ABSTRACT

MITTAL, KHUSHBOO SURENDER. Development of Dual Functional Polymeric Textile Materials Using Atmospheric Plasma Treatment. (Under the direction of Dr. Peter Hauser.)

Glow discharges and low temperature plasmas and their applications have increasingly entered various areas of industrial applications. The textile industry is a developing area for application of atmospheric plasma techniques with significant growth potential. Technological advances made possible by plasma processes can reduce the costs for production by reduction in process times, improve the quality of product, generate products with new surface or bulk properties, and contribute to an environmentally sustainable work environment. A novel dual functional textile material was developed which possesses co-existing hydrophobicity and hydrophilicity on opposite faces utilizing atmospheric pressure plasma. One side of the substrate repels water whereas the other side absorbs water. The sequence and chemistry of the plasma aided side specific treatment of poly (ethylene terephthalate)/ polyurethane blend knitted fabric and cellulose with fluorocompound namely 1, 1, 2, 2- tetrahydroperfluorodecyl acrylate (70- 90%) and 1, 1, 2, 2- tetrahydroperfluorododecyl acrylate (10- 30%) was demonstrated to obtain the dual functionality. Effect of process and device parameters such as variation of (1) flow rate of monomer, (2) flow rate of helium and (3) flow rate of argon, (4) RF power, (5) time of plasma exposure to the fabric, (6) gap between electrodes, (7) prewashing the material before treatments and (8) preliminary plasma treatment on the fabric performance was also studied in this research.
Development of Dual Functional Polymeric Textile Materials Using Atmospheric Plasma Treatments

by
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A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Master of Science

Textile Chemistry

Raleigh, North Carolina

2009

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DEDICATION

I dedicate this work to my grandparents (Late Dadaji, Late Dadiji, Late Naniji & Nanaji) whose perpetual blessings have always inspired me to aim for higher and achieve the highest! They have always taught me:

\[\text{राजस्व न च राजस्व न भातुभाज्यं न च भारकारिः}
\text{व्यये कृते वर्धेत एव नित्या विवर्धनं सर्वधनप्रधानम्}\]

English Translation of Sanskrit Quote:
It cannot be stolen by a thief.
It cannot taken away by a King.
It cannot be divided among brothers.
It does not cause load. It always increses when spent.
The wealth of knowledge is the greatest of all wealths.
BIOGRAPHY

Khushboo Mittal was born on December 17th, 1985 to Surender and Sangeeta Mittal. She stayed with her parents and younger sister Surbhi in Mumbai, India, where she received her Bachelor of Technology (Fibre & Textile Chemical Technology) from Institute of Chemical Technology (formerly UDCT) in May-2007. To pursue her goal further, she joined North Carolina State University, Raleigh, USA for dual Masters degree in 1) Textile Chemistry and 2) (Soft)Materials Science & Engg. Upon completion of the degrees, Khushboo aims to join specialty polymer/textile industry.
ACKNOWLEDGEMENTS

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Primarily I offer my sincerest and deepest gratitude to my advisor, Dr Peter Hauser, who has supported me throughout my research with his patience and knowledge whilst allowing me the room to work in my own way. I attribute the level of my Masters degree to his encouragement and effort and without him this thesis would not have been completed or written. He was, and will always be a fatherly figure for me in the School.

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1. Introduction
1.1. Motivation and goal

Although humans live in an environment of immense diversity, the human body maintains a tightly regulated core temperature. It has been shown that the stability of core temperature is dependent upon the balance of heat production together with heat gain from the environment and loss to the environment through the transfer of heat by conduction, convection, radiation and evaporation.\(^1\) Clothing, as an interactive barrier, greatly affects thermal balance. Clothing systems must be carefully planned to facilitate heat transfer with the environment. It has been shown that this reduces potential heat storage and loss that may decrease work capacity.\(^2\) Under normal stationary conditions, it has been demonstrated that the human body produces little sweat or saturated water vapor, and the wearer does not experience any significant discomfort while wearing either a cotton or polyester shirt.\(^3\) But, as the dry heat flux by conduction, convection and radiation is not sufficient to match metabolic heat production in a warm climate, while the human is exercising or working, it has been shown that reasonable sweating is started with the aim of creating a latent heat flux by the evaporation of sweat at the skin surface.

On the other hand, finishes that repel water, oil and dry dirt are important in all parts of textile market and applications- apparel, home and technical textiles. Water repellence is studied across a range of diverse disciplines, such as chemistry, materials, textiles and soil and reclamation science. In recent years many basic studies of water repellence of materials have focused on the role of the sub-mm surface topography of a material in modifying the intrinsic hydrophobicity imparted by the surface chemistry to create
superhydrophobicity. Surfaces with extreme water wetting properties have also been of considerable interest within the scientific community for the last two decades and are gradually finding applications in many areas of everyday life. Non-wetting surfaces that exhibit self cleaning effects are inspired by natural surfaces such as the Lotus leaf.\textsuperscript{4}

A textile garment with both the desired finishes- hydrophilic and hydrophobic has been developed in the past. Okubo et al.\textsuperscript{5} have developed functional, intelligent sportswear based on atmospheric pressure, non-thermal plasma graft polymerization process. It was possible to effectively disperse human sweat to the outside environment during the exercise by wearing the one-side treated apparel that has the hydrophilic property in the outer side and the hydrophobic property in the inner side. But this type of garment was not capable of repelling off any external liquid contaminants. Approach based on the use of both hydrophilic as well as hydrophobic fibers for moisture management has been explored in the past.\textsuperscript{6,7} Although these possess good water absorption properties, they lack the water repellency on the outer surface.

With the atmospheric pressure plasma jet (APPJ) laboratory unit installed in the College of Textiles at NCSU, it was possible to make side specific treatments and thus, a textile material with dual finish was targeted for development. This kind of dual functional intelligent fabric has co-existing hydrophilic and hydrophobic surfaces, making it water absorbent as well as water repellent simultaneously. A snapshot of this type of fabric is shown in Figure 1.1.
1.2. The Approach

Development of a multi functional textile material which possesses coexisting water absorbing as well as water repellent surfaces was attempted. Atmospheric pressure glow discharge plasma generated from RF power is used for surface activation and cross-linking of deposited perfluoroacrylate monomer by activated species in inert gas. Side specific plasma induced polymerization of fluorine based monomers results in superhydrophobic nanocoating of the textile material. Effect of process and device parameters such as variation of (1) flow rate of monomer, (2) flow rate of helium and (3) flow rate of argon, (4) RF power, (5) time of plasma exposure to the fabric, (6) gap between electrodes, (7) prewashing the material before treatments and (8) preliminary plasma treatment on the performance characteristics was studied in this research. Physical
and chemical interaction of the fluoropolymer with the substrate was studied and the dual functionality of the material was confirmed from neutron imaging which distinguishes between hydrophobic and hydrophilic faces based on hydrogen presence at atomic level. AATCC standard test methods were used to quantify the superhydrophobicity and excellent water absorption characteristics of the treated material. Figure 1.2 summarizes the process of development of dual functional fabric.

Figure 1.2: Process sequence for development of dual functional textile
1.3. References


2. Literature Review
2.1 Plasma- an overview

Plasma is an ionized gas, a distinct fourth state of matter. “Ionized” means that at least one electron is bound to an atom or molecule, converting the atoms or molecules into positively charged ions. As temperature or supplied power increases, molecules become more energetic and transform matter in the sequence: solid, liquid, gas and finally plasma, which justifies the title ‘fourth state of matter’. Plasma is often confused with the gaseous state, Table 2.1 illustrates the differences.

Table 2.1: Properties- Gas Vs Plasma

<table>
<thead>
<tr>
<th>Property</th>
<th>Gas</th>
<th>Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Conductivity</td>
<td>Very low</td>
<td>Usually very high</td>
</tr>
<tr>
<td></td>
<td>Air- 30 kilovolts per centimeter.</td>
<td>For many purposes the conductivity of plasma may be treated as infinite.</td>
</tr>
<tr>
<td>Independently acting species</td>
<td>One</td>
<td>Many</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrons, ions, and neutrals can be distinguished by the sign of their charge so that they behave independently in many circumstances</td>
</tr>
<tr>
<td>Velocity distribution</td>
<td>Maxwellian</td>
<td>Often Non-Maxwellian</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interactions</td>
<td>Binary</td>
<td>Collective</td>
</tr>
<tr>
<td></td>
<td>Two-particle collisions are the rule, three-body collisions extremely rare.</td>
<td>Waves, or organized motion of plasma, are very important because the particles can interact at long ranges through electric and magnetic forces.</td>
</tr>
</tbody>
</table>
Plasma is widely used in practice; it offers three major features that are attractive for applications in chemistry and related disciplines: 

- Temperatures of at least some plasma components and energy density can significantly exceed those in conventional chemical technologies.
- Plasmas are able to produce very high concentrations of energetic and chemically active species (e.g. electrons, ions, atoms and radicals, excited states, and different wavelength photons)
- Plasma systems can essentially be far from the thermodynamic equilibrium, providing extremely high concentrations of chemically active species and keeping bulk temperature as low as possible.

High or low temperature plasma can be obtained based on the activation methods and operating energy used to generate the plasma. Hot plasmas or thermal plasmas are usually at a Local Thermodynamic Equilibrium (LTE); conversely, cold plasmas or non-thermal plasmas are referred to as non-LTE because these are not in thermodynamic equilibrium as mentioned in the third feature above. If plasma is at LTE, then each kind of collision in the plasma is balanced by its inverse. Because hot plasmas have a very high operating temperature and textiles are polymeric materials which have a definite melting point, they have no applicability to textiles, thus only cold, non-LTE plasma are used for textile treatments.

Another classification of plasma is based on the pressure of the operation of plasma. There are two accepted plasma types: low pressure (vacuum) and atmospheric pressure
plasmas. Typical vacuum operating pressures are in the range between 10 mTorr and 10 Torr, while atmospheric pressure plasmas operate at one atmosphere or 760 Torr.

Atmospheric-pressure plasmas are used in an array of materials processes. Traditional sources include transferred arcs, plasma torches, corona discharges, and dielectric barrier discharges. However, since these discharges are not uniform, their use in materials processing is limited. Recently, APJeT, Inc. developed the atmospheric-pressure plasma jet (APPJ) process at the Los Alamos National Laboratory in collaboration with the University of California, Los Angeles. This process exhibits many characteristics of a conventional, low-pressure glow discharge. A laboratory unit and pilot plant unit of APPJ is installed and is fully functional at the College of Textiles, NCSU.

