

ABSTRACT

MAZLOUMPOUR, MARYAM. Durable Nanolayer Graft Polymerization of Functional Finishes Using Atmospheric Plasma. (Under the direction of Dr. Ahmed El-Shafei and Dr. Peter J. Hauser).

Various applications of atmospheric pressure plasma were investigated in conjunction with different chemistries on nonwoven materials including spunbond polyester (PET) and spunbond polypropylene for fuel separation and antimicrobial functionalities.

Hydrophobic/Oleophobic properties were conferred on nonwoven polyester (PET) via plasma-induced graft polymerization of different hydrophobic non-C8 perfluorocarbon chemistry including perfluorohexylethylmethacrylate, perfluorohexylethylacrylate, allylpentafluorobenzene, pentafluorostyrene, or 1,3-divinyltetramethyldisiloxane in the vapor form using both *in-situ* and *down-stream* plasma configurations. Different nanolayers of the grafted polymer were furnished on nonwovens to generate surfaces with different level of wettabilities for medical applications and water/fuel separation. The effect of various hydrophobic chemistry, different plasma conditions, and plasma device parameters including plasma power and plasma exposure time were studied and the performance was characterized by measuring the contact angle and the wettability rating against liquids with broad range of surface tensions.

Vapor deposition of 2-(perfluorohexyl)ethyl methacrylate and pentafluorostyrene on nonwoven PET followed by plasma-induced graft polymerization was investigated for possible use in water/fuel separation. Different nanolayer thicknesses (80-180nm) of the grafted polymer were achieved to generate surfaces with different wettabilities for water/fuel separation of different fuel compositions. The effect of different plasma conditions and device parameters including the flow rate of monomers, power of the device, and time of plasma exposure on the separation of different fuels was studied and characterized by measuring the surface energy of the treated substrates. The surface chemistry and morphology of the treated samples were characterized using XPS, SEM and TOF-SIMS techniques which confirmed the grafting of monomer onto the substrate.

Furthermore, spunbond nonwoven polypropylene fabric, commonly used for hygienic products, was treated with diallyldimethylammonium chloride (DADMAC). Atmospheric pressure glow discharge plasma was used to induce free radical chain polymerization of the ADMAC monomer, which conferred a graft polymerized network on the fabric with durable antimicrobial properties. The effect of different DADMAC concentration, and plasma conditions including the RF power and the time of plasma exposure were studied and the optimum treatment conditions were identified by calculating the surface charge density on the treated fabrics. The presence of poly-DADMAC on the polypropylene surface was confirmed using SEM, FT-IR and TOF-SIMS. Antibacterial performance was investigated using standard test methods (AATCC TM 100) for both gram positive and gram negative bacteria. The antimicrobial results showed 6 log reductions in the bacterial activities of *K. pneumoniae* and *S.aureus*, which was unprecedented using a plasma-induced graft polymerization approach.

Durable Nanolayer Graft Polymerization of Functional Finishes Using Atmospheric Plasma

by
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Chapter 1 Introduction

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. Plasma processes can be conveniently classified into four core processes:

- Etching
- Activation
- Grafting
- Deposition

In grafting, an inert gas 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, an initiation reaction occurs and chain polymerization results due to a propagation reaction. Hydrophobicity can be imparted to a fabric substrate by either plasma induced grafting or plasma deposition of low surface energy compounds on the textile substrate. In this research this process occurs in a two-step process: 1) creation of radicals at the fiber surface in inert plasma (e.g. helium) and 2) reaction of these radicals with unsaturated monomers (plasma grafting).

Textiles have been used for medical and surgical applications, including surgical gowns, bed sheets, etc. However, because of the large surface area and the ability of some of textile materials to absorb and maintain moisture, they are more susceptible to bacterial growth [1]. With the threat of infectious diseases in hospitals and the likelihood of disease transmissions [2], from blood-borne pathogens [3,4] such as HIV (human immunovirus) [5] and hepatitis, and air-borne viruses such as SARS among patients, nurses, doctors, and other employees, textile materials should be treated so that they possess antimicrobial, fluid repellent [6,7] and antiviral functionality. The Occupational Safety and Health Administration has issued a statement that protective garments for health care workers must provide protection against blood and other infectious materials [5,8].

Antimicrobial and water and oil repellent finishes have been studied and achieved on textile materials for surgical applications such as surgical gowns using textile wet processes [9]. However, textile wet processes have some disadvantages such as huge water and energy consumption, release of waste downstream and the enormous cost of waste treatment [10,11]. In addition, textile wet processes often change the bulk properties of materials. With all this in mind, plasma treatments of textile materials were investigated and found to change the surface properties of materials while the bulk of the materials remain intact. Plasma treatments offer many advantages over wet processes including being environmentally friendly, cost effective, and uniformity treatments.

In the textile field, non-thermal plasma has been used mostly to modify wetting characteristics including hydrophilicity [12-21], hydrophobicity [22-29] and oleophobicity [28, 30] and adhesion properties of fibers [31-38]. Also in the area with more focus on textiles, dyeing and printing, surface cleaning (desizing), inactivation of microorganisms (sterilization) [39-42], modification of physical properties of fibers (optical, mechanical and electrical properties), and shrink-proofing of wool [43] has been reported. Many researchers have been interested in using plasma for imparting antimicrobial properties on textiles, mostly by employing low-pressure plasma under vacuum conditions [44-48] and following the technology advancement, atmospheric pressure plasma has also been used recently for biocidal finishing of textiles [49-50] and other types of changing fiber surface properties [51,52]. Table 1-1 presents some examples of properties that plasma treatment can impart to textile substrates.

Plasmas offer significant advantages over conventional wet chemical processes for surface chemistry modifications of polymers, textiles, and other materials. Many commercial plasma processes perform surface functionalization, graft and plasma polymerization, cleaning, and etching of a large variety of substrates. Plasma process have the advantages of modification of surface properties without altering the bulk characteristics, using low quantities of monomeric compounds which makes the process more economical and also having less environmental impact. Table 1-2 lists some advantages of plasma processing over wet processing for atmospheric pressure plasma.

Table 1-1 Properties of textile materials that can be modified by plasma treatment [72]

Property	Material	Treatment
Wettability	Synthetic fibers	Oxygen, air, NH ₃
Hydrophobicity	Cellulosic fibers, wool, silk, PET	Fluorocarbons, SF ₆ , Siloxanes
Dyeability	Synthetic fibers, wool, silk	Oxygen, air, nitrogen, argon, SF ₆ , acrylates
Flame retardancy	Cellulosic fibers, synthetic fibers	Phosphorous compounds
Softness	Cellulosic fibers	Oxygen
Wrinkle resistance	Wool, silk, cellulosic fibers	Nitrogen, Siloxanes
Antistatic	Synthetic fibers	Chloromethylsilanes, acrylates
Adhesiveness	Synthetic fibers, cellulosic fibers	Air, oxygen, nitrogen, argon, acrylates
Antibacterial/Antimicrobial	Cellulosic fibers, synthetic fibers	Oxygen, argon
Bleaching	Wool	Oxygen
Antifelting	Wool	Oxygen, air

Most of these processes are performed in vacuum systems. Non-thermal atmospheric pressure plasmas offer the apparent advantages of eliminating the cost and complexity of operation under vacuum. With all this in mind, high density non-thermal plasma offers great potentials in revolutionizing the textile industry.

Non-thermal plasmas in vacuum environments have been widely used for materials processing applications for the past 30 years [53]. However, these applications have been restricted to the development of semiconductor devices, magnetic media or deposition of energy efficient films for certain types of glass. In these applications, plasmas are used because they provide a loaded foundation of chemically active species that react with a surface to produce secondary, short-lived chemical precursors required for thin film deposition. What makes plasma a very intriguing process is the fact that it operates at low temperature and has a nondestructive nature for material treatments.

Plasmas are usually used as a chemical reactor to furnish short-lived, energetic species that are produced by the interaction of electrons generated in the plasma with the gas being used for generating the plasma. Ions always live in any type of plasma and may boost the surface reactivity such as in etching processes [54], or they may generate undesirable side effects such as surface damage [55].

Table 1-2 Plasma processing advantages over conventional wet processing [72]

Manufacturing operation	Conventional processing	Plasma processing
Handling and storage of bulk chemicals	Yes	No
Mixing of chemicals/formulation of baths	Yes	No
Use of water	Heavy	None or very low
Raw materials consumption	High	Low
Drying ovens and curing operation	Yes	No
Need for solvents, surfactants, acids	Yes	No
Number of process steps	Multiple	Single
Energy consumption	High	Very low
Waste disposal/recycling needs	High	Negligible
Environmentally costly	Yes	No
Equipment footprint	Large	Small
Manufacturing versatility	Limited to single or few process options	Can be highly flexible with wide range of available processes
Innovation potential	Moderate	Very high

Chapter 2 Literature Review

2.1 Introduction to plasma

Plasma is the fourth state of the matter and a neutral medium of positive and negative particles, and electrons [56]. The term plasma was first used by Lewis Tonks and Irving Langmuir in 1929 [57] explaining the charged particles they observed in their studies concerning oscillations in the inner space of an electric discharge. Later this term has found broader applications mostly to describe a state of matter (the 4th state) in which a large number of atoms and/or molecule, ions, radicals and other electrically charged, excited and neutral particles exist with specific characteristics and collective behavior mainly due to the long-range coulombic interactions. On average a plasma medium is considered electrically neutral since any charge unbalance results in an electric field which tends to move the charges and neutralize the opposite charges. It is expected that more than 99.9 % of the whole universe is in the plasma state: gaseous nebulae, interstellar gas [58], stars and our sun with extremely high surface temperature (2000- 22000 K) which is entirely plasma [59, 60]. Overall plasmas can be generated in laboratories via different techniques including mechanical (similar to adiabatic compression), thermal (electrically heated furnaces), chemical (exothermic reactions), radiant (high energy electromagnetic and particle radiations), electromagnetic (arcs, corona, direct current (DC), radiofrequency (RF), microwave (MW), electron cyclotron resonance (ECR) discharges) energies and also by the combination of these methods similar to what happens in an atomic explosion [61].

Considering the plasma as the fourth state of the matter mainly means some phase transition happens in plasma creation providing it with unique features which distinguishes it from an ideal gas. One of these features is that plasma particles have interactions with each other because of the electromagnetic coupling and perturbations exist in the medium, meanwhile, and specifically in non thermal plasma, different temperatures are associated with different species since the plasma is a non-equilibrium thermodynamic regime. The fundamentals of plasma physics is extensively discussed in reference textbooks [62-66].

2.2 Plasma Classifications

In terms of plasmas thermodynamic properties, plasmas are classified as either thermal plasmas (TPs) or non-thermal plasmas (NTPs), which can be referred to as equilibrium (hot) or nonequilibrium (cold) plasma, respectively.

Hot and thermal plasmas are characterized by an equilibrium state, where the temperature of the three components of the plasma, electrons, ions and neutrals are equal: i.e., $T_e \approx T_i \approx T_n$, the pressure exceeds 103 Pa and the electron temperature is in the order of 10^4 °K and higher. The temperatures of thermal plasmas are several thousand degrees and the collision frequency is high enough with respect to the particle transit time in the plasma length which allows the electron to lose energy in favor of ions which provide thermalization of different particles to the thermodynamic equilibrium temperature. The ionization degree (number of ions over total plasma particles) is close or equal to 100%. Flames, certain arc discharges, plasma spraying and nuclear explosions are examples of thermal plasmas. This type of plasma generates huge values of energy in which the ionized gas at very high temperature is able to remove, fuse or thermally modify a material. The applications of thermal plasma depend on the temperature, gaseous reagents and small particles injected into it (plasma spraying, fusion or refining in metallurgy). The range of applications include different activities such as extraction of metals, the refining/ alloying of metals/alloys, synthesis of fine ceramic powders, spray coatings and also treatment and destruction of hazardous wastes. Recently a type of thermal plasma has found applications in areas of nanoparticle synthesis and fast quenching chemistry processes. In working with metals and thermally stable inorganic materials, hot plasma is the heat source for melting and remelting, it is also more economical than laser and electron beam for cutting and welding. Hot plasma sprayed coating has had great progress in the last twenty years in which the powder is injected into the plasma jet at desired locations relative to the plasma nozzle. However the destructive nature of this type of plasma makes it not well suitable for most materials processing applications [61].

Non-thermal plasmas are called “non-equilibrium” plasmas mainly because they are characterized by a large difference in the temperature of the electrons relative to the ions and neutrals. Since the electrons are enormously light, they move much faster and have almost no

heat capacity. In these plasmas, $T_e \gg T_i \approx T_n$. Ionization is maintained by the impact of electrons (which may have temperatures ranging from 0.1 to more than 20eV with neutral species, producing additional electrons and ions. These plasmas are typically maintained by the passage of electrical current through a gas [67-69].

Non-thermal plasma include low pressure DC and RF discharges from fluorescent illuminating tubes or dielectrical barrier discharges that exist at either atmospheric or low pressures. Cold low pressure plasmas (LPPs) are found in the range between 10^{-6} and 1 Pa and neutral densities between $10^{-5} n_0$ and $10^{-2} n_0$ (n_0 is the Loschmidt number [70]) while cold atmospheric pressure plasmas (APPs) such as radio frequency plasma are characterized by electron number densities of the order n_0 with an energy of 1-10 eV. Since the electrons in the plasma medium cannot heat large particles such as molecules, the temperature of the generated gas is almost at room temperature and electrons have the main role in forming the plasma chemistry. They are responsible for atomic/molecular excitation, disassociation and generating radicals and metastable states. LPPs have always been considered as techniques with great value in fundamental research however since their installations have the challenges of procurement and maintaining massive vacuum reactors, the new trend is more focused on developing atmospheric pressure plasma techniques. The APPs systems are regarded as providing devices with better substrate accessibility, high throughput and the ability to design continuous or semi-continuous processes. However atmospheric pressure plasma chemistry is more difficult to control and a variety of chemical and physical reactions such as plasma polymerization is imposed during processing. Different principles based on the different energy sources are applied to generate the NTPs. Micro plasmas, coronas , dielectric barrier discharges, electron cyclotron resonance ion source, and microwave plasma are examples of different methods for non-thermal plasma generation [71].