2.1.1 Atmospheric Pressure Plasma Jet

The Atmospheric Pressure Plasma Jet (APPJ) is a unique, non-thermal, glow-discharge plasma operating at atmospheric pressure. It is a capacitatively coupled device consisting of two coaxial electrodes between which a gas flows at particular rates. The discharge uses a high-flow feedgas consisting primarily of an inert carrier gas, such as He, and a small amount of an additive to be activated, such as O₂, H₂O or CF₄. This feedgas flows between closely spaced electrodes powered at 13.56 MHz radio frequency in a coaxial or parallel plate arrangement. The electric fields produced between the electrodes cause the gas to breakdown into a plasma state with electron temperature and density on the order of 2 eV and 10¹¹ cm⁻³, respectively. While passing through the plasma, the feed gas becomes excited, dissociated and/or ionized by energetic electron impact. Once the gas
exits the discharge volume, ions and electrons are rapidly lost by recombination leaving metastable species (e.g. O$_2^*$, He*) and radicals (e.g. O, OH, F). These reactive species are then directed onto a surface where the desired chemistry occurs. The electrons are not in thermal equilibrium with the ions and neutrals, so, although the electrons are quite hot, the overall gas temperature remains quite cold, typically 50-300°C.

The following section discusses the interaction of plasma with the materials.

2.2 Plasma-polymer interactions

Plasma chemistry is an area of research that has been explored for more than 35 years.$^6$ Plasma treatment has been found to be a tremendously remarkable and eco-friendly way to modify the surface chemistry and morphology of polymeric materials.$^7$ Surface modification using plasma treatments requires minimum use of water and chemicals; resulting in a more economical and ecological process.$^8$ An imperative aspect of plasma treatment is that the modifications are confined to a particular depth of a few nanometers at the surface because of the low level of penetration into the bulk.$^9$ More recently atmospheric pressure glow discharge processes have been developed and reported for treating polymeric materials in the form of fibers, bulk plastics,$^{10}$ films and fabrics,$^{11}$ and polyester supports. Plasma treatment effects in textile include increasing the hydrophilic character,$^{12, 13, 14, 15, 16, 17}$ enhancing adhesion,$^{18, 19, 20}$ and improving dyeing and printing properties,$^{21}$ among others.
2.2.1 Fundamentals of plasma modification of polymers

Non-thermal plasma treatment of polymers leads to significant modifications of particularly the surface properties including surface energy, wettability, adhesion, surface electrical resistance, dielectric loss tangent, dielectric permittivity, catalytic activity, tribological parameters, gas absorption, and permeability characteristics. The depth of interaction and modification, however, is independent of gas type and is limited to 5 µm.

Plasma processes can be conveniently classified into four core processes:

- **Etching**
- **Activation**
- **Grafting**
- **Deposition**.

2.2.1.1 Etching

In the process of physical etching, inert gas (Ar, He) and oxygen plasmas are used. The plasma-etching process removes, via ablation, organic contaminants such as oils and other production effluents released on the surface of most industrial materials. These surface contaminants are usually polymers that can undergo abstraction of hydrogen with free radical formation and repetitive chain scissions as shown in Figure 2.1. Etching can conveniently be compared to an evaporation process, where the bombardment of the polymer surface by energetic particles (i.e., free radicals, electrons, and ions) and radiation breaks the covalent bonds of the polymer backbone, resulting in lower-
molecular-weight polymer chains. As long molecular components become shorter, the volatile oligomer and monomer byproducts boil off (ablare) and are swept away with the vacuum-pump exhaust or feed gas.

![Figure 2.1: Plasma etching: Hydrogen abstraction and Chain Scission](image)

**Figure 2.1:** Plasma etching: Hydrogen abstraction and Chain Scission

Etching can occur by four basic plasma mechanisms commonly often in parallel or serial combinations as shown in Figure 2.2. 23, 24, 25, 26, 27

- Physical sputtering
- Pure chemical etching
- Reactive ion etching
- Ion inhibitor etching
2.2.1.2 Surface Activation

Activation plasma processes occur when a surface is treated with a non-carbon containing gas, such as $O_2^{28}$, air$^{29}$, $N_2^{30}$ and noble gases such as argon$^{31}$ and helium$^{32}$ in their mixtures. The primary result is the incorporation of different moieties of the process gas and/or its interaction with air, onto the surface of the material under treatment. The surface of polyethylene, normally consists solely of carbon and hydrogen: with a plasma treatment, the surface may be activated, anchoring on it functional groups such as hydroxyl, carbonyl, peroxy, carboxylic, amino and/or amines [Figure 2.3] depending on the type of gas used in plasma treatment. Hydrogen abstraction produces free radicals in the plasma gases and functional groups on the polymeric chain. Almost any fiber or polymeric surface may be modified to provide chemical functionality to specific adhesives or coatings, significantly enhancing the adhesion characteristics and
permanency. For instance, polymers activated in such a manner provide greatly enhanced adhesive strength and permanency, and resulting in a significant improvement in the production of technical fabrics.

![Surface Activation Diagram](image)

**Figure 2.3: Surface activation by oxygen plasma and nitrogen plasma**

2.2.1.3 Grafting

In grafting, an inert gas most often argon is employed as process gas to create many free radicals on the material surface. If a monomer capable of reacting with the free radical is introduced into the chamber, initiation reaction occurs and chain polymerization results due to a propagation reaction [Figure 2.4]. Typical monomers are acrylic acid, allyl amine and allyl alcohol. Polymeric materials are generally chosen and developed for their bulk properties; however, the inert nature of most polymer surfaces creates challenges for applications where coatings must be applied. By means of the plasma induced grafting processes some properties of the surface, wettability and adhesion in particular can be modified to attain extrapolated applications.
2.2.1.4 Deposition

Any species involved in the polymerization mechanism in plasma chamber can be deposited. Deposition occurs when an impinging particle fails to bounce back from a colliding surface. Such a deposition may result from the loss of kinetic energy or from the formation of a chemical bond with the target molecule or atoms. The sticking coefficient, or deposition co-efficient, can be defined as the number of particles deposited divided by the total number of impinging particles. Thus, as defined, the sticking coefficient is a function of the nature of species involved (mass, kinetic energy, chemical reactivity, etc.) and the surface temperature. In non-thermal plasmas, the observed difference in the deposition rate as a function of the substrate temperature is caused by the difference between the temperature of substrate and that of surrounding plasma, which is in steady state. In summary, polymer deposition can be prevented if the temperature of the substrate is raised far above the steady state ambient temperature of the plasma.
Plasma can also produce a material deposition: when a more complex molecule is employed as the process gas, a process known as plasma-enhanced chemical-vapour deposition (PECVD) may result. For instance, when methane or carbon tetrafluoride is employed, the gas undergoes fragmentations in the plasma, reacting with itself to combine into a polymer. Selecting the process conditions, pinholefree chemically unique films, may be deposited onto surfaces of materials within the plasma reactor. PECVD coatings alter in a permanent way the surface properties of the material onto which these have been deposited.

2.3 Plasma in textiles

Finishing is essentially the ultimate step in the fabric manufacturing process. In a broad sense, finishing is any operation for improving the appearance or usefulness of a textile material after it leaves the loom or knitting machine. Innovation is the lifeblood of the retailers who are always seeking products that are better, less expensive and delivered faster. In this way, niche markets have been opened up using lower volume, higher value functional textiles that can be marketed and expanded into major sectors of the industry. The whole area of finishing, giving water repellency and staining repellency has been explored for many decades. Some of the studies are based on conventional fluorocompound treatments, functionalization by sol-gel process, and functionalization by carbon nanotubes among others. These methods are wet processing techniques which conventionally entail post treatments processes like water recycling, water recovery, drying or curing, etc.
However, with the recent emphasis on alternate energy and energy concerns, plasma chemistry has revolutionized the textile processing industry. The potential of plasma technology for the treatment of textiles is varied. This is obvious in the numerous publications including scientific papers and books in the course of last four decades. Some of the applications include improving the water absorption by increasing the hydrophilic character, imparting water repellency and antimicrobial finishes among others.

Fibers are used in composite materials as a dispersed phase and also matrix phase, wherein, both cases adhesion between phases can be significantly improved by treatment in non-thermal plasma. The modification of properties of polymer/textile fibers after plasma treatment chiefly depend on the particular plasma gas and the treatment parameters such as type of discharge, pressure, plasma power and time of exposure. Table 2.2 gives a brief overview of such surface modifications.
Table 2.2: Modification of surface properties of textile polymers based on plasma treatment parameters.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Plasma gas</th>
<th>Plasma treatment parameters</th>
<th>Modification of surface property</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pressure [Pa]</td>
<td>Power [W]</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>Acrylic acid, hexamethyl disilazane, air</td>
<td>13.3</td>
<td>20-40</td>
</tr>
<tr>
<td></td>
<td>Tetrachloroethylene, trichloroethylene</td>
<td>13.3</td>
<td>20-40</td>
</tr>
<tr>
<td>Poly(ethylene)</td>
<td>Acrylic acid</td>
<td>6.6</td>
<td>30-70</td>
</tr>
<tr>
<td>Kevlar</td>
<td>Ar, O₂, ammonia (NH₃)</td>
<td>7-13.3</td>
<td>25</td>
</tr>
</tbody>
</table>
Enormous research on textile modification and finishing using vacuum or atmospheric plasma has been published and a few exemplary applications are summarized as follows:

2.3.1 Enhancement in mechanical properties
Yuan et al. studied the treatment of carbon fibers to improve the interfacial adhesion with polyphenylene sulphide. The carbon fibers were plasma etched by oxygen or argon plasma resulting in increased interfacial shear strength (IFSS) up to 2.5 times compared to non-treated fibers. A uniform treatment of carbon fiber surfaces by treatment with oxygen plasma was described by Huang et al. and they reported an improvement of the mechanical properties of their phenolic composites. The IFSS of the composites was strongly increased and the treated fibers exhibited a very significant increase in wettability.

2.3.2 Enhancement in electrical properties
The treatment requires the introduction of functional groups at the fiber surface which, by hydrogen bonding with atmospheric water, decrease the resistivity of the treated textile. Aubrecht et al. treated PET fabric with low pressure O$_2$/CF$_4$ 13.56 MHz plasma and surface resistance was significantly reduced from $10^{14}$ Ω to $10^8$ Ω. Hautojiärvi and Laaksonen studied on-line corona treatment of PP fibres during melt spinning which resulted in a decrease of electrical resistance by an order of magnitude and about 50% less static charge build up during carding.
2.3.3 Modification of optical properties

The treatment requires efficient physical removal of fiber surface polymers for the creation of microscopic pits. Treatments have been specifically done to decrease light reflection at the fiber surface, so that a dyed treated textile acquires a deeper shade; an effect especially desired with (microfiber) fabrics colored in black and other deep color. Byrne and Brown\textsuperscript{75} reported a decrease in reflection of PET fibers after treatment with low pressure argon plasma at 3.14 MHz for 3 hours to give a “sea-shore structure” due to creation of ripples. Effect of plasma treatments were also studied on disperse black dyed Technora, Kevlar (paraaramid), and Conex (meta-aramid) fabrics, and on yellow, red and blue dyed Technora (p-aramid) and Conex (m-aramid) fabrics by Kobayashi et al.\textsuperscript{76} Under identical conditions the micro craters produced on Conex fibers were much smaller than the ones created on Technora, which resulted in a smaller reduction in fiber reflection.

2.3.4 Modification of wettability of textile surface

2.3.4.1 Hydrophilicity

The most important result of the plasma treatment of textiles is the change in wettability by altering the surface energy of the substrate. Plasma treatments can make textiles both hydrophilic and hydrophobic. The change in wettability is usually characterized experimentally by the contact angle $\theta$, which is formed on the solid surface along the linear solid-liquid borderline of air. An increase in wettability or making the fiber more hydrophilic leads to a decrease in the contact angle. An example illustrating improvement
of wettability and decrease of contact angle as a result of plasma treatment is shown in Figure 2.5.

![Contact angle θ between water and polymer substrate](image)

**Figure 2.5: Contact angle θ between water and polymer substrate**

In a recent study, grey cotton fabric was treated in low pressure discharge plasma for improving to the surface properties. The surface hydrophilicity and surface energy were found to increase by Pandiyaraj et al.\textsuperscript{13} It was explained as due to the formation of polar groups on the surface of the fabrics. The reduction in contact angle was observed to be from 130° to 0°. Samples are shown in Figure 2.6.
The application of plasma treatments for improved wettability has been attempted on a range of fibers, with varying success. The treatment aims at the introduction of polar functional groups such as –COOH, –OH and –NH₂. Of all plasma effects, this is without a doubt the most studied because it influences many plasma applications. In most cases, it is difficult to determine the surface energy directly from contact angle measurements when evaluating the wettability of a treated fiber surface. The irregular surface of a textile reduces the accuracy of (large) contact angle values, while for lower contact
angles their porous structure immediately absorbs the liquid drop. Therefore, wettability of textile (fiber) surfaces is usually monitored by indirect methods such as absorption time and wicking. 77, 78, 17

2.1.1.1 Hydrophobicity

Hydrophobicity can be imparted to a polymer by either plasma induced grafting or plasma deposition of low surface energy compounds on the textile substrate. The most straightforward way is the treatment of a fabric in a non-depositing gas which grafts (or exchanges) single fiber polymer atoms with hydrophobic groups such as fluorine groups. In another method the fabric is immersed in a fluid consisting of or containing the hydrophobic prepolymer with added initiators, after which the textile is plasma-treated leading to the grafting of the prepolymer on the fiber surface. The method with the highest potential is the deposition of a polymer structure at the fiber surface while the textile remains in the plasma reactor. The deposition can occur (a) while the plasma is ignited (plasma polymerization) or (b) in a two-step process: (i) creation of radicals at the fiber surface in an inert plasma (e.g. argon) and (ii) reaction of these radicals with unsaturated monomers (plasma grafting).

Leroux et al. 63 deposited fluorocarbon coating on PET woven fabric using pulse discharge plasma treatment by injecting a fluoropolymer directly into the plasma dielectric barrier discharge. After atmospheric plasma treatments with fluoropolymer aerosol dispersion atomizing, the textile surface becomes hydrophobic but the fluoropolymer quantity deposited on the textile is not sufficient to get a good repellent behavior. This technique modifies the textile surface with a small quantity of chemical
product and water. Moreover atmospheric plasma treatments may result in an increase the 
wet pick up of a padding process and thus increases the treatment washing fastness. 
Contact angles of about 141° were obtained after 5 washes. 
Ruiz et al. 64 were able to fabricate engineered surfaces with controlled hydrophilic/ 
hydrophobic character by tailoring the substrate topography and chemistry. The surface 
was topographically modified chemically by controlled deposition of a thin polymer layer 
using plasma processing. In this way, both the surface texture and the surface chemistry 
could be varied independently, producing surfaces with variable wetting character, 
including super-hydrophilicity and super-hydrophobicity, depending on the choice of 
plasma polymer deposited. When the water contact angle is larger than 90°, the surface is 
hydrophobic, and surface becomes superhydrophobic for contact angles above 150°. 79, 80
2.4 References


3. Effect of flow rate of monomer and gases on the development of dual functional textile materials
Effect of flow rate of monomer and gases on the development of dual functional textile materials

3.1 Abstract

This research concerns a novel dual finished textile developed to have coexisting hydrophilic as well as hydrophobic nature on opposite faces. Garments made from such innovative materials can absorb the body sweat from the inner contact surface and at the same time have a self cleaning outer surface that repels any water/beverage/liquid spill. This dual functional textile utilizes the principle of in-situ atmospheric plasma polymerization. A polyester/polyurethane blend fabric is used for this purpose, on which 1, 1, 2, 2- tetrahydroperfluorodecyl acrylate layer is polymerized using helium gas glow discharge plasma treatment at atmospheric pressure. This paper will focus on the optimization of the amount of fluoromonomer, helium, and argon flow rates necessary to achieve this specialized fabric.

3.2 Keywords: dual finish, atmospheric plasma, polymerization

3.3 Introduction

Finishing is essentially the ultimate step in the fabric manufacturing process. In a broad sense, finishing is any operation for improving the appearance or usefulness of a textile material after it leaves the loom or knitting machine. Innovation is the lifeblood of the retailers who are always seeking products that are better, cheaper and delivered faster. In this way, niche markets have been opened up using lower volume, higher valued
functional textiles that can be marketed and expanded into major sectors of the industry. The whole area of finishing to give water repellency and staining repellency has been explored for many decades. Some of the studies are based on conventional fluorocompound treatments\textsuperscript{3, 4, 5, 6, 7, 8, 9, 10}, functionalization by sol-gel process\textsuperscript{11, 12, 13, 14} and functionalization by carbon nanotubes\textsuperscript{15, 16} among others. These methods are wet processing techniques which conventionally entail post treatments processes like water recycle, water recovery, drying or curing, etc.

However, with the recent emphasis on alternate energy and energy concerns, plasma chemistry has revolutionized the textile processing industry. The potential of plasma technology for the treatment of textiles is of great interest. This is clear in the numerous publications including scientific papers and books in the course of last four decades. Some of the applications include improving the water absorption by increasing the hydrophilic character\textsuperscript{17, 18, 19, 20, 21, 22}, imparting water repellency\textsuperscript{23, 24, 25, 26, 27, 28, 29, 30, 31} and antimicrobial finishes\textsuperscript{32, 33, 34, 35} among others.

The objective of the present study was to develop a dual finished fabric using atmospheric pressure glow discharge treatment at RF power. The atmospheric pressure glow discharge is particularly of special because of its potential for scaling to large areas, its relatively uniform surface interactions under controlled conditions and its freedom from vacuum and interlock requirements. The predominant active species in radio frequency plasma are positive ions and photons, with ability of breaking primary chemical bonds and inducing cross-linking. This type of functional textile is hydrophilic
on one side while hydrophobic on the other. The dual performance characteristics allow these types of textiles to keep moisture away from the skin whether coming in the form of precipitation from the outside or perspiration from the inside. After physical exertion, the body temperature of humans goes down due to removal of heat by evaporation. However, if rate of sweating is high and there is no escape for the vapors, then the evaporation process is hindered and more sweating occurs. This brings discomfort to the wearer. Also, the other side is water repellent making it suitable for outerwear garments. The paper describes the study of selectively processing one side of the poly (ethylene terephthalate) textile material with minimum or preferably no interference with the second side. This area of development and study of dual finished textile material has not yet been reported in the literature.

3.4 Experimental

3.4.1 Materials

Polyester/ polyurethane knitted, dyed ready-to-use fabric was used provided by Polartec (formerly Malden Mills) with 90/10 composition. The fabric was given a delicate wash in washing machine with standard AATCC detergent, thoroughly rinsed until total removal of the detergent and dried. Treated and untreated specimens (approximately 7” x 7”) were usually stored at 20±2 °C and 65±2 % relative humidity (conditioned atmosphere).

Industrial grade Helium and ultrahigh pure Argon 5.0 was used which was supplied by Machine and Welding Supplies Co.
Monomer based on perfluoroalkylacrylate derivates was used as obtained from Daikin (TG-10). The product was a clear to slight yellow liquid mainly composed of 1, 1, 2, 2-tetrahydroperfluorodecyl acrylate (70-90%) and 1, 1, 2, 2-tetrahydroperfluorododecyl acrylate (10-30%). The chemical structure of the monomer can be seen in Figure 3.1.

![Chemical structure of the monomer, 3D view of the monomer (inset)](image)

**Figure 3.1: Chemical structure of the monomer, 3D view of the monomer (inset)**

3.4.2 Equipment:
The treatments were carried with the **e‘ Rio™** atmospheric pressure plasma system APPR-300-13 from APJeT Inc. The machine uses RF electric fields, 1300 W @ 27 MHz RF/1 mm gap, to produce a unique, non-thermal, glow-discharge plasma that operates at atmospheric pressure with a cooling requirement of 1 gpm @ 20 psi max.

The plasma assembly also consists of an evaporator and applicator. The evaporator is a heated assembly that vaporizes the monomer that is to be applied to fabric samples. Heat
is regulated by a logic controller that is connected to a thermo-coupler attached to the evaporator. The applicator acts as a heated nozzle to apply vaporized monomer to the fabric sample. The heat is required to maintain the vapor property of the monomer. Heat is regulated by a logic controller that is connected to a thermo-coupler attached to the applicator. A schematic of the entire assembly can be seen in Figure 3.2.

![Figure 3.2: Atmospheric Plasma assembly](image)

3.5 Methods

3.5.1 Plasma treatment

For this study, the washed substrate was placed flat on the ground electrode with double sided adhesive tape to avoid any plasma exposure on the untreated side. The method included pre-treatment using plasma, deposition of monomer onto the knitted substrate.
attached to the electrode with the help of pressure from argon gas; exposing the monomer to helium atmospheric plasma, thereby causing polymerization of the monomer species. This step was followed by a second pass of the substrate through the plasma chamber. The process parameters and sequence is summarized in Figure 3.3. The flow rate of the monomer was varied using synchronous pump assembly from FMI pumps, while the flow rates of gases helium and argon were controlled with calibrated rotameters.