2.3 Properties of plasma

2.3.1 Plasma Chemistry

Plasma is a medium with different constituent species mostly resulted from the disassociation of molecules. The energy required to break down molecules into various species is listed in table 2-1. The dissociation energy is generally lower than the ionization

potential of the molecules; therefore there is always enough dissociation in ionized gas. These dissociate particles in the plasma are of much importance since they are the main source of interaction and reaction with the substrate surface. Figure 2-1 shows the approximate densities and temperatures or energies of the plasma particles in common low pressure plasma. Some atoms and molecules can contain an extra electron and therefore the ability to create negative ions. Furthermore the atoms and molecules could be excited from their ground state configurations to higher energy levels, usually in collisions with electrons. The additional energy from excitement released as light ranges from infrared to the ultra violet and this light emission can also provide chemical changes on the contact surface. The metastable state of the atom or molecule can play an important role in plasma transition and plasma chemistry when there is a delay in light emission [65].

Table 2-1 Energy characteristics of some atoms and molecules [72]

Atom or molecule	Ionisation potential (eV)	Electron affinity (eV)	Metastable energy level (eV)	Lowest excitation energy (eV)	Dissociation energy (eV)
H	13.6	0.75		10.2	
He	24.6		19.8	21.2	
O	13.6	1.5	1.97	9.2	
F	17.4	3.5		12.7	
Cl	13.0	3.6		8.9	
H ₂	15.6			11.5	4.5
O ₂	12.5	0.45	1.2	7.9	5.1
Cl ₂	13.2	2.5			2.5
C ₆ H ₆	9.6				

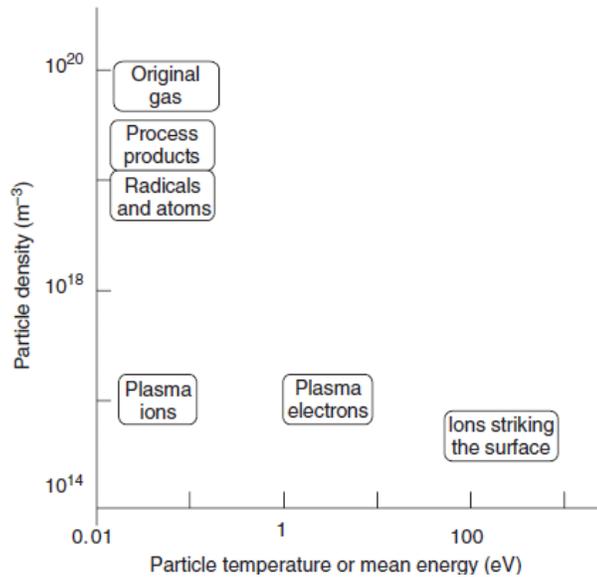


Figure 2-1 Densities and temperatures for the constituent species in low pressure plasma [72]

The plasma volume is a very dynamic medium, all the species are in constant motion of rotating and vibrating, however the motions have the lowest energy state that could be increased by the collision of particles. Broadly speaking there are three different types of collision between the constituents:

Elastic collision: the momentum is distributed between the colliding particles and the total energy of the particles after collision is unchanged.

Inelastic collision: the momentum distributed between the colliding particles but the kinetic energy transfers to the internal energy for involved particles. The result is dissociation, excitation or even ionization of participants.

Superelastic collisions: The momentum is redistributed between the particles and the internal energy form participants transferred to the total kinetic energy of both colliding species.

Table 2-2 lists some of the important types of reactions that occur in plasmas where there are mostly two particles participating in collisions. For the particles with a metastable state usually collision happens before radiation and the electronic energy is transferred to another involved species in the plasma. This energy is sometimes enough to ionize a neutral atom or molecule with lower ionization potential which is called Penning ionization. This situation is

very common in inert gas since they have large long-lived metastable states which have an important role in the kinetic behavior of plasmas [72].

Table 2-2 Some of the possible reactions of plasma constituents in the plasma medium [61]

Reaction type	Name		
Electron impact	Ionisation	$e + A \rightarrow 2e + A^+$	
	Dissociation	$e + AB \rightarrow e + A + B$	
	Dissociative ionisation	$e + AB \rightarrow 2e + A + B^+$	
	Dissociative attachment	$e + AB \rightarrow A^- + B$	
	Electronic excitation	$e + A \rightarrow e + A^*$	
	Ro-vibrational excitation	$e + AB \rightarrow e + AB (v, j \geq 1)$	
	Momentum transfer	$e + A \rightarrow e + A$	
Neutral	Dissociation	$AB + M \rightarrow A + B + M$	
	Penning Ionisation	$Am + B \rightarrow A + B^+ + e$	
	Atom transfer	$A + BC \rightarrow AB + C$	
	Rearrangement	$AB + CD \rightarrow AC + BD$	
	Recombination	$A + B + M \rightarrow AB + M$	
	Energy transfer	$A^* + B \rightarrow A + B^*$	
	Relaxation	$A^* + B \rightarrow A + B$	
	Momentum transfer	$A + B \rightarrow A + B$	
	Ion	Neutralisation	$A^- + B^+ \rightarrow A + B$
			$A^- + BC^+ \rightarrow AB + C$
Associative detachment		$A^- + B \rightarrow AB + e$	
Charge transfer		$A^+ + B \rightarrow A + B^+$	
		$A^- + B \rightarrow A + B^-$	
Dissociative charge transfer		$A^+ + BC \rightarrow A + B + C^+$	
	Momentum transfer	$A^+ + B \rightarrow A^+ + B$	

The effect of the collision can be categorized based on the level of energy that is transferred, denoted here as K [73-74].

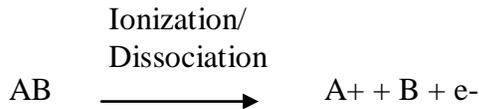
For $K > qV_i$, where q is the charge of the electron and V_i the ionization potential of the atom, the energy gain is more than the ionization potential so the electron is expelled from its orbital in its parent atom or molecule, yielding a new free electron while the atom (or molecule) becomes a positive ion:



The positive ion AB^+ is often unstable and dissociated into its constituents:

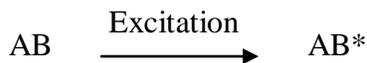


Where A and B are either free radical fragments or stable molecules. When ionization and dissociation occurs almost simultaneously, dissociative ionization occurs:



Where B is usually a free radical.

When the transferred energy is less than the ionization potential it may still be large enough to lift the electron from its ground state to an excited state ($qV_i > K > 0$):



It stays in the excited state for a very short period ($10^{-8} - 10^{-9}$ s) before returning to the ground state, releasing the excess energy as photons. This light emission ranges from infrared to the vacuum ultraviolet.

When $K = 0$, there is no transfer of energy so that electrons in the atom remain in the ground state. There is no change in the structure of the atom. The first two events, in which $K > 0$ and lead to ionization and excitation, are called inelastic collisions, whereas the last one is an elastic collision. The ionization potentials of some gases frequently used in plasma processing of material are summarized in Table 2-3. Helium has the highest ionization potential (24.5 eV), whereas oxygen is the lowest (12.3 eV). Hydrogen, nitrogen, and argon come second in the middle (15.4–15.7 eV). Helium has the highest ionization potential (24.5 eV), whereas oxygen is the lowest (12.3 eV). Hydrogen, nitrogen, and argon come second in the middle (15.4–15.7 eV). Because molecules consist of atoms, excitation can also take place at the vibrational and rotational levels of energy of the atoms, that is, internal energy for the vibration and rotation of atoms along the axis of a molecule. These energy levels are generally much lower than the energy levels of electrons in an atom. Accordingly, a low-energy electron, which cannot excite an atom electronically, can still excite a molecule by this energy transfer, giving rise to vibro-rotationally excited molecules. Other types of collisions in plasma are between ions and atoms or molecules, between molecules, and

between charged species. The number of collisions between ions and molecules, however, is much less than that between electrons and molecules, so that their effects in ionization process can be virtually disregarded, except for a phenomenon known as charge transfer. In non-equilibrium plasma, ionization of molecules by molecule-molecule collisions does not take place because extremely high temperatures are required. The effects of collisions between charged species in weakly ionized gas, i.e. non-equilibrium plasma, can be considered small, because the number of neutral species is predominant [76-78].

Table 2-3 Ionization potential for various gases [75]

G	Ionization Potential (eV)
H ₂	15.4
He	24.5
Ar	15.7
N ₂	15.6
O ₂	12.3

2.3.2 Plasma-Surface Interaction

The outcomes of the plasma constituent collision with the substrate surface are a major interest in plasma surface interactions. The collision of species with the surface delivers kinetic energy via accelerated ions in the sheath and vibrated molecules, potential energy through the charged ions and metastable states, chemical energy due to plasma-produced active atoms and radicals and electromagnetic energy from excited species to the surface. There are many known and unknown interactions with surface; a few important ones are listed in Table 2-4. The ions with low energy levels, < 15 eV, will exchange momentum with the outermost atomic layer of the surface while colliding on it. The ion can also be trapped on the surface if all its kinetic energy dissipates after collision with the substrate atom. It also can remove atoms from the surface from striking into it which is known as sputtering and is considered as a significant plasma effect in deposition and etching processes. The intensity of particle liberation (sputtering) from the surface is very dependent on ion energy, the ratios of masses of the incident and the target particles. Atoms can have the same behavior to ions if they first collide with the surface with similar energy and second

be relatively small. Molecules generally need higher energies than atoms and ions to provide the same effect. Not applicable to textile surfaces, atoms and ions can also generate electrons on the surface especially at metal electrode surfaces. In addition to the interactions on the very outer surface, plasma constituents can interact deeper into the substrate surface when arriving at the surface with a thermal distribution of energy. They can be absorbed due to the attractive forces such as Van der Waals or electrostatic attractions between the particle and the surface which is then called physisorption and is considered as a weak interaction with bond energies between 0.01 and 0.25 eV. In the case of forming chemical bonds, chemisorption occurs with an associated bond energy of about 0.4 to 4 eV [61,65,72,79]. Figure 2-2 shows the processes that can occur when the active particle strikes the surface.

Table 2-4 Some of the collisions and reactions of the plasma constituent with a surface [72]

Reaction type	Name	Reaction
Neutral	Adsorption	$A + (s) \rightarrow A(s)$
	Desorption	$A(s) \rightarrow A + (s)$
	Dissociative adsorption	$AB + (s) \rightarrow A(s) + B(s)$
	Associative desorption	$A(s) + B(s) \rightarrow AB + (s)$
	Reaction at surface	$A + B(s) \rightarrow AB(s)$
	Reaction on surface	$A(s) + B(s) \rightarrow AB(s) + (s)$
	Electron emission	$A_m + (s) \rightarrow A(s) + e$
Ion	Neutralisation	$A^+ + e(s) \rightarrow A + (s)$
	Sputtering	$A^+ + e + B(b) \rightarrow A + B$
	Assisted desorption	$A^+ + e + B(s) \rightarrow A + B + (s)$
	Enhanced etching	$A^+ + e + B(s) + C(b) \rightarrow$
		$A + BC + (s)$
	Incorporation into bulk	$A^+ + e \rightarrow A(b)$
	Electron emission	$A^+ + (s) \rightarrow A(s) + e$

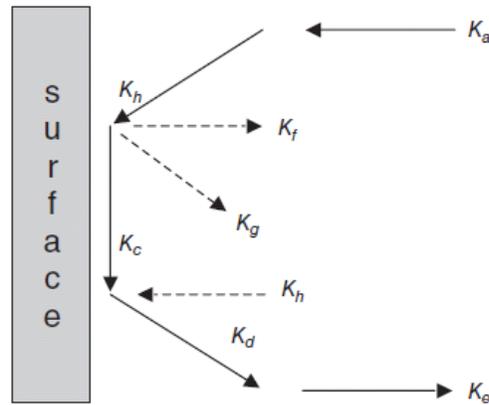
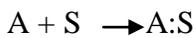


Figure 2-2 Schematic of the processes that can occur when a reactive species interacts with a surface [61]

The particle arrives at the surface with a rate of K_a ; it could be absorbed (K_b), react chemically (K_c), desorb (K_d) or flow into the gas phase (K_e). The particle can desorb without any reaction (K_f) or having associative desorption with another atom on the surface (K_g). The forming products in the gas phase can also return to the surface (K_h).

If A is the incoming particle and S is the surface, both physical and chemical absorptions can be presented by the following reaction:



For a striking molecule ($A=B$) with multiple bonds, the chemical absorption could happen by breaking any of the bonds,



However for a molecule with single bond, dissociation of the bond is expected,



All the colliding particles do not have the opportunity to get absorbed by the surface. The striking coefficient (s) is defined as the flux of molecules that are absorbed (Γ_{ads}), over the flux of the molecules incidents onto the surface (Γ_A), as in the following equation:

$$\Gamma_{ads} = S \Gamma_A = \frac{1}{4} n_A S C_A$$

Where nAS is the gas density close to the surface and CA is the mean atom or molecule speed. The striking coefficient not only depends on the reactivity of the species but also on the gas temperature and the available site on the surface that the particle could occupy.

Desorption also is another possible mechanism happens on the surface. In thermal equilibrium adsorption and desorption are in balance.



2.4 Plasma surface modification

When plasma is applied to a substrate, it changes its surface chemically and morphologically. With enormous number of electrons available in plasma, free electron or other metastable particles collide with the surface of the substrate and homolytically break bonds and generate free radicals on the polymer surface [72]. Hence, chemical modification of the polymer surface can be achieved without changing the bulk properties of the materials. In textiles arena, plasmas have been used to provide better adhesion than conventional thermal and chemical treatments, clean surface, hydrophilic and hydrophobic surfaces, and for medical application and devices sterilization [80-85].

The fact that non-thermal plasmas have low temperatures makes them suitable for processing materials applications including heat-sensitive fabrics such as silk, rayon, wool, and Kevlar. Kevlar fibers undergo negative thermal expansion in the axial direction when heated, due to an increase in entropy with axial contraction of the crystalline areas [68]. However, unlike thermal plasmas, non-thermal plasmas normally have required vacuum, or low pressure processes [67].