**Figure 3.3: Process parameters and sequence**

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate of monomer</td>
<td>0.45 ml/min</td>
</tr>
<tr>
<td>Flow rate of Helium</td>
<td>40 SLM</td>
</tr>
<tr>
<td>Flow rate of Argon</td>
<td>1.0 SLM</td>
</tr>
<tr>
<td>Operating plasma power</td>
<td>650 W</td>
</tr>
<tr>
<td>Gap between electrodes</td>
<td>3.5 mm</td>
</tr>
<tr>
<td>Exposure time (plasma)</td>
<td>3 sec</td>
</tr>
<tr>
<td>Exposure time (monomer)</td>
<td>~0.4 sec</td>
</tr>
</tbody>
</table>

3.5.2 Characterization

Hydrophilicity of the untreated surface of sample was characterized using a method based on the measurement of absorption time of water droplet onto the fabric. The drop was placed onto the fabric and the time for absorption of water was noted with the help of a stopwatch. Absence of any specular reflection of water on the substrate surface
confirmed the complete absorption of water by the fabric. Specular reflection is the reflection without diffusion, in accordance with the laws of optical reflection, as in a mirror.\textsuperscript{37}

Hydrophobicity of the treated surface of the sample was characterized on qualitative as well as quantitative basis. AATCC Test Method 193- 2005 was used to qualitatively determine the water/ alcohol solution resistance of the treated sample. In this method, drops of standard test liquids, consisting of a series of water/ isopropyl alcohol solutions with varying surface tensions (59.0 to 24.0 dynes/ cm), are placed on the fabric surface and observed for wetting/ wicking. The aqueous repellency grade is the highest numbered test liquid which does not wet the fabric.\textsuperscript{38}

Static contact angle measurement was done using Rame Hart manual contact angle goniometer (100- 00- (115/ 220)). A calibrated syringe from Gilmont Instruments was used to place a drop of 0.016 ml of water on the hydrophobic surface of the fabric. ASTM D 5946- 04 standard test method for corona treated polymer films using water contact angle was used for analysis.

3.6 Results and Discussion

3.6.1 Surface Chemistry

The method involves initial passage of fabric through plasma chamber to activate the surface of the polyester/ polyurethane surface. Plasma treatment of polymers especially polyester encompasses a variety of plasma technologies for a wide range of applications.
and dates back to at least the 1960s. Studies in the past have shown that after the inert gas plasma is irradiated on to the surface of polyester; active radicals are induced on the surface. If monomer vapors are condensed on to this activated surface, then it initiates the cross-linking of the monomer by free radical polymerization mechanism. This is followed by the irradiation of plasma for two more time to ensure complete cross-linking of the fluorocarbon monomer. The reactions are depicted in Figure 3.4.

Figure 3.4: Plasma induced fluoropolymer grafting on poly (ethylene terephthalate)
3.6.2 Effect of monomer flow-rate

The effect of variable flow rate of monomer and thus the amount of monomer deposition on the substrate was studied. Only the flow rate was varied and other parameters were kept constant as mentioned in Figure 3.3. As the flow rate of liquid monomer input increases, more monomer enters the evaporator and more amount of monomer is

Figure 3.5: Effect of monomer flow rate on (a) contact angle and time of absorption of water droplet (b) water/alcohol repellency of the sample
deposited on the fabric substrate. The results for hydrophobic surface tests as well as hydrophilic surface tests are shown in Figures 3.5(a) and 3.5(b).

3.6.2.1 Hydrophilic surface

As the monomer flow rate is increased, the time of absorption of water droplet by the hydrophilic side increases. This infers that with increase in monomer flow rate, penetration of monomer on the other side increases, which polymerizes giving decrease in water absorption values. For textiles, to be labeled as superhydrophilic—meaning a little more than usual hydrophilicity usually exhibited, the wetting time is expected to be less than 3 sec. Thus, the hydrophilic surface for flow rates of 0.45 ml/min and 0.75 ml/min can be called superhydrophilic.

3.6.2.2 Hydrophobic surface

AATCC test rating is 5 for the first three samples as seen in Figure 3.5(b). This means that the samples are resistant to 30/70 alcohol/ water solution. This rating is constant for all flow rates but plummets for high flow rate (1.15 ml/ min). The reason for this decrease is speculated to be inadequate polymerization of all the deposited monomer. It must be noted here that monomer without any plasma does not give any water repellency. Thus, high amount of monomer but same amount of time (3 second) of plasma exposure results in non- polymerized or unreacted monomer on the surface. Moreover, higher concentration will also increase the pressure and thus the penetration of monomer to the other side increases, but the plasma treatment time is not correspondingly increased.
Figure 3.5(a) shows the trend of the change in contact angle observed with the change in flow rate of monomer. The contact angle slightly increases initially to $154.5^\circ$ with increase in flow rate to give superhydrophobic surface. After this point, the flow rate decreases. As the flow rate of monomer increases, the thickness of monomer layer on fabric surface increases as well as the penetration also increases. By the initial plasma passage of the fabric, the surface is activated and also the latter treatment of plasma treatment initiates the polymerization and cross-linking of the monomer on to the fabric surface. But this initiator is inadequate to completely polymerize the increasing amount of monomer, thus reducing the contact angle at higher amounts of perfluoro compound.

This phenomenon for increase in contact angle is represented by a schematic in Figure 3.6.

![Schematic](image)

**Figure 3.6:** Proposed surface characteristics after plasma treatment (A) monomer flow rate- 0.45 ml/min (B) monomer flow rate- 0.75 ml/min
Effect of flow rate of helium

Figure 3.7: Effect of helium flow rate on (a) contact angle and time of absorption of water droplet (b) water/alcohol repellency of the sample

Figures 3.7(a) and 3.7(b) show the results for 3 different flow rates for dual functionality testing. From the trend observed in Fig. 3.7(a), with increase in helium flow rate, the
contact angle of the hydrophobic surface decreases while the time of absorption gradually increases for the water droplet on the hydrophilic side. Overall, the dual functionality of the fabric is not lost as the contact angle is higher than $140^\circ$ while time of absorption is less than 3 seconds.

The polymer surface modifications are a fingerprint of the plasma discharge action. Gheorghiu et al. have studied the surface properties of poly (ethylene terephthalate) and point out that treatments on a helium plasma discharge induce both a functionalization and a cross linking of the uppermost layers of the polymer film. The authors confirm the distinct values of surface energies of polyester film, with the greatest values for surface energy of polyester obtained for lowest gas flow rates. This infers that with higher gas flow rates, plasma penetrates into the bulk of the sample and is not restricted to the surface, explaining the fall in the contact angle as fluoropolymers are not restricted to the surface but also the bulk of sample. This phenomenon also hampers the wicking of the water on the hydrophilic side, resulting in slight increase of time of absorption of water droplet. The increase in the time of absorption for increase in helium flow rate by two times is $\sim 1.2$ seconds. This rise is almost insignificant for most textile applications. Thus, when helium at 20 SLPM (Standard Liters Per Minute) is purged into the plasma chamber, the best dual functionality is obtained. Schematic in Figure 3.8 depicts the phenomenon of surface and surface as well as bulk activation in case of lower and higher flow rates of helium respectively, thus providing a rationalization for the trend of graph seen in Figures 3.7(a) and 3.7(b). It must be noted that while studying the effect of helium flow rate, flow rate of monomer and other parameters were kept constant.
Figure 3.8: Proposed surface characteristics after plasma treatment (A) helium flow rate- 20 SLPM (B) helium flow rate- 40 SLPM
3.6.3 Effect of flow rate of argon

![Graph showing the effect of argon flow rate on contact angle and time of absorption of water droplet and water/alcohol repellency.]

**Figure 3.9:** Effect of argon flow rate on (a) contact angle and time of absorption of water droplet (b) water/alcohol repellency of the sample

The effect of flow rate of argon was studied by characterizing the hydrophobicity and hydrophilicity of the two surfaces of the sample keeping other parameters listed in Figure 3.3 unchanged. Flow rates of argon from 0.6-1.0 SLPM were used as in Figures 3.9(a) and 3.9(b). The main function of argon gas is to provide the required pressure for
monomer vapors to flow in vertical direction from evaporator to the surface of the fabric. Higher pressure yields more amount of monomer transfer onto the fabric. Thus, the trend of contact angle and time absorption change is comparable to Figure 3.6. The changes are tolerable till an argon flow rate of 0.9 SLPM, beyond which the contact angle of the treated surface reduces and the time of absorption of water droplet on the untreated surface increases. AATCC rating increases from 3.5 to 5 for argon flow rates from 0.6 SLPM to 1.0 SLPM, giving better resistance to alcohols as seen in Figure 3.9(b).

3.7 Conclusion

In this study, dual finished fabric was achieved and the effect of parameters to control this functionality was studied and reported. The parameters which give a contact angle of $>150^\circ$ on the hydrophobic side and time of absorption $< 3$ seconds were considered to be the ideal in this case. Thus, best results are achieved when 20 SLPM of helium generates plasma and argon at 0.9 SLPM is used to impinge the fluoromonomer at 0.75 ml/ min. The textile industry is searching for innovative production techniques to improve the product quality, as well as the society requires new finishing techniques working in environmental respect. Plasma surface treatments show distinct advantages, because they are able to modify the surface properties of inert materials, most times with environment friendly devices. Dual finished textiles serve as one of the solutions to the current needs.
3.8 References


4. Effect of preliminary treatments on the development of dual functional textile materials
Effect of preliminary treatments on the development of dual functional textile materials

Abstract

The study involves development of dual functional textile material using atmospheric plasma glow discharge treatments, which are hydrophilic and hydrophobic on opposite sides. The method includes deposition of perfluoroacrylate monomer followed by plasma exposure for 3 seconds thereby causing polymerization of the monomer species to give side specific hydrophobic properties to the fabric. This paper mainly discusses the role of removal of surface hand modification finish before plasma treatments and also the exposure to plasma prior to the monomer condensation on the fabric to activate the surface.

Keywords: dual finish, atmospheric plasma, preliminary treatments.

4.1 Introduction

Plasma chemistry is an area of research that has been explored since more than 35 years.\(^1\) Plasma treatment has been found to be tremendously remarkable and eco-friendly way to modify the surface chemistry and morphology of polymeric materials.\(^2\) Surface modification using plasma treatments does not require the use of water and chemicals; resulting in a more economical and ecological process.\(^3\) An imperative aspect of plasma treatment is that the modifications are confined to a particular depth of a few nanometers at the surface because of the low level of penetration into the bulk.\(^4\) More recently
atmospheric pressure glow discharge processes have been developed and reported for treating polymeric materials in the form of fibers, bulk plastics, films and fabrics, and polyester supports. Plasma treatment effects in textile include increasing the hydrophilic character, enhancing adhesion, and improving dyeing and printing properties, among others.

In this study, a dual finished fabric was developed using atmospheric pressure glow discharge treatment. In the present case, dual finished fabric implies a textile substrate which has two functionalities, a fabric that absorbs water from one side while the other side repels water; giving it hydrophilic as well as hydrophobic finishes concurrently. Such class of textiles finds use in sportswear and corporate wear primarily for people dwelling in tropical climate allowing the user to keep moisture away from the skin whether coming in the form of precipitation from the outside or perspiration from the inside. After physical exertion, the body temperature of humans goes down due to removal of heat by evaporation. However, if the rate of sweating is high and there is no escape for the vapors, then the evaporation process is hindered and more sweating results. This causes discomfort to the wearer. The paper describes the study of effect of preliminary treatments on the selective processing of one side of the poly (ethylene terephthalate) textile material with minimum or preferably no interference with the second side.
4.2 Experimental

4.2.1 Materials
A 90/10 blend of polyester/polyurethane dyed ready-to-use substrate in the form a knitted fabric used provided by Polartec (formerly Malden Mills) was used for both experiments. Industrial grade helium and ultrahigh pure argon 5.0 supplied by Machine and Welding Supplies Co. was used.

Monomer based on perfluoroalkylacrylate derivates was used as obtained from Daikin (TG-10). The product was a clear to slight yellow liquid mainly composed of 1, 1, 2, 2-tetrahydroperfluorodecyl acrylate (70-90%) and 1, 1, 2, 2-tetrahydroperfluorododecyl acrylate (10-30%).

4.2.2 Equipment
The plasma treatments and monomer deposition were carried out with the eRío™ atmospheric pressure plasma system APPR-300-13 from APJeT Inc. The machine uses RF electric fields, 1300 W @ 27 MHz RF/1 mm gap, to produce a unique, non-thermal, glow-discharge plasma that operates at atmospheric pressure with a cooling requirement of 1 gpm @ 20 psi max.

The plasma assembly consists of RF generator, RF electrodes, RF matching unit evaporator and applicator and logic controllers. The evaporator is a heated assembly that vaporizes the monomer to be condensed on to fabric samples. Heat is regulated by a logic controller that is connected to a thermo-coupler attached to the evaporator. The applicator
acts as a heated nozzle to impinge vaporized monomer to the fabric sample. The heat is required to maintain the vapor property of the monomer. Heat is regulated by a logic controller that is connected to a thermo-coupler attached to the applicator. A schematic of the entire assembly can be seen in Figure 4.1.

![Figure 4.1: Atmospheric Plasma assembly](image)

4.3 Methods

4.3.1 Plasma treatment

For both the experiments, the fabric was given a delicate wash in washing machine with standard AATCC detergent, thoroughly rinsed until total removal of the detergent and dried. Treated and untreated specimens (approximately 7” x 7”) were usually stored at 20±2 °C and 65±2 % relative humidity (conditioned atmosphere). This pre-wash was not given to the sample that was used to study the effect of washing prior to plasma
treatments. The substrate was held flat on the ground electrode with double sided adhesive tape to avoid any plasma exposure on the untreated side or the hydrophilic side as shown in Figure 4.1. The method essentially integrated the activation of the surface to be made hydrophobic; deposition of monomer onto the knitted textile substrate attached to the electrode with the help of pressure of argon gas; and exposing the monomer to inert gas helium atmospheric plasma, thereby causing polymerization of the monomer species. This step was followed by a second pass of the substrate through the plasma chamber. The plasma enhanced activation of surface preceding the monomer deposition was not carried out for the sample that was used to study the effect of this activation. The parameters for the whole process are tabulated in Figure 4.2.

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate of monomer</td>
<td>0.45 ml/min</td>
</tr>
<tr>
<td>Flow rate of Helium</td>
<td>40 SLPM</td>
</tr>
<tr>
<td>Flow rate of Argon</td>
<td>1.0 SLPM</td>
</tr>
<tr>
<td>Operating plasma power</td>
<td>650 W</td>
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<tr>
<td>Gap between electrodes</td>
<td>3.5 mm</td>
</tr>
<tr>
<td>Exposure time (plasma)</td>
<td>3 sec</td>
</tr>
<tr>
<td>Exposure time (monomer)</td>
<td>~0.4 sec</td>
</tr>
</tbody>
</table>

**Figure 4.2: Plasma process and monomer deposition process parameters**

This process makes the substrate selectively hydrophobic on one surface while the other surface is not affected and remains hydrophilic. A dual functional textile material is thus obtained.
4.3.2 Characterization

The substrate was tested for hydrophilicity of the untreated surface using a drop test. A water droplet was placed onto the fabric with the help of a disposable pipette and the time for complete absorption of this water droplet placed from the untreated (hydrophilic) surface was noted using a stopwatch. Absence of any specular reflection of water on the substrate surface ensured the complete absorption of water by the fabric. Specular reflection is reflection without diffusion, in accordance with the laws of optical reflection, as in a mirror.\textsuperscript{18} In simpler words, it is the glossiness of water seen when it spreads on any surface.

The performance of the hydrophobic surface of the sample was characterized quantitatively and qualitatively; using AATCC Test Method 193-2005 to qualitatively determine the water/ alcohol solution resistance of the treated sample and static contact angle measurement for quantitative analysis. AATCC methods involves the placement of drops of standard test liquids, consisting of a series of water/ isopropyl alcohol solutions with varying surface tensions (59.0 to 24.0 dynes/ cm) on the fabric surface and observation of the liquid’s wetting/ wicking if any. The aqueous repellency grade is the highest numbered test liquid which does not wet the fabric.\textsuperscript{19}

Static contact angle measurements were carried out using a Rame Hart manual contact angle goniometer (100-00- (115/220)). A calibrated syringe from Gilmont Instruments was used to place a drop of 0.016 ml of water on the hydrophobic surface of the fabric.
ASTM D 5946-04 standard test method for corona treated polymer films using water contact angle was used for analysis.

4.4 Results & Discussion

4.4.1 Effect of pre-wash

Table 4.1: Study of effect of pre-wash on the dual functional sample.

<table>
<thead>
<tr>
<th>Type</th>
<th>Hydrophilicity</th>
<th>Hydrophobicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time of absorption [sec]</td>
<td>AATCC rating</td>
</tr>
<tr>
<td>Pre-wash</td>
<td>2.27</td>
<td>5</td>
</tr>
<tr>
<td>No pre-wash</td>
<td>15.12</td>
<td>4</td>
</tr>
</tbody>
</table>

The effect of washing of the textile material before all plasma and monomer deposition treatments was studied. One of the fabrics was washed before all the treatments while the other fabric was treated as obtained from the mill. These fabrics were then tested for their performance as dual functional textiles. The results for the hydrophilic surface and hydrophobic surface characterization are shown in Table 4.1.

4.4.1.1 Hydrophilic surface

Softeners act mainly on the surface of the fabric. Almost all apparel fabrics in the textile industry are treated with softeners, because the hand of a textile is a very important quality for most buyers/users. The basic molecular structure of softener consists of long chain alkyl chain hydrophobe and hydrophilic groups. The characteristic soft feeling and handle imparted by softeners is due to these long chain groups which also provide slight
water repellency or relatively less water absorbency to the fabric. The table 4.1 shows that after washing the ready-to-sew fabric from the mill, followed by the dual functional treatment, the fabric absorbs water faster. This infers that firstly, washing removes this hand modification finish from the surface. This removal of the silicone softener finish does not interfere with the dual functional finish given with the aid of plasma treatment; moreover, it enhances the required hydrophilicity on the untreated surface of the textile material.

4.4.1.2 Hydrophobic surface

It is apparent from Table 4.1 that the difference in the contact angle of the hydrophobic surface before and after the wash prior to the plasma treatments is about $15^\circ$ and increase in AATCC test rating by one rank. The difference in contact angle is noteworthy especially since it categorizes the fabric from being hydrophobic to superhydrophobic as the contact angle increases from $\sim145^\circ$ to $\sim160^\circ$. A surface is defined as superhydrophobic when the contact angle of the surface with water is more than $150^\circ$.\textsuperscript{21} The reason for decrease in contact angle for the sample without washing is speculated to be the insufficient grafting of the fluoropolymers onto the polyester surface due to the blockage by the polysiloxane softener chains. This mechanism is demonstrated in Figure 4.3. After washing, the surface is free of any foreign chemical/softener layer and this clean surface facilitates the grafting of the more amounts of fluoropolymers imparting the required superhydrophobicity.
Thus, it is recommended to wash the fabric to remove any surface contamination before atmospheric plasma treatments to obtain hydrophilic as well as hydrophobic surface in this study.

![Proposed surface characteristics of the substrate with and without surface contamination](image)

**Figure 4.3: Proposed surface characteristics of the substrate with and without surface contamination**

4.4.2 Effect of pre-plasma treatment

Table 4.2: Study of effect of pre- treatment with plasma on the dual functional sample.

<table>
<thead>
<tr>
<th>Type</th>
<th>Hydrophilicity</th>
<th>Hydrophobicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time of absorption [sec]</td>
<td>AATCC rating</td>
</tr>
<tr>
<td>No pre-treatment</td>
<td>6.5</td>
<td>5</td>
</tr>
<tr>
<td>With pre-treatment</td>
<td>2.27</td>
<td>5</td>
</tr>
</tbody>
</table>

To study the effect of plasma treatment of the surface before the deposition of the monomer, two samples treated with the algorithm as shown in Figure 4.4 were used. Table 4.2 shows the response of the dual functional surfaces towards the pre- treatment
done with atmospheric plasma exposure for 3 seconds. The difference in the contact angle for the pre-treated and non pre-treated surfaces is very trivial ($\approx 2^\circ$). Thus, it can be concluded that the hydrophobicity of the surface is not affected by the initial surface activation by plasma exposure.

![Treatment Algorithm Diagram](image)

**Figure 4.4: Treatment algorithm**

The time of absorption for pre-treated sample is less than that observed for the sample without pre-plasma treatment for the hydrophilic surface. Surface of a poly (ethylene terephthalate) is activated upon exposure to atmospheric plasma. This activated surface serves as the initiation site for the graft polymerization of the forthcoming fluoromonomer. The polymerization of the fluoromonomer begins immediately and is enhanced by plasma treatment post monomer deposition. The instant polymerization of the incoming fluoromonomer prevents its penetration into the bulk and the other side of
the sample substrate as shown in Figure 4.5. This explains the hydrophilicity or good wick ability of surface due to the lower penetration of the fluoropolymer.