As explained so far plasma chemistry includes several different types of reactions in which ionization is the key process to convert the active constituents into the final products. In agreement with the literature [86,87] the plasma processes can be categorized into 3 main functions including etching, activation, and graft-induced polymerization. These three processes are in fact the overall results of several steps which take place in the plasma operation with different kinetics illustrated in Figure 2-3 and 2-4. These processes can be

divided into 5 steps as following and can take place either in the same volume or separated as the treatment ages:

- Creation of the primary plasma (ionization of the gas within the reactor)
- Formation of the secondary chemistry in the plasma volume (like disassociation of the injected monomers)
- Plasma-surface interaction
- Reformation and production of new molecules in the same volume and on the surface
- Clustering of reformed species

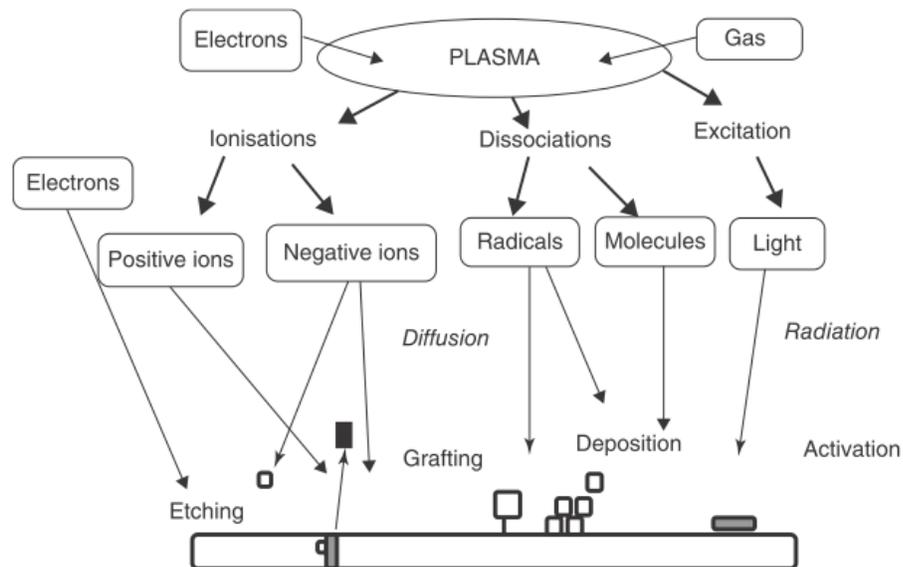


Figure 2-3 Processes in cold plasma and on the substrate surface [72]

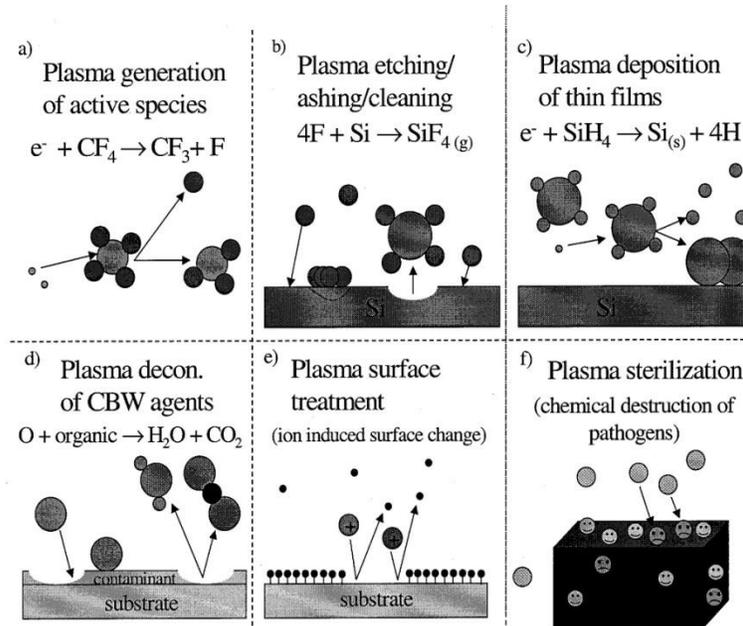


Figure 2-4 Illustration of some of the processes used in plasma processing of materials. Some processes are entirely chemical in nature, and some involve physical contributions, e.g. the impact of ions with the surface [67]

Depending on the plasma mode and parameters, the results of such dynamic equilibria are the effects plasmas bring to the substrate. These results can be divided into three major processes which are discussed in more detail in the following sections.

2.4.1 Surface Activation

Plasma surface activation never happens alone and is always during or after plasma cleaning [61]. When the substrate is exposed to the plasma volume with reactive species, the atoms and ions striking on the surface will react with organic chains and the contaminants present on the surface breaking the loosely bound hydrocarbon atoms. Both H and C will react with oxygen and will create volatile forms of H₂O and CO₂ on the surface. In the case of not having organic contamination on the surface, the active particles of plasma can react with oxygen atoms (especially in APPs) and form carboxy-, carboxyl- or hydroxyl functional groups on the surface changing the surface properties. Surface activation changes the surface properties of the substrate such as surface energy, adhesion and electrical properties [43].

The shelf-life of activation depends on the type of material and plasma condition. For example polypropylene has a relatively good shelf-life of several weeks; however silicon substrates show a shelf-life less than a day. Furthermore an intense plasma treatment will provide higher surface densities of functional groups which take longer to totally dissipate. In fact surface activation is a temporary increasing of the surface energy which also increases the affinity of the substrate to other surfaces and provides many advantages to the synthetic polymeric surfaces which have a relatively low intrinsic surface energy. The active species created on the surface after exposure to the plasma reorient themselves as the time passes, therefore the treatment effect is not permanent and it is better to be done very close to the subsequent process targeted to improve. Aging is an important issue in plasma processes since the effect of the plasma treatment decreases with time and most often reaches a partially steady state condition after some weeks. However there are some plasma processes which are affected by aging much more than other treatments such as surface functionalization and there are some in which aging is not an issue such as etching or coating. In surface functionalization, first only the outer most layer of the surface is treated and then the grafted chemical groups added via different processes can reorient themselves on the surface under the influence of thermal energy and undergo various reactions with the surface and the smaller molecules from the bulk. Therefore the fewer reactive species on the surface, the fewer grafted chemicals on the surface will be obtained and the impact of functionalization will decrease. This argument is very probable when the surface activation is done by oxygen-based plasma since the generated groups reorient easily. A research study showed that dye exhaustion reduced due to aging which indicates a reduced hydrophilicity already achieved by plasma treatment [88] and in contrast, wettability has been improved upon adding water vapor to the discharge [89].

2.4.2 Etching

The other result of treating a polymeric surface with plasma is weight loss caused by the chemical degradation reaction of the most outer polymeric layer located on the surface which is called plasma etching. Plasma etching is a chemical etching not a physical one and occurs when charged particles (ions and electrons) in plasma bombard and dislodge the

hydrogen atoms directly from the polymer chains in the surface region, causing C – C bond scission and the formation of carbon radicals at the end of broken polymer chains [91-92]. The formed radicals then initiate the degradation reaction, leading to fragmentation and detachment of low molecular weight species from the substrate and hence loss of weight. The intensity of this weight loss depends on the polymer type, the plasma power, and also the way polymeric chains break down. Polymers with a functional group containing oxygen are more sensitive to etching than polyolefins. Plasma generating gas is also important in how severe etching occurs on the surface. Noble gas based plasmas are less harsh than halogenated gas based plasmas, while the latter has the effect of chemical modification as well which is beneficial in decontaminating the surfaces and removing the organic pollutant, also imparting hydrophilic properties into the surface. Etching has a significant effect in changing the micro surface roughness of the substrate which alters the interaction characteristics of the surface with contact liquids through changing the surface energy of the substrate and the wetting behavior of the surface. Table 2-5 shows an example of measuring water contact angle on the surface of the Polyethylene treated with different plasma gases. The contact angle values explain how different plasmas have different effect on surface wettability.

Table 2-5 Values of water contact angle measured on PE film after plasma treatment.

Plasma	Contact Angle (°)
CO ₂	8
CO	16
NO	25
O ₂	35
NO ₂	37
Untreated	102

2.4.3. Grafting

Plasma grafting is the use of plasma to create covalent bond between a suitable chemical precursor and a polymeric substrate with the objective of modifying chemical characteristics of the substrate. This process does not change the bulk properties of the polymer and interestingly occurs at room temperature. Depending on the nature of the

precursor or chemistry of the grafting monomer, different properties can be introduced into the polymer surface just by applying a variety of functional groups. The grafting precursor can have functional groups such as carboxylic acid, hydroxyl, amine, fluorine, chlorine and so on. Grafting of monomers with hydrophilic functional groups (like acrylic acid) or applying precursors with oxidant groups (like air, oxygen or nitrogen) significantly increase the hydrophilic properties and wettability of the substrate which is closely tied to the generation of polar groups on the surface [93]. Increasing the hydrophilic properties of the fibrous assembly used in textiles has many advantages in increasing the adhesion properties, dye uptake and printability of the fabrics [94]. Applying the well-defined functionality through choosing a suitable monomer to render the desired properties on the surface could be processed in two direct and indirect ways. In the direct process the monomer is placed directly into the plasma volume while in the indirect process the activation is done through plasma exposure but the monomer is subsequently applied on the surface via different methods such as dipping, padding or vapor phase exposure. Theoretically, if fragmentation of monomer, which could lead to plasma polymerization and the formation of homopolymers, can be minimized during the second pass, e.g., by lower Yasuda factor (W/FM), grafting should be achievable and predominant. Even with the best (optimum) process conditions, the formation of homopolymer cannot be totally excluded, which also occurs in wet chemical processes and UV-induced graft-polymerizations. A cleaning procedure is necessary in all cases.

2.5 Atmospheric Pressure Plasma

Because of the capital equipment cost and the high operation and maintenance costs necessary for vacuum plasmas, the technical society started looking for a better and cost-effective option. Several atmospheric pressure plasmas have been reported [95]. These plasmas include Corona Discharge, Dielectric Barrier Discharge (DBD) and atmospheric pressure plasma jet (APPJ) [97]. Figure 2-5 shows their modes of generation. Table 2-6 summarized the comparison between different sources of plasma. It can be seen that the atmospheric pressure glow discharge APGD and plasma jet have characteristics that are

comparable to the advantages of low-pressure plasma: low breakdown voltage and high plasma density.

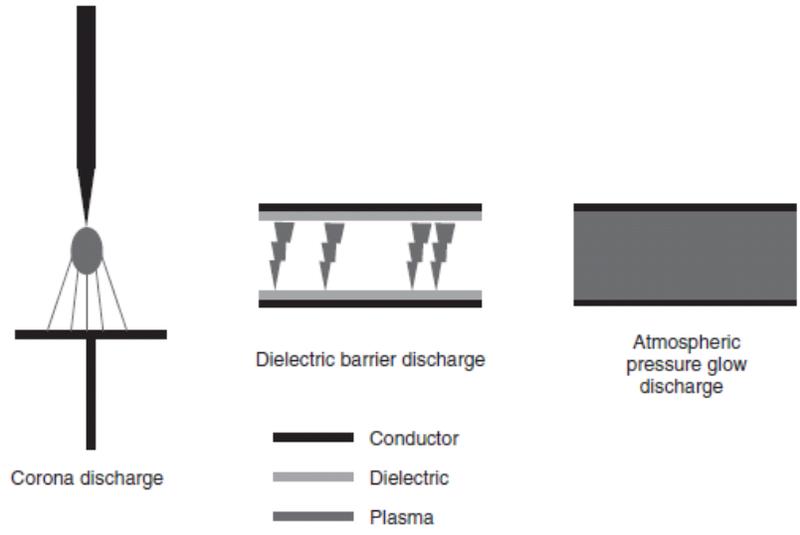


Figure 2-5 Schematic of the modes of generation of the three APP types for textile treatment

Table 2-6 Comparison of plasma sources [73]

Source	Breakdown voltage	Plasma density (cm ³)	Electron temperature (eV)	Density (cm-3)		
				O ⁺ , O ₂ , O ⁻	O	O ₃
Low-pressure discharge	0.2-0.8	108-1013	1-10	1010	1014	<1010
Corona	10-50	109-1013	10	1010	1012	1018
DBD	5-25	1012-1015	2-5	1010	1012	1018
APGD	0.2	10-10	1-2	-	-	-
Plasma Jet	0.05-0.2	1011-1012	1-2	1012	1016	1016

2.5.1 Corona discharge

Corona discharges are plasmas resulting from high electric fields surrounding an electrically conductive spatial singularity when a voltage is applied. Corona systems have the form of two opposing conductive electrodes separating by a gap the gas flows through and are connected to a high voltage source. The geometry of the electrodes is mostly like a pointed needle or a thin wire. The high electric field around the electrodes provides the breakdown and ionization of the gas and discharges in a fountain like spray form of plasma.

The generated plasma is characterized by the number, density and temperature of the free electrons in the system. Coronas are very weakly ionized and have an electron density about 10^8 electrons/cm³ and electron temperatures in excess of 100 000 K. The corona is relatively non uniform and the plasma density drops off from the point of generation rapidly, requiring a small electrode gap. The big disadvantage of the corona for textiles with large areas is that the discharge is too narrow with a very short time of residence which it makes it very impractical for commercial operations.

2.5.2 Dielectric barrier discharge

If a system is set up with a symmetrical electrode arrangement including two parallel conducting plates separated by a gap of ~10mm and a high voltage of 1-20 kV is applied, then the gas between the plates is electrically broken down and a plasma discharge is generated. This type of plasma has generally a form of a hot thermal plasma arc which jumps from one spot on one electrode plate to a spot on the opposite electrode and is absolutely useless for textile applications since it just leaves a burning hole in the fabric. However if one or both of the electrode covered by a dielectric like a ceramic or glass, then the plasma cannot discharge as an arc and has to spread itself over the surface of the electrodes to carry the current and becomes stable. This type of plasma is called Dielectric Barrier Discharge (DBD) and is very suitable for textile applications. The DBD system is run by high voltage and is powered by alternating current at the frequencies of 1 to 100 kHz. The typical free electron density is about 10^{10} electrons/cm³ (denser than corona) and the electrons temperatures are in order of 20 000 to 50 000 K (cooler than corona). The DBD can have two forms: filamentary and homogenous. The homogenous type is sometimes confusingly called atmospheric pressure glow discharge; however the most common form is the filamentary one where the plasma looks like a bunch of discrete arrays of microdischarges of short duration. Each microdischarge has limited charge transport and energy dissipation which typically provides less gas heating leaving a considerable part of free electron energy to be utilized for exciting atoms and molecules in the volume gas and therefore creating more precursors for initiation of surface reactions which is very desirable. The homogenous DBD is more

preferred for textile processing since is spatially more uniform and does not have the risk of causing pinholes in the fabric.

2.5.3 Atmospheric pressure plasma jet (APPJ)

Atmospheric pressure plasma jet (APPJ) or plasma jet represents the latest development in non-thermal atmospheric pressure glow discharge for surface modification of materials, especially polymers and textiles. The discharge was invented by Selwyn in 1998 (US Patent 5961772) and was introduced to the scientific community by Jeong et al [61] and shortly afterward by a report paper on its design and operation in etching of materials. APPJ is the only true non-thermal plasma, because of the vast difference in ion and electron temperature. The APPJ source produces a stable, homogenous and uniform discharge at atmospheric pressure using 13.56 MHz radio frequency power and a predominate fraction of helium feed gas. APPJ operates without any dielectric electrode cover, yet is free of arcing and this is the type of plasma we intend to use for the proposed research herein. High density atmospheric plasma uses RF electric fields, at 13.56 MHz to 60 MHz, to produce a unique, non-thermal, glow-discharge plasma that operates at atmospheric pressure and at power densities up to 500 W/cm³. Using RF excitation, together with a helium carrier gas and unique electrode geometry, the technology is free of arcing. High density atmospheric plasma furnishes a non-thermal, stable, homogeneous discharge that is 1,000 times more efficient in producing active chemical species than conventional atmospheric pressure plasma systems such as corona or dielectric barrier discharges (DBDs). APPJ operates in a capacitive configuration using RF power and produces a stable, uniform glow discharge between two bare metal electrodes, without any dielectric between them. The stable discharge in APPJ is realized by cooling both electrodes, appropriately restricting the current density and mostly with the use of a large volume (high flow rate) of helium gas. With helium the feed gas, a small percentage of a reactive gas such as O₂ can be fed into the gas stream, which becomes dissociated to produce the active, short-lived species required for changing the chemistry and morphology of material surfaces. The dissociation occurs when the gas is passed through the plasma, due to collisions with energetic electrons present in the plasma. Figure 2-6 shows the three basic electrode configurations of APPJ. Concentric and solid plate parallel electrodes

APPJ are commercially available by ApJet, Inc. (Santa Fe, NM), whereas perforated plate electrodes plasma technology is available by Surfex Technologies (Culver City, CA).

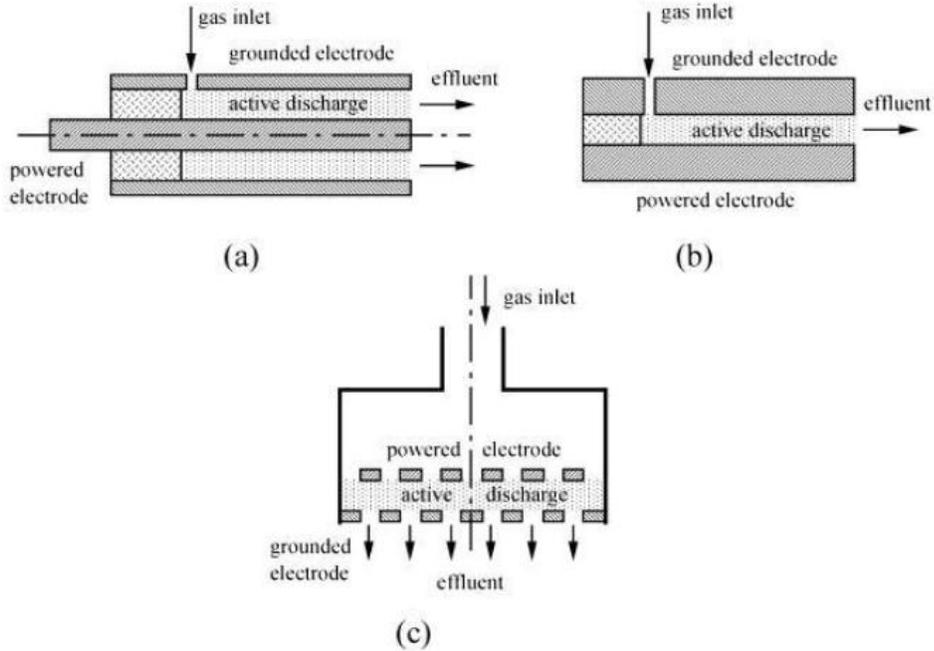


Figure 2-6 Schematic illustration of three different configurations of APPJ: (a) concentric electrodes or zero-dimensional plasma, (b) solid plate parallel electrodes or large area one-dimensional plasma, (c) perforated plate parallel electrodes. [73]

Because APPJ is non-thermal plasma, thermal degradation to materials is completely avoided. High density atmospheric plasma surface treatment can be performed in either a downstream or an in-situ mode. In the in-situ mode the substrate passes between the RF electrode and ground electrode while in the downstream the substrate passes beneath the ground electrode. Figure 2-7 shows a schematic diagram of the atmospheric plasma device. The features of the devices are as following:

2.5.3.1 The Stage

The stage is a flat, motorized platform to place fabric samples for testing. The motorized stage travels on tracks. The movement of the stage facilitates fabric samples to

travel under the monomer applicator, then into the plasma chamber, and finally out of the plasma chamber in a single operation. The stage is water cooled to allow the applied monomer to adhere to the target sample. The cooled stage allows the vaporized monomer to condensate onto the fabric sample. Without the cooling, a relatively warm stage could actually evaporate the monomer off the sample. This could prevent the plasma from efficiently polymerizing the applied monomer. The stage is manually operated by a motor control. When the stage reaches either end point, installed limit switches will automatically turn off the motor control.

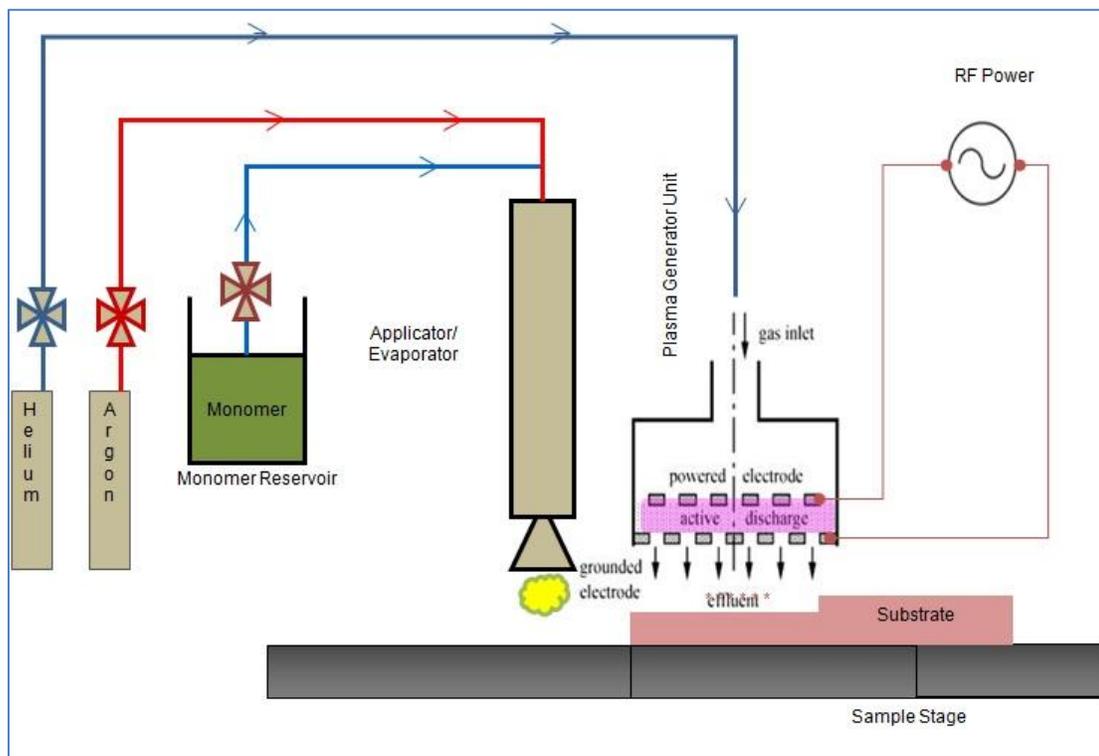


Figure 2-7 Schematic diagram of APPJ device.

2.5.3.2 The Evaporator

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 thermocouple 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. Helium (He) or argon (Ar) are species that less likely interact with most monomers and therefore less likely to alter a monomer's characteristics before polymerization. The He or Ar gas is passed through the evaporator to move the monomer vapor from the evaporator to the applicator.

2.5.3.2 The Applicator

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. After the monomer is applied the sample travels into the plasma field for polymerization.

2.5.3.3 Radio Frequency Generator

The RF Generator provides the RF power that creates the plasma field. The RF comes from the generator, passes through the matchbox, then to the electrode which then lights up supplied helium and creating a plasma field. The RF power is a variable that can be changed to manipulate properties of the plasma field. Arcing is an event that can occur when too much power is supplied or the distance from the RF electrode to the ground electrode is too large.

2.5.3.4 Radio Frequency Matching Unit "Matching Network"

The RF Matching Unit or Matchbox matches the impedance change as fabric samples travel through the plasma. As a sample passes under the electrode, the distance between the electrode and the stage will change the impedance. Therefore, the matchbox adjusts the reflective power to maintain a consistent RF load.

2.6 Introduction to nonwovens

2.6.1 Nonwoven Defined

Since the emergence of nonwovens there have always been challenges in their definition mainly to make a distinction from paper. Table 9 shows definitions of nonwovens

from different sources. Early definitions do not differentiate paper from nonwovens and later definitions did not propose any specifications to clarify the difference between paper and nonwovens. Batra et al [97] suggested a definition based on the structure of the nonwovens in which discriminate them from paper by specifying the fiber length between bond points. Both INDA [98] (number 6 in the table 9) and EDANA [99] (number 7 in table 2-7), have definitions based on ISO 9092:1998 with the criteria including fiber L/D (length/diameter ratio) and bulk. In both definitions a nonwoven is different from paper if:

- 50% of its mass is composed of fibers whose L/D is 300 and greater.

Or

- INDA: 30 % of its mass is composed of fiber with L/D is 600 and greater or 30% of its mass including fibers with L/D over 300 or greater and with the density less than 0.4 g/cm³
- EDANA- 30% of its mass composed of fiber with L/D over 300 or greater and its density is less than 0.4 g/cm³.

Note that INDA and EDANA differ in that INDA allows a nonwoven to be defined as such if it contains 30% by mass of fibers having an L/D ratio of 600 or higher, whereas EDANA makes no allowance for the higher L/D ratio fibers.

Table 2-7 Definitions of nonwoven

Number	Source	Definition
1	Manual of Nonwovens [100]	"Nonwoven fabrics are textile fabrics made of a fibrous layer, which may be a carded web, a fiber web, or any system of randomly laid or oriented fibers or threads, possibly combined with textile or non-textile materials such as conventional [woven] fabrics, plastic films, foam layers, metal foils, etc., and forming them with a mechanically bound or chemically bonded textile product "
2	Annual Book of Standard, 1989 ASTM International [101]	"Nonwoven fabrics": A structure produced by bonding or interlocking of fibers, or both, accomplished by mechanical, chemical, thermal, or solvent means and the combination thereof.
3	Man Made fibers and Textile Dictionary [102]	Nonwoven fabrics: An assembly of textile fibers held together by mechanical interlocking in a random web or mat, by fusing of the fibers (in the case of thermoplastic fibers), or by bonding with cementing medium such as starch, glue, casein, rubber, latex, or one of the cellulose derivatives or synthetic resins. Initially, the fibers may be oriented in one direction or may be deposited in a random manner. This web or sheet of fibers is bonded together by one of the methods described above. Normally crimped fibers are used which range in length from 0.75 to 4.5 inches.
4	"Nonwovens, theory, process, performance and testing", Chapter 2: Nonwoven Terminology, p.14 [103]	Nonwoven: A manufacturing sheet, web, or batting of directionally oriented fibers, made by bonding or entangling fibers through mechanical, thermal, or chemical means. They exclude paper and products which are woven, knitted, tufted, or felted by wet milling. The fibers may be natural or man-made origin.
5	The Dictionary of Paper, Fourth Edition, p. 285 [104]	Nonwoven fabric: A cloth like material made of fibers longer than those normally used in papermaking which, instead of being woven on a loom, is formed by felting on a line mesh screen from all air or water suspension with or without binders.
6	Nonwoven Fabric Handbook (INDA) [98]	Nonwoven: A sheet, web or batting of natural and/or man-made fibers or filaments, excluding paper, that have not been converted into yarns and that are bonded to each other by any of several means.
7	ISO 9092: 1988 (extract) from EDANA website [99]	Nonwoven: A manufactured sheet, web or batting of directionally or randomly orientated fibers, bonded by friction, and/or cohesion and/or adhesion, excluding paper (see note) and products which are woven, knitted, tufted, stitch-bonded incorporating binding yarns or filaments, or felted by wet-milling, whether or not additionally needed. The fibers may be of natural or man-made origin. They may be staple or continuous filaments or be formed in situ.
8	A New System for Classifying Nonwovens TAPPI Press [103]	Structure-based definition of nonwoven: Fiber web structures: Includes all textile sheet structures made from fibrous webs, bonded by frictional/mechanical restraints and/or covalent bonds obtained through the use of resins, thermal fusion, or formation of chemical complexes. Here, fibers or filaments are bonded so that the average bond-to-bond distances are greater than 50-100 times the fiber diameter giving textile-like qualities of low bending and low in-plane stiffness. Net-like structures: Structures formed by extruding one or more fiber-forming polymers in the form of a network or film. The film may then be uniaxially or biaxially oriented to fibrillate into a net-like structure. Multiplex structures: This class of fabrics combine and utilize characteristics of several primary and/or secondary structures, at least one of which is a recognized nonwoven textile structure, into a single unitized structure.

2.6.2 Classification of Nonwovens

The best way to classify nonwovens is based on the process by which they are produced [104]. Each process uses a unique method and materials and produces a different

type of nonwoven web. The first major sorting consists of two basic forming processes: dry formed and wet laid. The process names are almost self-explanatory since in the dry process the web is formed in air medium and in the wet laid the web formation is in water. The major dry formation processes are:

- Airlaid
- Dry laid (carding operation)
- Spunbond
- Meltblown
- Electrospun

Each method of manufacturing results in a defined set of attributes that overlaps with other processes but clearly characterizes each technology. The design of a filter for a specific application will require a specific media.