![Figure 4.5: Proposed surface schematic for hydrophobic surface and hydrophilic region of sample with and without pre-treatment](image)

4.5 Conclusion

In this study, dual finished fabric is achieved and the effect of preliminary treatments including pre-wash and plasma exposure of textile prior to monomer deposition to control this functionality are studied and reported. Washing removed the silicone softener layer from the surface of the fabric effectively facilitating enhanced hydrophilicity as well as hydrophobicity. Activation of the surface by atmospheric plasma exposure before the deposition of the monomer does not affect the hydrophobicity significantly but the improvement in the time of water absorption of the hydrophilic surface recommends this pre-plasma treatment of the polyester substrate.
4.6 References:


5. Study of effect of variations in atmospheric pressure plasma device parameters on the development of dual functional textile materials
Study of effect of variations in atmospheric pressure plasma device parameters on the development of dual functional textile materials

Abstract

A dual functional textile material was prepared with one side having hydrophilic and another with hydrophobic characteristics. Side specific atmospheric pressure glow discharge plasma treatment was used to generate active sites on the polymeric textile substrate and a hydrophobic surface was created by plasma induced surface grafting of perfluoroalkyl acrylate based polymers. Effect of variation in device and process parameters including RF power, time of plasma exposure and gap between electrodes on the hydrophobicity and hydrophilicity was studied. The hydrophobic surface was quantitatively analyzed by static contact angle measurements and qualitatively by AATCC tests for water/alcohol resistance. The hydrophilicity of sample was characterized by the measurement of time of absorption of water droplet from the hydrophilic surface. A textile material which absorbs water in less than 3 seconds being superhydrophobic on the other side is developed.

5.1 Introduction

Historically, polymers formed under plasma conditions were recognized as an insoluble deposit that provided difficulties in cleaning the plasma device. This insoluble deposit, however, is now being explored to give important applications mainly such as imparting hydrophilicity, hydrophobicity, superhydrophobicity,
adhesion enhancement\textsuperscript{19, 20, 21} among others. Moreover, non thermal plasma treatment of polymers leads to significant changes in their surface properties, in particular surface energy, wettability, activate surface to initiate polymer grafting, surface electric resistance, dielectric loss tangent, dielectric permittivity, catalytic activity, tribological parameters, gas absorption and permeability characteristics.\textsuperscript{22}

In this research, a dual functional textile fabric is produced utilizing the principles of side specific atmospheric pressure plasma treatment based on polymer surface activation producing initiation sites for surface grafting, and then plasma induced polymerization of the monomer on the surface. Novel development of a fabric that was hydrophilic on one side whereas hydrophobic on the other side was achieved. A snapshot of the resultant dual finished fabric is shown in Figure 5.1. The effectiveness of plasma treatment, that is the degree of hydrophilicity and hydrophobicity in the present case, largely depends on the device parameters such as RF power of operation, speed of fabric which governs the time of plasma exposure and the gap between RF and ground electrodes where the plasma is generated.
Figure 5.1: An image of untreated and treated fabrics. The untreated fabric absorbs water on both sides whereas the treated fabric absorbs water on one side only

5.2 Experimental

5.2.1 Materials

Polyester/ polyurethane blend knitted, dyed ready- to-use fabric provided by Polartec (formerly Malden Mills) with 90/10 composition was used for experiments. The fabric was given a delicate wash in washing machine with standard AATCC detergent, thoroughly rinsed until complete removal of the detergent and dried. Treated and untreated specimens (approximately 7” x 7”) were usually stored in conditioned atmosphere at 20±2 °C and 65±2 % relative humidity.

Industrial grade helium and ultrahigh pure argon 5.0 was used, supplied by Machine and Welding Supplies Co., North Carolina, USA.

Monomer based on perfluoroalkylacrylate derivates was used as obtained from Daikin (TG-10). The product was a clear to slight yellow liquid with chemical composition of 1, 1, 2, 2- tetrahydroperfluorodecyl acrylate (70–90%) and 1, 1, 2, 2-
tetrahydroperfluorododecyl acrylate (10- 30%). The structure of the monomer can be seen in Figure 5.2.

![Monomer Molecule Diagram](image)

**Figure 5.2: Three-dimensional structure of the monomer molecules. Green-Fluorine, Blue- Carbon, Red- Oxygen**

5.2.2 Equipment

The treatments were carried with the e' Rio™ atmospheric pressure plasma system APPR- 300- 13 from APJeT Inc. The machine uses RF electric fields, 1300 W @ 27 MHz RF/ 1 mm gap, to produce a unique, non-thermal, glow-discharge plasma that operates at atmospheric pressure and cooling requirement of 1 gpm @ 20 psi max.

The plasma assembly consists of an evaporator and applicator. The evaporator is a heated assembly that vaporizes the monomer that is to be applied to fabric samples. Heat is regulated by a logic controller that is connected to a thermo-coupler attached to the evaporator. The applicator acts as a heated nozzle to apply vaporized monomer to the
fabric sample. The heat is required to maintain the vapor property of the monomer. Heat is regulated by a logic controller that is connected to a thermo-coupler attached to the applicator. A snapshot of the whole assembly can be seen in Figure 5.3.

![Figure 5.3: APPR- 300- 13 Atmospheric Pressure Plasma assembly](image)

5.3 Methods

5.3.1 Plasma treatment

For the study, the washed substrate was attached flat on the ground electrode with double sided adhesive tape to avoid any plasma exposure on the untreated side. The method included activation of polymer substrate by initial plasma exposure, followed by deposition of monomer onto the knitted substrate laid on the electrode with assistance of pressure of argon gas; exposing the monomer to inert gas helium atmospheric plasma, thereby causing polymerization of the monomer species. This step was followed by
another short plasma exposure. The process parameters and sequence is summarized in Figure 5.4. The flow rate of the monomer was controlled using synchronous pump assembly from FMI pumps, while the flow rate of gases helium and argon was controlled with calibrated rotameters.

![Figure 5.4: Process parameters and sequence](image)

5.3.2 Characterization

Hydrophilicity of the surface of sample was characterized using a method based on the measurement of absorption time of water droplet onto the fabric. The drop was placed onto the fabric and the time for absorption of water was recorded with the help of a stopwatch. Absence of any specular reflection of water on the substrate surface confirmed the complete absorption of water by the fabric. Specular reflection is reflection without diffusion, in accordance with the laws of optical reflection, as in a mirror. The experiment was repeated five times and average of these readings was reported.
Hydrophobicity of the treated surface of the sample was characterized on qualitative as well as quantitative basis. AATCC Test Method 193-2005 was used to qualitatively determine the water/alcohol solution resistance of the treated sample. In this method, drops of standard test liquids, consisting of a series of water/isopropyl alcohol solutions with varying surface tensions (59.0 to 24.0 dynes/cm), are placed on the fabric surface and observed for wetting/wicking. The aqueous repellency grade is the highest numbered test liquid which does not wet the fabric. The test was repeated five times and the rating which was obtained the most number of times was reported.

Static contact angle measurement was done using Rame Hart manual contact angle goniometer (100-00- (115/220)). A calibrated syringe from Gilmont Instruments was used to place a drop of 0.016 ml of water on the hydrophobic surface of the fabric. ASTM D 5946-04 standard test method for corona treated polymer films using water contact angle was used for analysis. Two measurements each from the left side and the right side of the droplet were taken and the average of four readings was reported.
5.4 Results & Discussion

5.4.1 Effect of variance of power

Figure 5.5: Effect of RF power on (a) contact angle and time of absorption of water droplet (b) water/ alcohol repellency of the sample

The effect of variation in RF power on the plasma induced polymerization of fluoromonomers and the depth of penetration of fluoropolymers were studied. All parameters listed in Figure 5.4 were kept constant while the RF power was varied from
250 – 650W and the hydrophobicity as well as hydrophilicity of the samples were characterized as shown in Figure 5.5. From Figures 5.5(a), it is interpreted that as the RF power increases, the contact angle decreases with a difference of ≈2° for an increase in RF power by 100W, while highest time of absorption was taken by the sample which was treated with 400W plasma.

5.4.1.1 Hydrophobic surface

AATCC water/ alcohol resistance test rating for the sample increases from 1 to 5 as the RF power increases as seen in Figure 5.5(b). The AATCC test rating was 1 for sample treated with 250W generated plasma meaning that the sample is resistant to 2/98 alcohol/water solution. Test ratings 4 and 5 imply the resistance of fabric to 20/80 and 30/70 alcohol/water solution corresponding to the surface tension of 33.0 and 27.5 dyne/cm respectively. Figure 5.5(a) depicts the decrease in contact angle by 5° with the increase in RF power from 250-650W. This infers that the resistance of the sample to alcohol penetration increases but the contact angle which is a function of surface energy decreased. Higher RF power generates high density of ionized species which activated the substrate polymer beyond the surface into the bulk resulting in ‘through grafting’. In ‘through grafting’, the grafted polymer had penetrated all the way through the substrate and not concentrate at the surface. But the APJeT plasma device used for treatment allows only side specific treatment, allowing the grafting to take place till a certain fabric thickness but not through to the other side. The schematic depicted in Figure 5.6 explains the rationalization speculated for the decrease in contact angle observed.
5.4.1.2 Hydrophilic surface

The measure of time of absorption of water droplet by the hydrophilic surface gives an estimation of the degree of hydrophilicity of the sample. With the increase in RF power, the time of absorption increased initially till 400W, thereafter, a decrease in time of absorption was observed with increase in RF power as shown in Figure 5.5(a). The energy density of activated species increased at higher RF power values. Absorption of water depends on the rate of diffusion of water from the surface to the bulk of the sample. The rate of diffusion of water is controlled by the presence or the absence of fluoropolymers. Water diffuses at a very slow rate in presence of fluoropolymers, because the surface tension of these polymers is 10-20 dyne/cm² thus repelling any incoming water (73 dyne/cm). Figure 5.6 represents a schematic explaining the rationalization for the trend of hydrophilicity observed.