Wet laid processes are very similar to the paper making process and even the machinery used to produce them is referred to paper machines. Wet laid media can be made with nominal or absolute filter ratings. They typically contain binders which can have poor chemical and thermal resistance and high extractables when compared to air laid media. Wet laid media can also be made using FDA compliant materials. New wet laid media have begun to compete with microfiltration membranes in many applications. High efficiency wet laid media have equivalent efficiency as MF membranes but with significantly higher dirt holding capacity or life.

The dry form processes including carded, needled, spunbond and meltblown webs are less similar to paper production and more prevalent for producing nonwovens in which each process produces a web with specific properties. Following is a brief description of each process, extensive information about each method can be found in the literature [105-106].

2.6.2.1 Airlaid webs

Airlaid nonwoven fabrics are mostly formed from cellulosic fluff pulp and generally are used as diaper fluff or personal hygienic pads. The fluffy pulp is hammered milled into separated fibers and then is air conveyed to a moving belt to form into a fabric. Staple synthetic fibers such as polyester, polypropylene, nylon and rayon could be incorporated in

their structure with hydrophilic absorbent polymers such as carboxymethyl cellulose (CMC). If the web contains a lot of long fibers then it could be spunlaced (hydroentangled).

2.6.2.2 Dry laid webs

Dry laid is a very common process to produce many carded webs and felt materials used in filtration. The process is fully described by Crook [107]. The dry laid webs are different from air laid product in the point of raw materials and the way of processing. The air laid webs are basically made of cellulosic wood pulp fibers and partially (up to 20%) mixing with staple fibers. Whereas the dry laid webs are mainly composed of longer staple fibers which are mostly synthetic and the process is more complicated than the airlaid and includes a greater number of mechanical processes to separate, disperse, mix and orient the fibers into webs. Briefly explaining the process, the main core of the dry laid line is the carding machine which is called garnett. The processing line is very similar to the process used to separate the fibers from bales and prepare the skeins before the spinning process in traditional yarn spinning methods. After the loose final web is prepared, it should be bonded together to provide a consolidated structure. There are several different methods to bond the carded webs which are:

- Mechanical bonding
- Needle punching
- Hydroentanglement
- Thermal bonding
- Chemical bonding

Table 2-8 shows the type of bonding technique employed for different nonwoven web systems.

- Mechanical bonding

Mechanical bonding basically involves fiber entanglement. This can be achieved through needling or fluid jet action. In many applications, mechanical bonding is used as a first stage of bonding, followed by chemical or thermal bonding which imparts additional strength and

other desirable characteristics not attainable through mechanical bonding itself. Table 2-9 shows the comparison of mechanical bonding processes.

Table 2-8 Different bonding techniques for different nonwoven webs

Process	Bonding technique
Dry laid	Mechanical, chemical, ultrasonic
Wetlay	Chemical and thermal bonding
Spunbond	Thermal, hydroentanglement, needle punching
Meltblown	Thermal, Hydroentanglement, needle punch

Table 2-9 Comparison of mechanical bonding process

Mechanical process	Structural characteristics	Fiber lay in the web
Needle punching	Tuft	Partial fiber bundling with reorientation in the vertical web plane
Hydroentangling	Ball	Fiber displacement and entanglement
Stitch bonding	Stitch	Fiber bundling and horizontal conversion to stitches

- Needle punch

The fibers are entangled mechanically by puncturing the web with a series of barbed needles. Needle punch webs are the most leading form of nonwoven used for filtration application. Needle felt filter media are more often used in air filter applications; there are a number of liquid applications. They are a popular choice for bag filters and pocket filters. They are also used in vacuum belt filters. Because of the broad range of fibers that can be chosen for needle felt production, the media can be designed for filtration efficiency, for temperature, and for desired chemical exposure.

- Hydroentanglement (spunlace)

The method was first introduced by DuPont in 1973 with the product Sontara which is a spunlaced web formed of two components of wood pulp and polyester. Spunlace is the

generic name of hydroentanglement. In this process the webs are bonded together mechanically through very high velocity water jets with header pressure usually ranging from 0.5 to 25 MPa. The bonded web properties depend on the fibers type as well as the jet velocity. In hydroentanglement, fiber entanglement is accomplished by directing fine, columnar, high energy jets of water from a series of manifolds, arranged perpendicular to the machine direction, against a nonwoven web supported by a porous substrate. The number, size and pressure level of the water needling jets will depend on the type of fiber being processed and the amount of entanglement required. The hydroentanglement system has some specific advantages compared with needle punching, chemical or thermal bonding system. They are listed as following:

1) The spunlace process is suitable mainly for weights between 20-350 g/m² whereas heavy webs of more than 350 g/m² are produced by mechanical needling. The hydroentanglement system also has higher speeds compared with mechanical needling and the fiber damage in hydroentanglement is much less than mechanical needling by barbed needles.

2) Binder-free nonwovens can be produced which are very much suitable for the applications where chemicals are not desired for various reasons.

3) Nonwovens made of 100% natural fibers can be bonded optimally without adding melting fibers such as bicomponent fibers, used for thermal bonding. Textile softness and physical strength can thus be achieved by use of entangling energy and the cost of more expensive bonding fibers can then be saved.

4) The application of hydroentanglement to fibrillating the fibers can be favorable for obtaining a soft nonwoven material, as the mechanical effect of water jets is suitable for splitting these fibers. Table 2-10 shows the different parameters that affect the nonwoven product characteristics.

Table 2-10 Parameters that determine the nonwoven fabric characteristics

Parameters	Needle punching	Hydroentangling	Stitch bonding
Constant	Needle type and gauge Needle density Needle layout Needle punching direction	Hole diameter Number of holes holes layout	-Needle density Needle gauge
Variable	Stroke frequency Stitch density Stitch depth Entry and exit speed	Water jet pressure Entry and exit speed Drying temp	Shaft speed Stitch length Entry and exit speed

-Chemical bonding

Chemical bonding is a process of adding a nonfibrous material to a web during or after formation. The nonwovens are held together chemically using a bonding agent or a binder. There is wide range of chemicals that can be used and also of techniques for applying the chemicals. Post application treatment is necessary to dry, cure and fuse the binder.

- Thermal bonding

Thermal bonding is the use of heat energy to activate an adhesive system for the purpose of interlocking fibers. The adhesive may be a fibrous material or a dry applied powder.

The specific advantages of thermal bonding process are as follows:

- Widely successful with number of thermoplastic fibers.
- Significant energy conservation with respect to latex bonding because of effective thermal contact and because no water needs to be evaporated after bonding
- Environmentally friendly
- The bonding options available are:
 - Area bond calendaring
 - Point bond calendaring
 - Through air bonding
 - Ultrasonic bonding
 - Radiant bonding

A study carried out by James Westphal [104], compares properties of air laid web formed by chemical, thermal and combination of chemical and thermal bonding. It shows that

bonding by both chemical and thermal bonding results in improvement of the air laid web characteristics.

- Stitch bonding

Stitch bonding is another mechanical method in which knitting elements with or without yarns or sewing threads is used to entangle the fibers together. Quilted structures are the good examples of stitch bonding method.

2.6.2.3 Spunbonded webs

Figure 2-8 shows the generic layout of spun bond process provided by Malkan and Wadsworth [108]. The process mainly is the extrusion of melted polymer in a die block consisting of a spinneret and then cooling and drawing the molten spun filaments by air stream through a venturi. Following the venturi the filaments pass through a distributing chamber in which randomly entangled by the turbulence of the air and then is deposited by suction onto the moving belt. As the filaments touch the surface of the moving belt and also considering the suction of the air below the belt, the thermal bonding between them increases and the web layer is formed. Polymers generally used in the spunbond process include polyester (Reemay®), nylon (Cerex®), polyethylene (Tyvek®), polypropylene (Typar® and Tekton®), polyurethane and rayon. The mentioned trade names are those spunbond nonwovens originally introduced to the market. An alternative to the spunbond process is flash spinning in which a high density of a solvent solution is extruded and then thermally bonded. This process is the common method for Tyvek® production. Fabric structure is between paper and woven. The structure is random, shingled, and includes high content of voids which results in high liquid retention. The fabric has high in-plane shear resistance, low drape ability.

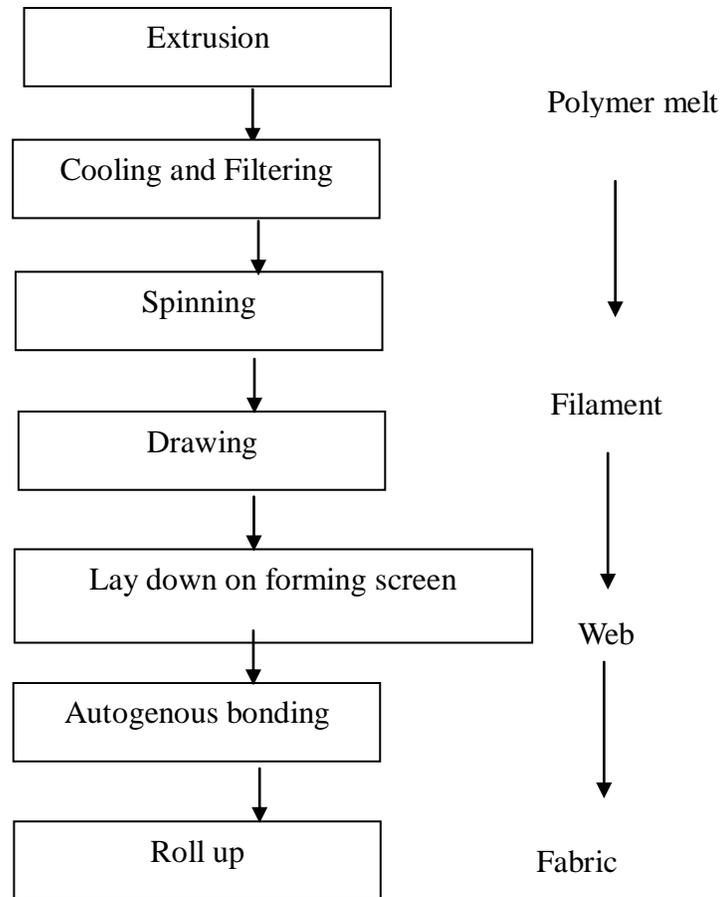


Figure 2-8 Generic of the spun bond process [104]

2.6.2.4 Meltblown process

Meltblown webs are directly formed from the melting polymer. The process is similar to the spunbond method due to the extrusion and spinning die steps however is different because of production at very high velocity and applying heated air near the die tips which attenuate the filaments at the very beginning and resulting in very fine diameter fiber. The filaments are then cooled and collected onto the moving screen. Figure 2-9 illustrate a diagram of a meltblown process. Air temperature, polymer/die temperature, die collector distance, collector speed, polymer throughput and air throughput are the process parameters which influence structure properties of final web properties. Polymer, die, air temperature and air flow rate determine the web uniformity, rope and fly formation, shot formation, fabric appearance and feel. Die to collector distance affects the openness of the fabric, thermal

bonding among fibers and weight. All these parameters are named on-line variables and may be changed during production. On the other hand, there are some off-line process parameters such as air gap, air angle, die setback, and die hole size. Fiber size is affected by both die hole size along with die set back. Air gap affects the degree of fiber breakage by controlling the air exit temperature. Direction of air flow is controlled by air angle. A 90° air angle results in a high degree of fiber separation or turbulence that leads to random fiber distribution. At an angle of 30°, roped or parallel fibers deposited as loosely coiled bundles are generated. This structure is undesirable. At angles greater than 30°, attenuation as well as breakage of fibers occurs. Uniform fiber distribution in air flow and optimum air suction inside collector enhance fibrous web uniformity. Poorly designed die and variation in air flow may result in non-uniform fiber distribution. The closer the die assembly is to the collector surface, the more uniform web structure is obtained. Meltblown fabric has an isotropic structure because of random distribution (like airlay) of fibers in both machine and cross direction. In polypropylene production, increasing throughput results in an increase in fiber diameter (due to die swell), tensile strength, initial modulus, web density, and stiffness. On the other hand, high throughput decreases breaking strain and creates a brittle fabric structure. Fiber diameter is not greatly influenced by the air flow rate. An air laying system enable isotropic web structures. Meltblown webs have good squareness properties, while carding webs have higher machine direction strength than cross direction.

Among all the thermoplastic polymers, polypropylene and polybutylterephthalate are the most common ones used in melt blown process. The significant difference between a web produced by spunbond and meltblown is that the meltblown web has finer diameter fibers and is generally softer and weaker than the spunbond web. Butler [109] indicates that approximately two-thirds of meltblown consumption is used in composites structures. The most common nonwoven composite is SB or spunbonded/melt-blown structure.

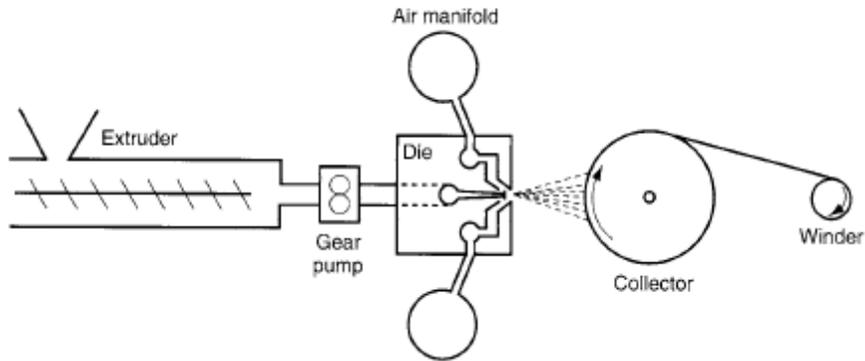


Figure 2-9 Schematic of melt-blown process [104]

2.6.2.5 Electrospun process

The earliest trace of electrospinning backs to 1934 when Anton Formhals [110] patented the invention of this method. The process is simply based on the production of nanofiber webs by applying a high voltage charge to a polymer solution or melt in which the nanofiber is drawn from a tip of a charged capillary to a grounded electrode. The applied voltage should be enough to overcome the surface tension of the polymer. Figure 2-10 is the schematic of the principle of this method. The collected web has very fine fibers (in order of 1 micron or less) and has limited mechanical properties. Graham et. al [111] mentioned that in the current market, electrospun webs are mainly used for air filtration applications including engine air intake filters, turbine air filters and vacuum bag filters.