![Schematic of proposed fabric cross section after treatment at various RF power](image)

**Figure 5.6: Schematic of proposed fabric cross section after treatment at various RF power**
5.4.2 Effect of variance of time of plasma exposure

Figure 5.7: Effect of time of plasma exposure on (a) contact angle and time of absorption of water droplet (b) water/ alcohol repellency of the sample

The effect of variation in exposure time of plasma on the polymerization of fluoromonomers and on the depth of penetration of these fluoropolymers was studied. Three different exposure times corresponding to low (3 sec), medium (10 sec) and high (30 sec) were used for this study. All parameters listed in Figure 5.4 were kept constant
while the exposure time was varied from 3-30 sec and the hydrophobicity as well as hydrophilicity of the samples was characterized, results shown in Figures 5.7(a) and 5.7(b). From Figure 5.7(a), it is interpreted that as the exposure time increases, the contact angle decreases with a difference of $\approx 2^\circ$ for an increase in exposure time by 10 times, while hydrophilicity decreases with increase in exposure time almost linearly.

5.4.2.1 Hydrophilic surface

The time of plasma exposure refers to time of pre-treatment with plasma as well as the final plasma treatment after the monomer deposition. The time of absorption was least for the smallest duration of plasma treatment, increasing mostly linearly with time. For the low exposure time (3 sec), the time of absorption of water droplet was 2.27 sec on an average, whereas the water droplet was very difficultly absorbed on the substrate that is plasma treated for 30 sec. Higher treatment time corresponds to higher contact time of the sample surface with plasma which suggests that more number of sites are activated for initiation of plasma induced polymerization. Higher numbers of fluoropolymer chains reduce the ability of water diffusion, thus taking a longer time to absorb the water.

5.4.2.2 Hydrophobic surface

The graph in Figure 5.7(b) shows that the AATCC water/alcohol test rating for 3 and 10 sec exposure time is 5 implying that the surface was resistant to 30/70 alcohol/water solution with a surface tension of 27.5 dyne/cm. At 30 sec exposure time, the rating increased to 6 indicating the resistance of the fabric to 40/60 alcohol/water solution with a surface tension of 25.4 dyne/cm. The contact angle was $151^\circ$ for both 3 and 10 sec
plasma treatment time, but decreased by $2^\circ$ for 30 sec of plasma treatment. The decrease in contact angle suggests that less fluoropolymer chains were present on the surface to reduce the surface tension indicating the advent of ‘through grafting’ along with decrease in ‘surface grafting’. This can also verified by the plummeting hydrophilic response of the other side as indicated in Figure 5.7(a).

5.4.3 Effect of variance of electrode gap

![Graph showing the effect of gap between electrodes on contact angle and time of absorption of water droplet.](image)

**Figure 5.8:** Effect of gap between electrodes on (a) contact angle and time of absorption of water droplet (b) water/alcohol repellency of the sample
The gap between the RF and ground electrode was varied and its effect on the hydrophilic and hydrophobicity was studied. From Figures 5.8(a) and 5.8(b), it is apparent that the time of absorption of water droplet (hydrophilicity) was not significantly affected by variation in gap between electrodes, whereas it played a vital role in case of hydrophobic surface generation. A difference of 0.0475” (1.2 mm) in the gap between the electrodes resulted in a difference of more than 30° in contact angle.

5.4.3.1 Hydrophobic surface

Figure 5.8(b) shows that the AATCC water/alcohol resistance test rating increased from 2 to 5 for the increase in electrode gap from 0.09 to 0.1375 inch. This infers that the surface tension of the fabric substrate was reduced from 50.0 dyne/cm to 22.5 dyne/cm for higher electrode gap.\(^{25}\) From Figure 8, it can be seen that the contact angle was 120.5° for the lowest electrode gap of 0.09 inch which gradually increased to 151.25° for 0.1375 inch electrode gap making it superhydrophobic.\(^{28}\) The plasma distribution during exposure is affected by the electrode gap.\(^{29}\) If the gap is larger, the surface activation rate in the center part of the substrate will be faster than at the edge. Further, if the gap is made smaller, the etching rate in the edge of the substrate surface will be higher than in the center, which results in non-uniform activation of the surface by helium plasma and correspondingly uneven polymerization of fluoromonomers. This proposes that the contact angle was low for lower electrode due to insufficient initiation sites produced by helium plasma to polymerize the incoming monomer to give high contact angles; whereas higher gap between electrodes produced sufficient amount of active sites to polymerize
fluoromonomers to give high contact angles. The phenomenon of non-uniform plasma distribution is depicted in Figure 5.9.

![Diagram of plasma chamber with RF generators, matching units, and substrate samples at different electrode gaps]

**Figure 5.9: Side view of the plasma chamber with the substrate sample at (a) lower and (b) higher electrode gap**

5.4.3.2 Hydrophilic surface

The water droplet took 1.39 sec to completely diffuse into the bulk of the hydrophilic side when the electrode gap was 0.09 inch and 2.27 sec for 0.1375 inch electrode gap as seen from Figure 5.8(a). This slight increase in the time of water droplet absorption is speculated to be due to the decrease in rate of diffusion resulting from the obstruction by the fluoropolymer chains. Overall, the effect of change in gap between electrodes on the hydrophilic side is very trivial.

5.5 Conclusion

In this study, dual finished fabric is achieved and the effect of variations in plasma device parameters such as RF power, gap between the RF and the ground electrodes and stage
speed that is the time of plasma exposure to control this functionality is studied and reported. At the RF power of 300W, a contact angle of 153.25° with surface tension of 27.5 dyne/cm for the hydrophobic surface and an absorption time of 5.13 sec was reported. Best conditions of dual functionality were obtained with 300W plasma power. Low amount of exposure time is recommended as the hydrophilicity of the sample was chiefly affected at higher plasma exposure times, although a trivial difference in hydrophobicity was observed. Due to uneven distribution of plasma when the electrode gap is arrow, a wider electrode gap is suggested for further treatments. The contact obtained for 0.1375 inch electrode gap was 151.25° and the surface tension of the hydrophobic surface was reported to be less than 27.5 dyne/cm, whereas the hydrophilic face absorbed water in 2.27 sec.
5.6 References


(AATCC Technical Manual, 2006)


6. Development of novel dual functional textile materials by atmospheric plasma polymerization
Development of novel dual functional textile materials by atmospheric plasma polymerization

Abstract

Development of multi functional textile material which possesses coexisting water absorbing as well as water repellent surfaces is successfully attempted. Atmospheric pressure glow discharge plasma generated from RF power was used for surface activation and cross-linking of deposited perfluoroacrylate monomer by activated species in inert gas. Side specific plasma induced polymerization of fluorine based monomers resulted in superhydrophobic nanocoating of the textile material. Physical and chemical interaction of the fluoropolymer with the substrate was studied and the dual functionality of the material was confirmed from neutron imaging which distinguishes between hydrophobic and hydrophilic faces based on hydrogen presence at atomic level. AATCC standard test methods were used to quantify the superhydrophobicity and excellent water absorption characteristics of the treated material.

6.1 Introduction

Polymeric materials are generally chosen and developed for their bulk properties; however, the inert nature of most polymer surfaces creates challenges for applications where coatings must be applied. A widespread approach to tailor surface properties of polymer materials is to expose them to an electrical discharge or plasma to modify their surface chemistry. Functionalization of polymers with plasma allows the modification
of the surface layers down to few nanometers with chemically different atoms or functional groups to modify surface properties. Plasmas are generated by applying large amounts of energy to a gaseous state where neutral atoms or molecules of the gas are broken up by energetic collisions to produce electrons, positively or negatively charged ions and other species. New environmental laws, as well as cost and quality aspects have motivated research on the application of plasma to textile materials in order to continuously improve the surface characteristics of a polymeric material. Numerous studies have focused on plasma-polymer surface interactions to impart water repellent surface, hydrophilic property, adhesion improvement, surface electrical property modifications among other applications.

However, an inherent ageing process affects any plasma treatment of polymer surfaces, due to the surface’s tendency to minimize its energy, which takes place within the first one or two monolayers of the surface. Textile material with co-existing hydrophilic as well as hydrophobic surface was developed in the present research as shown in Figure 6.1. These materials have extensive applications in polymeric membrane finishes, textile industry with concentration on sportswear, workwear and high-end tropical corporate wear in particular. This ageing effect is slowed down or may be completely avoided with the plasma induced surface grafting and cross-linking of water repellent polymers.
Figure 6.1: Dual functional cellulose (left) and poly (ethylene terephthalate) (right).

The area where water is absorbed on hydrophilic side is circled in red, whereas unabsorbed droplet of water is seen on hydrophobic side

6.2 Materials and equipment

Poly (ethylene terephthalate) (PET) in the form of a textile material- polyester/polyurethane blend knitted, dyed ready- to- use fabric provided by Polartec (formerly Malden Mills) with 90/10 composition was used for experiments. Cellulose in the form of 100% percent cotton fabric obtained Cotton Incorporated, Cary, NC with twill weave and density of 6.7 oz/yd² was used for treatments.

The fabrics were given a delicate wash in a washing machine with standard AATCC detergent, thoroughly rinsed until complete removal of the detergent and dried. Treated and untreated specimens (approximately 7’’ x 7’’) were usually stored in conditioned atmosphere at 20±2 °C and 65±2 % relative humidity.
Industrial grade helium and ultrahigh pure argon 5.0 was used, supplied by Machine and Welding Supplies Co., North Carolina, USA.

Monomer based on perfluoroalkylacrylate derivates was used as obtained from Daikin (TG-10). The product was a clear to slight yellow liquid with chemical composition of 1, 1, 2, 2- tetrahydroperfluorodecyl acrylate (70-90%) and 1, 1, 2, 2- tetrahydroperfluorododecyl acrylate (10-30%).