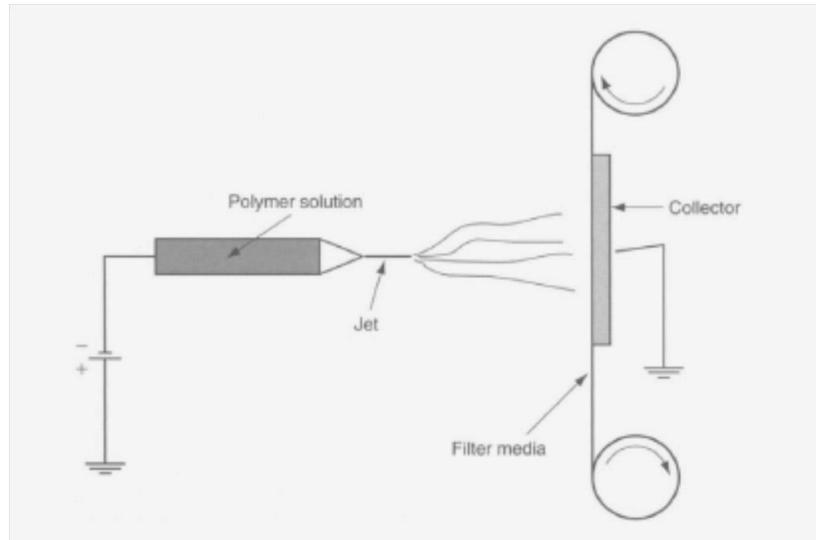


Figure 2-10 Schematic of the elctrospinning process [104]

2.6.3 Nonwoven Filter Media

The most simple nonwoven filter media is defined as a random fiber structure usually in sheet form which is used for the purpose of separating one or more phases from a moving fluid passing through the filter media. There are several ways to produce this sheet form. The constituents of fibers and filaments may be either bonded together as they are formed or bonded by a downstream process of a fabric former which could be in-line or off-line of the manufacturing process. The post bonding process in the most common technologies include entanglement of the fibers by needlepunching, hydroentanglment, stitch bonding, water-based latex treatment, solvent-based resin treatment and thermal bonding. Table 2-11 shows different nonwoven processes and their application specifically as a filter media. The interesting point about the table is that almost every filter media can be used in almost every application.

Table 2-11 Classification of nonwoven filter media based on the formation process [104]

Forming process	Application	Medium Type
Dry laid	Industrial air filters (bags) Industrial fume Air demisters Paint spray booth Furnace and ventilation	1. Needle-punch and spunlace 2. Membrane w/felt support Needle punch and spunlace- heat and chemical resistant Glass microfiber High loft mat 1. High loft 2. Mat from polyester, cotton, hogs hair, coir, filament glass, fibrillated film and/or etc.
	General ventilation Vacuum bag Air Purifier Turbine and rotating machinery (bag) Milk filter Beverage - beer and wine (bag) Belt filters Roll filters	1. High loft panel or mat 2. Monofilament glass mat 3. Phenolic treated glass mat Needle-felt, electrostatic Needle-felt. Electrostatic 1. Needle-felt or spunlace 2. Nanofiber w/felt support-electrostatic 3. Membrane w/felt support Resin bonded Needle-felt Scrim reinforced needle felt - chemical and mechanical finishes Chemical bonded, needle punched, or spunlace
Spunbond	Cartridge dust filter Furnace and ventilation Residential ventilation - panel Respirator Cabin air filtration Turbine and totaling machinery (cartridge)	Polyester and nylon Panel filters - polyester, nylon, and/or polypropylene Gradient density Activated carbon layer Activated carbon layer Pleated
	Milk filter Beverage - beer and wine (bag) Beverage - beer and wine (cartridge) Swimming pool filter Roll filters	Polyester Polyester Pleated Pleated – antimicrobial Rolls slit to size
Melt-blown	Residential ventilation (panel and pocket filters) Surgical face mask/Respirator Vacuum bag Micron rated filter bag Depth filter Pleated cartridge	Composite w/support substrate Laminated composite Composite Composite w/resin treated paper Composite w/needle-felt Pleated Melt-blown w/support medium
Electrospun	Ventilation filters - panel Cabin air filtration Vacuum cleaner Turbine and rotating machinery (bag)	Nanofiber - Cellulose support Nanofiber - Cellulose or synthetic fiber Support Nanofiber - Cellulose support Nanofiber- needle-felt or spunlace felt support

The random structure of fibers is the backbone of the nonwoven fabric, however other components may add to this basic structure during the formation process to fit it for final application. Particulate fillers such as clays, calcium, adsorptive powders, sizing agents, plasticizers and pigments are examples of additives. On the other hand the nonwoven fabric could always be exposed to different post chemical and mechanical treatments to change or

improve the properties, processes such as coating and finishing. Flame retardants, water repellents, antimicrobial, dye and softening agents and mechanical operations such as creping, corrugating, embossing, pleating, bag making, sheeting and stamping are very general to prepare the nonwoven sheet properly for end use in filtration/separation. In order to have a more specific definition from the nonwoven filter media some of the very well-known filter media are should be excluded including filter types such as woven filter media, screens (metal, plastic,etc.), sintered metals, sand bed filters, membrane filter media, cake filters, ceramic media, and fluidized bed filters. Filtration is generally defined as the removal of a particulate phase from a moving fluid by entrapment of particulate matter in the convoluted structure of the filter medium. INDA, the Association of the Nonwovens Fabrics Industry [112] explains filtration as follows:

“Filtration is the mechanism or device for separating one substance form another. Filtration may be used to separate contaminants from fluid or separate value-added materials, such as minerals, chemicals, or foodstuffs in a process operation.”

However there are plenty of discussions about the other forms of separation or filtration where a nonwoven medium is applicable including adsorption, absorption, extraction coalescence, electrostatic effects and antimicrobial activity. This means that it is possible to extend the definition of filter media from Sutherland and Purchas argument to broader more comprehensive definitions. They define “A filter medium is any material that, under the operating conditions of the filter, is permeable to one or more components of a mixture, solution or suspension, and is impermeable to the remaining components.” Focusing more on liquid filtration, there is a wide range of industries that use nonwoven media for liquid filtration applications. They range from food and beverages, biotech, pharmaceutical, potable water, hydraulic oils, fuels, solvents, acids and bases. Each application has a different contaminant that must be removed. In liquid filtration we understand the separation of solid substances being removed from suspensions whereby the filter media divides the particles from the fluids. The systems to be dispersed may consist of solid substances in fluids, which are called suspensions and the fluid dispersed is named a filtrate. A very simple illustration is shown in Figure 2-11.

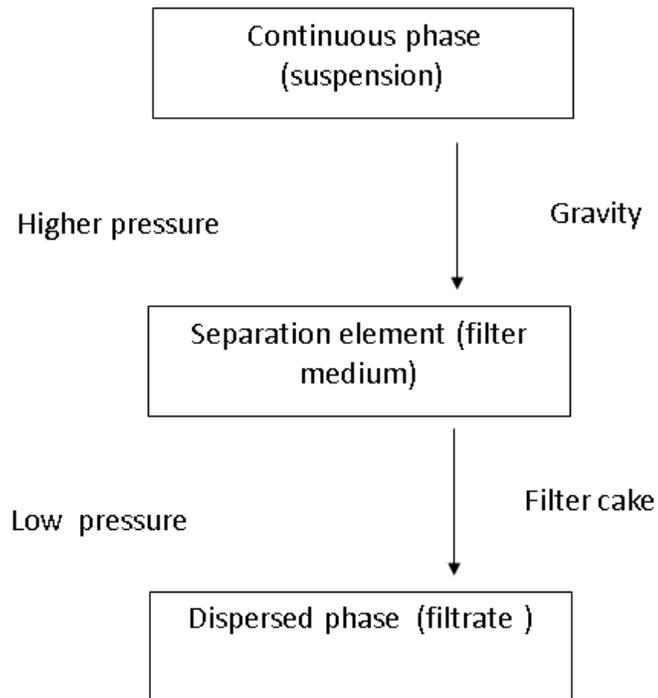


Figure 2-11 Liquid filtration

The difference in pressure, which drives the filtrate fluid, the filter medium and filter cake deposited, may be created by means of gravity, low pressure on the filtration side and by means of high pressure on the suspension side. Depending on the process, in liquid filtration we differentiate between surface filtration and cake filtration. Large scale liquid filtration is accomplished mostly by cake filtration. Selecting a suitable nonwoven for use in liquid filtration, the filter-technical properties are, in addition to the chemical and thermal resistance of the fiber materials essential. In addition to that, the type of filter designs, the wear and tear behavior of the nonwoven when in operation and economy has to be taken into consideration. Also

- They must provide high separation performance at a pressure differential as low as possible in relation to the flow characteristics. Separation performance and efficiency largely depend on the fiber fineness as well as the density of the nonwoven.
- Chemical and Thermal Stability: Nonwoven media are used in many different industries and applications with each having a wide range of operating conditions. Nonwoven liquid filtration media are thermally or resin bonded and uses polymers that are susceptible to

thermal and chemical attack. The polymers can swell, fracture and/or soften which may change the filtration performance. The change in filtration performance can be gradual or sudden based on the concentration, exposure time, temperature and additives. Chemical and thermal compatibility is also important.

- For specific applications like water treatment of drainage more specific requirements must be met :

- Have a high water permeability over its entire surface
- Have an effective aperture width, which holds back any eroding granules but
- Allow granules to pass through
- Have a mass per unit area and strength which can resist mechanical loading from the soil and during laying, without being damaged

The advantages of using nonwovens for liquid filtration can be summarized as:

- Removal of a wide range of contaminants from water (bacteria, viruses, metals, minerals etc.)
- Uniform structure
- Tear and puncture resistance
- Chemical resistance
- High retention capacities
- High air permeability
- Excellent abrasion resistance
- Flame retardancy
- Absorption of fats and oils
- High level of flow capacity
- High tensile strength

In the meantime nonwoven fabrics like most filtration media, have disadvantages compared to other media choices such as polymeric membranes, woven fabrics, metal media etc. No single media can or will ever satisfy every filtration requirement. In the case of nonwoven fabrics, the disadvantages are not so much the shortcomings of nonwovens, but the advantages of other media. For example, membranes provide narrow pore size distribution, particularly below 1 micron mean flow pore. Monofilament fabrics and wire

cloth offer strength and straight through holes for use in sifting and excellent sieving capabilities. All three of these are surface filters, a feature not easily achieved for nonwoven fabrics, because of the nature of the manufacturing processes and resultant constructions; at least, not yet. Many filtration and separation applications require stiffness, minimal flex, and rigidity or even low stretch as is the case of dewatering belts, which by their nature are less favorable to the use of nonwovens. All, which proves, that even with the tremendous growth of nonwoven fabrics in filtration, there are many unmet market opportunities for nonwoven fabric manufacturers to further expand their business.

Following are possible separation processes other than simple particle entrapment in which nonwoven products are applicable:

2.6.3.1 Adsorbent media

Filter media containing adsorbents remove liquid and soluble contaminants from fluid streams by surface adsorption in a way that contaminants are attracted to the surface of the medium and held by physical chemical phenomena. Good examples of it are activated carbon impregnated layers used in air and gas masks, respirators, water filter, automotive cabin air filters, and HVAC (heat, ventilation, air conditioning) systems.

2.6.3.2 Absorbent media

An adsorbent medium removes the contaminant from bulk stream by surface effects while an absorbent media eliminates the particulates by absorbing them into the porous structure of the medium. Nonwovens are often used with absorbent structures to have both the absorbent material and acting as a transport layer for fluid to flow to the absorbent material.

2.6.3.3 Coalescing media

Coalescence is a process in which the filter media enhances the removal of smaller droplets of the dispersed phase from the continuous phase by improving their growth to form bigger drops. The dispersed phase includes hydrocarbons in water, oil mist in air, moisture and vapor in air and moisture in aviation fuel. The process is a particulate filtration requiring a matrix of fine fibers to trap the liquid particles and hold them on the fibers.

2.6.3.4 Electro-filtration

The filter media or the fiber made out of material that can be electrostatically charged to boost their filtration properties. Charged filter media or fibers are often referred to as electrets which are dielectric materials that exhibit an external electric field in the absence of an applied field. Electrostatic filters are considered among the most important products in the current market of filtration.

2.6.3.5 Antimicrobial media

Antimicrobial filter media are incorporated with agents providing antimicrobial activity to protect the media from the growth of bacteria, fungi and yeast. This property could be in the form of protecting the media against the migration of microorganisms into it.

2.6.3.6 Extraction

This method of separation just uses the filter media as a structural support for the extraction process. Teabags and coffee filters are in this category.

2.6.3.7 Filter support

Some nonwoven processing methods provide webs that are not strong enough to be used as a single filter media, however they have found the wide application as supports for a filtration assembly. Meltblown or electrospun layers are generally weak or too thin and do not have the needed structural solidity, therefore they require a stronger material such as woven fabrics or needle punch felts or even metal meshes to provide them with enough strength. The nonwoven support layer participates in the filtration process in many cases.

2.6.3.8 Composite structure

Robert Murphy from Hollingworth and Vose Co. defines composites as “Two or more different web technologies that are combined to optimize the characteristics of a filter medium”. Composite media give the chance of more than one step of separation to the filtrate.

2.6.4. Nonwoven Filtration Market

Nonwoven fabrics continue to grow and in some cases, take market share from other media. However, filtration industry trends provide many challenges for nonwoven fabrics. These trends could be

- Environmental consciousness
- Finer filtration
- Specialized media

The field of filtration is tremendously diversified. There are more than 1,000 different applications characterized by different profiles and conditions and consequently requiring different filter materials. One of the most important segments of filter materials are nonwovens. Due to their variability and their economical manufacture they can be easily adapted to nearly all kinds of filtration jobs. This explains that already in 1994 such products had a 89% share of the world filtration market (836 million m²). The annual sales in 1995 for all nonwovens amounted to US \$ 1.4 billion worldwide. This represents growth of approximately US \$ 100 million for the previous year and more than US \$ 600 million compared to 1988. In 2002 North American filter converters were reported to have consumed close to 1.1 billion m² of nonwoven media, representing a market value of US\$ 370 million. Therefore, few would disagree that filtration remains a significant end use market for the nonwoven industry in this region.

Furthermore, according to Kimberly-Clark, together air and liquid filtration are within the top three end use markets for nonwoven fabrics in North America. The liquid filtration market for nonwoven materials is slightly smaller and more fragmented, but nonetheless it maintains an annual growth rate of 5-6%, according to Kimberly-Clark. The North American market for nonwoven filter media was worth \$588 million in 2005, \$617 million by the end of 2006 and in 2007 this figure increased to approximately \$639 million and at an average annual growth rate (AAGR) of 4.4% will reach \$792 million by 2012. The market is broken down into several different manufactured categories, including airlaid, wetlaid, spunbonded, meltblown, and apertured film. Of these sectors, spunbonded material maintains more than 30% of the market throughout the forecast period-the highest of share of

the market. Meltblown material worth \$181 million in 2007 and will grow at an AAGR of 4.9% to \$230 million in 2012. Meltblown material has the highest growth rate of the material types and will hold 29% of the market share by 2012. The market for filter media worth US\$25 billion in 2010 according to new research in a series of reports published by the McIlvaine Co. filter media sales will grow at a faster rate than GDP because of applications like water treatment and growth markets such as China. Sales of indoor air filters reached US\$6018 million in 2010, while liquid cartridge sales are forecast at US\$13 644 million and cross flow membranes at US\$1890 million. [98]

The market will continue to look for the perfect filter. This product can only be made with the development of more versatile and complex components than those currently available today. It will be essential to increase the complexity and capability of the product to allow for its universal acceptance. This will inevitably increase the cost of the material. This cost increase must be offset by the product's increased durability and ability to be cleaned, thereby increasing its lifespan. To provide a cleaner environment with toxin free air and water it will be necessary to improve the filtering efficiencies to filter nano particle sizes, gases, complex chemical compounds, and individual elements. Expanding these limits will further enable the filtering of subatomic particles for research in space and here on earth. Not all of the materials have been developed to accomplish these demanding tasks. The technology needed to provide a foundation for future developments is needlepunch nonwoven dual and multiple density composites. Currently, highly engineered needlepunch multiple density composites are being used for the filtering of hazardous gases, viruses, bacteria, and subatomic particles in accelerators. The ability of needlepunch nonwovens to produce high performance and consistently uniform composites will demand the attention of engineers when designing solutions for our future needs.

2.7 Fuel Filtration

One of the most important results of the plasma treatment of textiles is the change in wettability by altering the surface energy of the substrate. Plasma treatments can make textiles hydrophilic and as well as hydrophobic. Hydrophobic finishing reduces the surface energy at fabric surfaces. Surfaces that exhibit low interactions with liquids are referred to as

low energy surfaces and their critical surface energy or surface tension must be lower than the surface tension of the liquid that is to be repelled. For the specific application of fuel filtration or water/fuel separation it should be considered that the term fuel filtration includes filtration for vehicle engines and fuel transportation system [104]. The former is related to the engines powered by gasoline or diesel fuel and the latter is for a number of distribution systems that mainly distribute oil and fuel to various locations through pipeline or different motor vehicles. The issue of filtration in fuel transportation systems is more challenging since oil/fuel is exposed to different contaminants between the source and the destination.

2.7.1 The need for fuel filtration

Fuel contamination and its contaminants are important topics in the field of fuel mixing, storage and transportation systems, aviation fuel industry and engine efficiency [104]. Most common fuel contaminants, except those arising from comingling of different fuels, include particulate matter and moisture. Moisture could be in the form of free or dissolved water. Free water can be seen in the fuel as a form of cloud, emulsion, droplets, or in large amounts at the bottom of a tank, sample container, or filter/separator reservoir. Dissolved water is water that has been absorbed by the fuel. It cannot be seen and cannot be separated out of the fuel by filtration or mechanical means. Fuel surfactants are also considered as interference since they inhibit water droplet coalescence in separation processes [113-117].

Water has a more dangerous role than solid particles mostly because the presence of water in fuel, not even in large amounts, is considered as the main source of many significant problems that can easily alter the fuel function. As ethanol blended fuel usage increases, the problem of water contamination exacerbates in a similar trend [115]. Water is definitely the main reason for pipeline and instrument corrosion when the oil or fuel is in contact with them. It can either contain corrosive material such as chloride or easily dissolved polar corrosive compounds such as sulfuric acid and cause considerable damage over time. Water reacts with some antiwear additives in fuel to produce hydrogen sulfide, sulphuric acid, and precipitate sludges. In addition to promoting corrosion due to increased oxidation, water reacts with antioxidants and rust inhibitors to form precipitates. Water contamination is the

major contributor to tank and reservoir bottom corrosion, it also provides the ideal conditions for flourishing of micro-organisms such as bacteria and fungi in the fuel which gradually form solid particulate that can plug the engine and influence the filtration effectiveness by plugging the filter media. Microbiological growth in the fuel could either be an indicator for water presence, since if there is no water in the fuel, microbes cannot grow. In hydraulic equipment water changes the physical properties of the hydraulic fuel such as density and bulk compressibility. After a length of time it is very likely to come across a hydraulic system with cloudy oil. Oil becomes cloudy when it is contaminated with water above its saturation level. The saturation level is the amount of water that can dissolve in the oil's molecular chemistry and is typically 200 - 300 ppm at 68°F (20°C) for mineral hydraulic oil. This water content can strip some additives and react with others and produce corrosive agents, it also reduce the lubricant film-strength which speeds up the fatigue wear rate of the engine parts, it also reduces the filterability and increases the filter clogging, air entrainment ability and the chance of cavitations occurring [116].

Water contamination is much more critical in aviation fueling. Very small free water droplets which are not dissolved in the fuel may freeze at high altitudes or cold outside air temperatures and plug the fuel screens, causing the engine to cease operation/flame out and possible loss of the aircraft. Salt water is extremely dangerous because of its potential effect on certain aircraft instruments. For this reason the most important component in any aircraft refueling facility is the filtration system which provides the report of water contamination check based on the allowable water in parts per million (ppm). The danger of dissolved water in aviation fuel is that it settles out as free water when the fuel is cooled to a temperature lower than that at which the water dissolved. Such a cooling of fuel is likely at high altitudes. Once freed, all the dangers of free water are present [114]. Optimal separation of free water from fuels prevents freezing at great altitudes and the accumulation of microorganisms. Water concentration as low as 100 ppm can cause a product to be off-specification due to haze, color or overall water concentration, detergents and additives make the water removal more complicated since they lower the interfacial tension between water and the fuel [118].

2.7.2 Water- Fuel Separation

Almost all fuel filtration media should provide the desirable function in three steps; primary separation of the solid particles following by water coalescence and final precise water separation. In the first step a pre-filtration is carried out to separate the solid particles which adversely affect the next steps. In the coalescence process, liquid droplets, usually water, existing in the immiscible mixture clott together and settle due to their density differences. There are some techniques which accelerate the rate of coalescence. One of the most common methods is to pass the fluid through resin treated media. Phenolic resins were found to be good chemicals for fuel filtration since they provide the right surface tension values which makes the media hydrophilic increasing the attraction of water droplets and holding them close together to eventually form larger droplets with faster settling rates . This is why for the last step of filtration; the filtering media surface should be completely hydrophobic so as to be wettable by fuel and unwettable by water. This treated surface requires a specific low surface tension which repels every small water droplet in the fluid and passes the pure fuel mixture. The mechanism is illustrated in Figure 2-12. Factors that affect this separation include interfacial tension, viscosity, relative density and temperature:

- Interfacial tension is the measure of the attraction force between each phase for its own species that significantly determines the ability to remove water. As the interfacial tension (IFT) value increases between two phases the separation improves. It is a critical factor in liquid/liquid coalescence because the largest possible stable droplet size that will form by the coalescence process will be dictated by IFT values. Systems with high values of IFT provide more stable droplet sizes which can be easily separated, also systems with low level of IFT form smaller droplets which are harder to separate and require more efficient separators. The emulsion droplet size also depends on the system dynamics including the relative droplet velocity, density and viscosity. The lower the IFT value, the more challenging will be coalescing. Using surfactant-containing inhibitors, detergents and additives in the fuel are among the factors that make coalescing more difficult.
- Viscosity: The viscosity of the emulsion is another important factor in its breakdown and the removal of water droplets, the higher viscosity means the higher drag forces in the liquid for droplets to reach one another, therefore more resident time is required to have the same level

of coalescing compared to a low viscosity fluid. To make up this effect the flow rate should be lower or higher surface area of the filter media should be used.

- Relative density: As the density of the coalescence part approaches the density of the bulk liquid's density, separation becomes more difficult.
- Temperature: Increasing the bulk temperature will decrease the IFT and makes the separation more difficult. High temperature of the fuel also increase the concentration of the dissolved water which is hard to remove by regular coalesce and will have to be challenged with separators. As the temperature decreases, water transforms more into the suspended state and can be removed in the coalescing step.

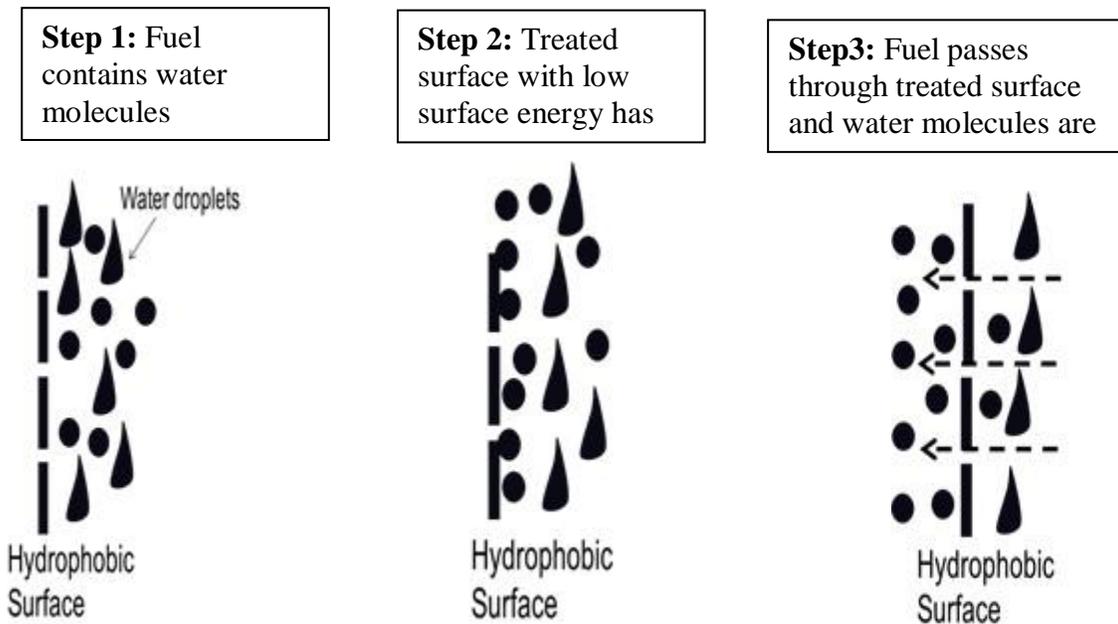


Figure 2-12 Simplified mechanism for effective separation

2.7.3 Repellent Theory

The name textile finishing covers an extremely wide range of activities which are performed on textiles before they reach the final customer. They could be temporary processes or permanent. However all finishing process are designed to increase the attractiveness or serviceability of the textile products [119]. In case of repellent finishing many terms have been used to describe the water repellency of a textile material, shower

proof, rainproof, rain resistance, rain repellent and so on [120]. Therefore the literature on water repellency and water-proofing are confusing because of firstly the dependency of repellency effect to the test method and test conditions[121], and secondly to the reality that in the earliest publishing researches and endeavors there had not been any distinction between the terms waterproofing and water repellency. In general, water repellent fabrics are those which resist being wetted by water. A fabric's resistance to water will depend on the nature of the fiber surface, the porosity of the fabric and the dynamic force behind the impacting water. Water repellent fabrics have open pores and permeable to air and water vapor, in fact they permit the passage of water once the hydrostatic pressure is high enough. In contrast, waterproof fabrics are resistant to the penetration of water under higher hydrostatic pressure in comparison with water repellent fabrics [122].

2.7.3.1 Wetting theory

Wetting phenomena play a dominant role in different surface treatment strategies. The wetting of a surface is determined by the interfacial tensions of the wetting liquid, the wetted solid and the surrounding gas phase. Besides these three parameters, which are caused by molecular interactions, the surface roughness or specific structures play a key role in wetting phenomena. Surfaces can be divided into hydrophobic (water hating) and hydrophilic (water loving) surfaces. Functional finishes to the fibers such as oil- and water-repellent, softening, antimicrobial, antistatic, flame-retardant, easy-care and soil-release agents modify the surface properties of fibers. This results in a change of the surface free energy, which depends on the chemical structure of the agent used. Surface free energy is an important parameter in evaluating chemical properties of solid surfaces and represents a measure of the solid wettability. It is directly related to the adhesion forces between a solid and a liquid, expressed by the work of adhesion [120,123,124] .

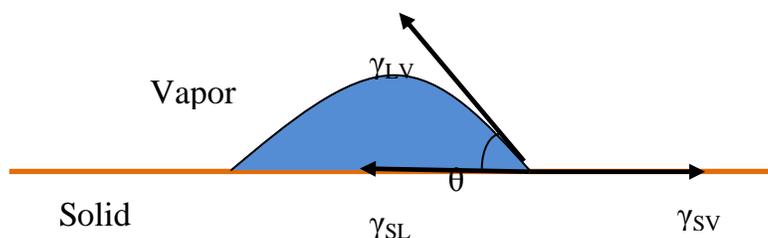


Figure 2-13 Equilibrium contact angle

The equilibrium of forces on a liquid drop on a plane solid surface as shown in figure 2-13 is given by the Young equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

Where θ is the contact angle in the liquid at the solid-liquid vapor boundary. The work of adhesion between the liquid and the solid is given by the Dupre equation :

$$WA = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

Therefore we can have the relationship between the work of adhesion and contact angle:

$$WA = \gamma_{LV} (1 + \cos \theta)$$

Now it can be reasoned that as the contact angle approaches 180 degrees, the work of adhesion approaches 0 and the liquid drop will not stick on the fabric surface.

2.7.3.2 Repellent finish

Water and soil repellency has been one of the major targets for fiber and textile chemists and manufacturers for centuries. Combinations of new materials for fiber production with a variety of surface treatments have been developed to reach the condition of limited wettability.