The treatments were carried with the e’ Rio™ atmospheric pressure plasma system APPR-300-13 from APJeT Inc. The machine uses RF electric fields, 1300 W @ 27 MHz RF/1 mm gap, to produce a unique, non-thermal, glow-discharge plasma that operates at atmospheric pressure and cooling requirement of 1 gpm @ 20 psi max. The plasma assembly consists of both the evaporator and applicator. A schematic of the device is shown in Figure 6.2.
6.3 Principle Methods

6.3.1 Surface Activation:
A range of physical and chemical processes can simultaneously occur in the plasma-polymer interaction. Conventionally, these interactions are driven by impact of species from the plasma with the species constituting the surface of the polymer. A number of species can be used in the plasma generation, mainly gases including O$_2^{24}$, air$^{25}$, N$_2^{26}$, PEG$^{27}$ and noble gases such as argon$^{28}$ and helium$^{29}$ or their mixtures. Depending on the type and composition of the gas in the discharge, the functional groups present on the polymer surface being treated, and the placement of the polymer sample in the discharge, the dominant effects of the plasma treatment can vary considerably. Chen et al.$^{30}$ used plasma as a pre-treatment step before graft polymerization of acrylamide on
polypropylene (PP) fabrics to enhance the long term water absorption of PP. In the current research, irradiation of helium gas plasma was used for treatment of polymeric textile substrates cellulose and polyester/polyurethane blend. Yasuda describes two types of reaction between species in the plasma and the polymer surface: (1) direct reaction of “activated gases” and (2) formation of free radicals and the subsequent reaction of the free radicals (with species from the plasma environment). 31,32

The pre-treatment with helium gas plasma in the present case, therefore sputters the surface physically, and chemically etches free radicals on the surface of the substrate. Physical sputtering is due to simple ion bombardment, while chemical etching is due to surface reaction33 as mentioned earlier. The phenomenon of modification of surface topography by plasma etching and the activation of the surface by formation of free radicals on the surface is depicted in Figure 6.3.
6.3.2 Monomer deposition

After the surface was physically sputtered and chemically etched, the monomer vapors were impinged on the activated surface of fabric. The plasma assembly as shown in Figure 6.2 consists of an evaporator and applicator which allows the vaporization of the incoming perfluoroacrylate monomer at a flow rate of 0.45 ml/min with the deposition of $\approx 0.095$ milliliter of monomer per square meter of the sample substrate. Heat is regulated by a logic controller that is connected to a thermo-couple attached to the evaporator. Monomer is pumped into the evaporator chamber that contains a substrate. The substrate provides more surface area for monomer to spread across as vaporization occurs. Argon gas at the flow rate of 1.0 SLPM (Standard Liters Per Minute) is passed through the
evaporator to move the monomer vapor from the evaporator to the applicator. Argon gas species are inert and do not interact with perfluoroacrylate monomers and therefore less likely to alter the characteristics of monomer before deposition on the substrate and subsequent polymerization. The applicator acts as a heated nozzle to apply vaporized monomer to the fabric sample. The heat is required to maintain the vapor property of the monomer which is regulated by a logic controller that is connected to a thermo-coupler attached to the applicator. The textile substrate is laid on the ground electrode which is cooled with the help of water further accelerating the monomer vapors to condense onto the substrate. After the monomer is applied the sample travels into the plasma field for further processing. Figure 6.4 illustrates the phenomenon of monomer deposition.

![Figure 6.4: Monomer deposition- physical and chemical interactions of fluoromonomer with sample substrate](image)

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6.3.3 Plasma induced polymerization and crosslinking

Free radicals formed on the surface of the substrate exposed to plasma were utilized to initiate graft polymerization in a manner similar to pre- irradiation grafting as some studies in the past.\textsuperscript{34, 35} Non-thermal plasma can be applied for effective stimulation of more conventional chain polymerization processes such as plasma initiated polymerization of methyl methacrylate with a production of practically important polymethyl methacrylate.\textsuperscript{9} In the present study, plasma induced grafting of perfluoroacrylate onto the substrate surface also occurred with the same mechanism. After the initiation, the propagation reaction of the grafted intermediate took place and perfluoroacrylate polymer was attached to the surface of the substrate resulting in ‘surface grafting’. It was worthwhile to note that the substrate was highly water absorbent before the final plasma treatment and hydrophobicity was imparted only after this plasma induced polymerization of the monomer and the crosslinking. Moreover, the effect of surface grafting on the bulk properties of the substrate polymer and the effect of substrate polymer on the properties of the grafted surface layer was very crucial in the present study. The surface grafting of perfluoroacrylate was limited to a certain depth and penetration to the other surface was strictly controlled. The penetration of grafted fluoro copolymer can interfere with the hydrophilicity of the second face in particular. Hydrophobicity is imparted to the polymer substrate due to the reduction in surface tension by the perfluoroacrylate chains.

By exposure to 650W atmospheric pressure glow discharge plasma of helium @30 SLPM for 6 seconds, cross-linking of the fluoropolymer and fluoropolymer as well as
fluoropolymer and polymer substrate took place enhancing the durability of the nanolevel coating on the substrate. The surface chemistry and physical illustration is shown in Figure 6.5.

**Figure 6.5:** Physical and chemical depiction of polymerization and crosslinking of perfluoroacrylate
6.4 Results and Discussion

6.4.1 Dual functionality

The dual functionality of textile material with coexisting hydrophilic as well as hydrophobic property on the opposite faces was characterized with help of neutron imaging equipment. The Thermal Neutron Imaging facility set up at the PULSTAR reactor at North Carolina State University was used for this purpose. The PULSTAR is an open pool type light water moderated research reactor with a full power of 1-MWth and fuel that is enriched to 4% in U-235. Unlike x-rays, neutrons interact with various materials with very specific cross-sections largely independent of atomic number (Z) of the material. Examples of high absorption cross-section materials include hydrogen and boron while iron has a lower neutron cross-section. Hence with neutron imaging it is possible to image materials composed of light nuclei even if they are present in minute quantities in the specimen. This varied nature of interaction of neutrons with matter is due to the fact that neutrons being neutral interact with the nucleus of atoms unlike the photons which interact mainly with electrons. Thus, due to higher absorption, neutrons are scattered the most and produce bright spot on the image.

In the present study, the surface of poly (ethylene terephthalate) substrate is selectively grafted with perfluoroacrylate copolymer. Neutron imaging was used to substantiate the dual functionality of treated PET. The sample fabric was mounted between two aluminum bars and folded in such a manner that on one side the hydrophilic surface faces the ground (left side of the image) and the hydrophobic side faces the ground on the
other. Water was then poured from both the sides. This water rolls off and accumulates in the center of the sample from the hydrophobic side, whereas it is absorbed completely by the hydrophilic surface. Since, neutrons produce brightest spots in hydrogen rich areas, the water droplet and the hydrophilic portion wetted with water are seen prominently in the neutron image in Figure 6.6.

![Figure 6.6: Scanned neutron image of the dual functional sample fabric](image)

Table 6.1: Characterization results of the dual functional samples.

<table>
<thead>
<tr>
<th>Fabric Type</th>
<th>Hydrophilicity</th>
<th>Hydrophobicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time of absorption [sec]</td>
<td>AATCC rating</td>
</tr>
<tr>
<td>PET/Lycra</td>
<td>2.27</td>
<td>5</td>
</tr>
<tr>
<td>Cellulose</td>
<td>1.31</td>
<td>5</td>
</tr>
</tbody>
</table>
6.4.2 Quantitative analysis of hydrophobic surface

Static contact angle measurements were done using Rame Hart manual contact angle goniometer (100- 00- (115/ 220)). A calibrated syringe from Gilmont Instruments was used to place a drop of 0.016 ml of water on the hydrophobic surface of the fabric. ASTM D 5946- 04 standard test method for corona treated polymer films using water contact angle was used for analysis. Two measurements each from the left side and the right side of the two drops were taken and the average of four readings was reported for statistical significance. As seen in Table 6.1 the average contact angle observed for the hydrophobic surface of the PET substrate was 156.5° and for cellulose substrate was 165° defining these as superhydrophobic.36

6.4.3 Qualitative analysis of hydrophobic surface:

AATCC Test Method 193- 2005 was used to qualitatively determine the water/ alcohol solution resistance and the respective range of surface tension of the treated sample. In this method, drops of standard test liquids, consisting of a series of water/ isopropyl alcohol solutions with varying surface tensions (59.0 to 24.0 dynes/ cm), are placed on the fabric surface in order of decreasing surface tension and observed for wetting/ wicking. The aqueous repellency grade is the highest numbered test liquid which does not wet the fabric.37 The test was repeated five times and the rating which was obtained maximum number of times was reported considering statistical significance. As shown in Table 6.1, AATCC rating 5 was obtained for the treated polyester and cellulose which approximates the surface tension of fabrics to be in the range of 27.5 dynes/cm and 25.4 dynes/ cm at 25°C.37
6.4.4 Qualitative analysis of hydrophilic surface

Hydrophilicity of the surface of sample was characterized using a method based on the measurement of absorption time of water droplet onto the fabric. The drop was placed onto the fabric and the time for absorption of water was recorded with the help of a stopwatch. Absence of any specular reflection of water on the substrate surface confirmed the complete absorption of water by the fabric. By specular reflection one means the reflection without diffusion, in accordance with the laws of optical reflection, as in a mirror.\textsuperscript{38} The experiment was repeated five times and average of these readings was reported. The average time of absorption for hydrophilic side of polyester sample was 2.27 sec and of cellulose was reported 1.31 sec as seen in Table 6.1. A textile substrate with a wetting time less than or equal to 3 seconds is termed as superhydrophilic.

**Summary:**

Wettability is a fundamental property of a solid surface, which plays important roles in daily life clothing, industry, and agriculture. Functional surfaces with special wettability have aroused much interest because of their imperative advantages in miscellaneous applications such as antifogging and self-cleaning, inhibition of phenomena like contamination, snow sticking, erosion, and even current conduction.\textsuperscript{39, 40, 41, 42} A dual finished textile material with coexisting hydrophobic and hydrophilic surfaces was successfully developed by atmospheric pressure plasma treatments and sequence of following steps: (1) Physical etching and chemical sputtering, (2) Condensation of
vaporized monomer on the substrate, and (3) Plasma induced polymerization and crosslinking. Dual nature of the material was clearly seen in the neutron image and results were substantiated by AATCC test methods.
6.5 References


7. Conclusion and Summary
Conclusion and Summary

The development of dual functional textile material with co-existing hydrophobic and hydrophilic surfaces was successfully achieved. Apparels made from such high performance textile will have the ability to control moisture and expel human sweat to the outside environment effectively as well as repel any undesired external liquid contaminants. Atmospheric pressure plasma jet (APPJ) device from APJeT, Inc. was used for site specific treatment of polymeric textiles. The dual functionality of the textile material at sub- molecular level was confirmed with neutron imaging technique. The primary process sequence can be summarized by the chart in Figure 7.1.
Figure 7.1: Primary process sequence to achieve dual functionality

Each process and device parameter has significant effect on the hydrophobicity as well as hydrophilicity of the polyester/polyurethane fabric. All the process and device parameters including flow rates of (1) monomer, (2) helium and (3) argon, (4) RF power, (5) time of plasma exposure to the fabric, (6) gap between electrodes, (7) prewashing the material before treatments and (8) preliminary plasma treatment were optimized according to the results obtained for water absorption as well as water repellency qualitatively and quantitatively.
Plasma processing as a dry and easily controllable technology is a potential candidate for innovations along these lines of side selective treatments. Such kind of dual functional intelligent wear has enormous applications in outdoor sportswear, comfort-wear, workwear and corporate wear especially for tropical climate.