The early water- repellent finishes were all based on the application of a mixture of waxes which were applicable at normal temperature. The products were emulsions that contained heavy metal salts of fatty acids. These heavy metal soaps did have water repellent properties and the first attempt at the production of durable treatment was to use the chromium salt of fatty acids which were applied on cotton and then baked [120,123]. The paraffin repellent process is not only available at low cost, it also delivered good repellent effects, however

they are not durable to laundering and have low vapor permeability which adversely affects the comfort properties of the fabric. Following these early attempts numerous chemical components were introduced to the market and in the research area of repellent effects, chemicals such as esters, urethanes, amines, amides and related compounds, aldehydes, ethers, epoxides and related compounds, cyanates, thiocyanates, urea derivatives, and silicon derivatives were studied [125]. In the meantime it could be found in the literature that water and oil repellency could be conferred to natural cotton fabrics by spraying synthetic high polymers of suitable composition, or by resin coating with perfluoroester aziridines [126,127] , zirconium compounds [128] , radical crosslinking of methyl or cyanoethyl silicones [129] , crosslinking of fluorocarbon resins on the fabrics [130], or covalent condensation of stearamidomethyl-pyridinium chloride on the fabric surface [131].

- Fluorocarbon Finishing

The conventional paraffin or silicone based water repellent finishing agents are not sufficient to protect the textiles from liquid and oil stains and hence fluorocarbon polymers are used. Fluorocarbon polymers, commonly known as fluorocarbons, today represent an indispensable part of the technology of oil, water and soil-repellant finishing. They make it possible to keep the beauty and character of the textile, and to dramatically change its wetting behavior at the same time. Fluorochemicals are well known with their low surface free energy.

These fluoropolymers are used mostly by padding processes and exhaustion, it is also possible (to some extent) to modify the surface properties of the textiles with regard to staining and dirt repellency. Fluorocarbons reduce the surface energy of the treated fibers to such a low level that neither aqueous nor oily substances impregnate the surface of the material. Unlike silicones, fluoropolymers do not have the property of attracting fatty dirt because they are naturally oil repellent. New chemical combinations are also patented as new inventions in the field of water repellent chemistry. In one of latest registered ones, oil and water repellency is imparted to the substrate by a water repellent composition comprising a cationic dispersion of fluoroacrylate copolymer with a glass transition temperature at ambient temperature and a cationic dispersion comprising a fluoroacrylate copolymer with a glass

transition temperature of about 80 degrees which makes it suitable to have a LAD (Landry-air-dry) effect and low curing fluorocarbon condition[132]. Due to long concern of the textile industry about water consumption and environmentally hazardous chemicals in effluents, new methods in attaining repellent effects on fabric are being developed [133].

Low-temperature plasma treatments have been investigated for the enhancement and/or replacement of conventional wet chemical processing for textile materials. In this method high energy electrons and low energy molecular species are generated through electrical discharges in low temperature plasma without excessive heating of the substrate. In the case the low energy molecular species are fluorocarbon (FC) compounds, repellency is induced on the fabric by changing the surface chemistry from hydrophilic to hydrophobic. McCord et al. [134] discussed a detailed surface analysis on cotton fabric treated with FC compounds in RF plasma method and evidenced the chemical and physical alteration of the fabric surface due to plasma treatment by different characterization methods. The water repellency and hydrophobicity of the CF₄ and C₃F₆ treated cotton fabric is judged by measuring the contact angle of the droplet and wet out time measurement. Furthermore, to have a deeper insight into what happened on the surface after the treatment, the researchers performed chemical composition analyses by applying XPS photospectrometer high-resolution scans of the F1s and O1s regions after CF₄ and C₃F₆ gas plasma treatments which lead to deconvolution results of the C1s spectra for cotton fabrics. Thilagavathi and Kannaian [133] reported the procedure in which dual antimicrobial and blood-repellent finishes are applied on cotton fabrics used as hospital gowns, while the repellent step is done by deposition of Teflon sputter using argon plasma. The authors also discuss the effect of argon plasma on the surface of the fabric and indicated that the argon gas sputters fragments of CF₁, CF₂ and CF₃ from the Teflon target on the fabric, altering the surface chemistry and leading to a very good water repellency. However it is surprisingly concluded that the spray rating of 4% FC treated fabric is the same as that of the Teflon finishing. However the plasma treated samples has a smoother handle which is a valuable point to skilled end users. Leroux et al. [135] imparted repellent properties on the polyester fabric through a novel method of nano-coating the fabric with FC using a direct aerosol dispersion in the plasma machine. They indicated that using ionized aerosol in a plasma method is not sufficient to get

the desired repellency and this is mainly because of the low concentration of repellent chemical on the surface. Therefore it should be considered a post step in which the fabric goes through a bath in pad-dry-cure process. Rajpreet et al. [136] treated the nonwoven fabric Sontarax®, commonly used for surgical gowns, with antimicrobial finishes and plasma containing fluorocarbon gas to achieve water repellent effect [20]. In the plasma-induced graft-polymerization (PIGP) process, an inert gas (argon for instance) is able to initiate polymerization at the surface of non-volatile liquid or solid monomers. The plasma itself is also well known for activation of various surfaces. The coupling of these two behaviors of the cold plasma process will allow the simultaneous grafting and polymerization of a monomer onto the surface of a substrate. Tsafack and Grützmacher [137] discussed water-repellent treatment combined with fire retardant finishing on cotton fabric applying the PIGP method. The results are encouraging in conferring two different properties on cotton fabric via a cold plasma technique.

Nature has already developed an elegant approach that combines chemistry and physics to create super repellent surfaces. Lotus leaves are unusually water repellent and keep themselves spotless, since countless miniature protrusions, coated with a water repellent hydrophobic substance, cover the leaves' surface. The "lotus effect" is based on the surface roughness caused by varying microstructures combined with hydrophobic properties of the wax covering the leaves' surface (Figure 2-14).

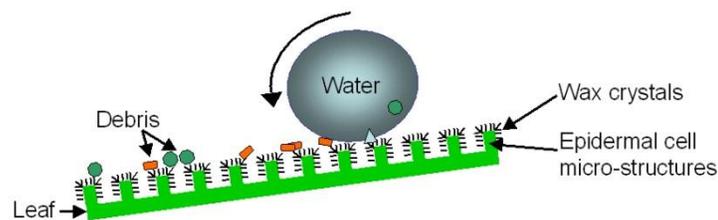


Figure 2-14 The Lotus effect

The preparation of ultrahydrophobic fibers/fabrics using different approaches that resemble the "lotus effect" was demonstrated recently. Mimicking lotus leaf properties on textiles is considered an application of nanotechnology in textiles. Luzinov et al. [138]

approach to mimic lotus roughness and hydrophobicity by imparting permanent grafts of polystyrene and on the polyester surface. Ramaratnam et al. [139] has imbedded silver nano particles and a repellent chemical, silicon polymer, on the fabric surface in a multi stage procedure. The attachment of silver nano particles to the fabric is considered durable, however it is indicated in the results that having a real superhydrophobic fiber is very dependent on the roughness of the fabric and just nano particles and repellent chemical is not enough.

In some literature [140-142] the relationship of superhydrophobicity with contact angle and contact angle hysteresis is discussed. It is mentioned that a surface having a water contact angle greater than 150 degrees is called a superhydrophobic surface. A droplet of water easily rolls off a surface having such excellent hydrophobicity. However it was found the contact angle hysteresis is very important in understanding the drop motion on a surface.

2.8 Antimicrobial Treatment

With the threat of emerging new bacteria and old bacteria capable of reinventing themselves by changing their DNA to surpass different antimicrobial agents and the threat of blood-borne pathogens such as HIV and hepatitis, and air-borne viruses such as SARS, the need for garments that can disinfect wide spectra of bacteria and viruses is highly desirable. Antimicrobial fabrics include variety of natural, synthetic or blended fibers made from nonwovens and woven fabrics.

2.8.1 Antimicrobial Agents

Microbes grow at an incredible speed, for example, the bacteria population doubles every 20 to 30 min under ideal condition (36-40°C, pH 5-9). At this rate, a single bacteria cell can increase to 1,048,567 cells after just 7 hours. This unique duplication of bacteria add complexities to how quick and effective an antimicrobial should be in killing bacteria [123]. Ideal antimicrobials should exhibit the following characteristics:

- has a wide range of effectiveness against both bacteria and fungi
- Matching durability with the life of the product
- Absolutely non-toxic to humans at the applied concentration

- Safe in handling and applying
- Colorless and odorless
- Moderate costs and effective at low concentration
- Not affecting the handle or other properties of the fabric
- Compatible with water-repellent and fire retardant finishes, also with dye and other chemical finishes applied on the fabric
- Not to accelerate or catalyze the degenerative process
- Applicable in the processes of standard textile machineries
- Holding up to the processing conditions and temperature
- Environmentally benign
- Fibrous materials can be protected by one of the following approaches:
 - Killing the microorganism
 - Blocking the secreted degrading enzymes
 - Applying a barrier (like coating)
 - Modifying the fiber (top surface or whole)

The first approach applies to hygienic and aesthetic antimicrobial/antiviral finishes and the other three are more theoretic or applicable for rotproofing finish which out of this context.

There are two mechanisms to kill a microorganism using a biocide: first the metabolic process of the microorganism can be stopped through a chemical reaction with the cell membrane. For example, metallic ions like silver and mercury with biocidal properties kill the cell by replacing the hydrogen ion in the bacteria with the metallic ion and then the biocide penetrates the cell wall and poison the cell wall within. In the second mechanism, the enzymes secreted by microorganism are blocked and the microorganism is disarmed.

The biocides developed based on these two mechanisms are divided into two categories: the first category includes compounds operating based on the controlled-release mechanism in which the antimicrobial is released slowly from a reservoir which could be incorporated either into the fabric or on the surface, and this type of biocides is generally called leaching antimicrobials. This type of antimicrobials is characterized by its effectiveness against microbes both on the surface and around, however, as the reservoir is depleted the biocidal

activity is lost. The second category of antimicrobial compounds is chemical structures that have the ability to chemically bond to the fiber surface. The main advantage of this type is that they exist only on the surface and do not leach into the environments.

Antimicrobials can fit into a larger category based on their mode of action. The group that controls the rate of the growth and spread of the micro-organism are called biostats, and the compounds that kill microbes are known as biocides. Biocides are strongly under the supervision of the governmental regulations since they may have many side effects including killing useful microorganisms in the surrounding environment [123]. The latest general trend for new antimicrobial agents is toward fully organic products that possess good environmental and safety properties. Some of the most common antimicrobials are shown in Table 2-12.

Table 2-12 Typical modern antimicrobials [120]

Name	Comment
2,4,4'-Trichloro-2'-hydroxy-diphenyl ether	Originally developed by Ciba
Triclosan	Have a very good toxicity profile and is considered very safe, used in textiles where skin contact is involved.
2,2'-Dihydroxy-5,5'-dichloro-diphenyl methane	Effective biocide with good biodegradability.
Dichlorophen	Suitable for many applications although not recommended for skin contact.
Isothiazolones e.g 1,2-Benzisothiazolin-3-one (BIT) 2-n-Octyl-4-isothiazolin-3-one (Octhilinone) 5-Chloro-2-methyl-4-isothiazolin-3-one Ortho phenyl phenol	These antimicrobials are used in wide range of applications from preservatives in aqueous latex systems and cosmetics to mildewcides, slimeicides and textiles applications.
Poly hexa methylene biguanide (PHMB)	The structure of this molecule enables it to bond to cellulosic materials and give very good durability. It has a long history of safe use in applications such as swimming pools and cosmetics.

2.8.2 Chemistry of antimicrobial finishes

2.8.2.1 Controlled- release antimicrobial

In textiles, the product chosen to apply as an antimicrobial agent should not only have good application and durability, but also follows the environmental regulation, therefore, many of the antimicrobials used formerly are now strictly prohibited and their application is extinct. Compounds such as copper naphthenate, copper-8-quinolate and many of the organo mercury compounds are seized to use. There are chemicals such as dichlorophene and 3-iodopropynylbutylcarbamate which have a broad range of activity against many bacteria and fungi, however, they do not have the desired durability. Other products such as benzimidazol derivatives, salicylanilides and alkylolamide salts of undecylenic acid showed better durability using with resins but there is a risk of deactivation due to the resin presence. 2,4,4'-trichloro-2'-hydroxydiphenyl ether is one the most common antimicrobials known as “triclosan”, the structure of this compound is shown in Figure 2-15. Although triclosan is very effective against bacteria, it is not effective against fungi. While triclosan has low water solubility and requires dispersing agent for textile application, quaternary ammonium salts with antibacterial properties are water soluble and can be grafted to textiles if they have active sites for covalent bond formation such as monomer containing quaternary ammonium salts. The most recent controlled-release agents are based on organo-silver and silver zeolite chemistry with low toxicity and high durability. Several types of synthetic fibers were modified by incorporating silver particles in both wet and dry spinning processes. Another novel approach to the leaching antimicrobials is microencapsulation in which the filled capsules are integrated into the fiber during the spinning or in a separate coating process. However, gradual release of active substance can provide the conditions for the development of antimicrobial resistance.

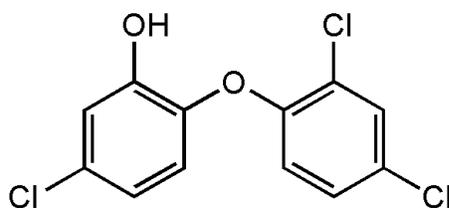
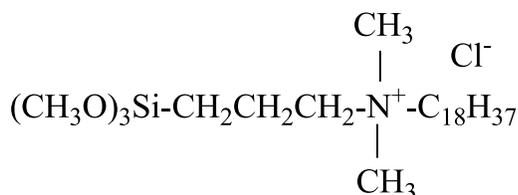


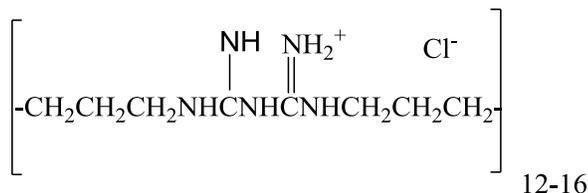
Figure 2-15 Triclosan structure as control released antimicrobial

2.8.2.2 Bound antimicrobials

Developing non-leaching antimicrobial agents received significant interest in recent years. Immobilization of the substance on the substrate via chemical bonds not only enhances the durability, but also decreases the toxicity compared to leaching antimicrobials. Octadecylaminodimethyltrimethoxysilylpropylammonium chloride (Figure 2-16) is a popular compound that can be exhaust and or pad applied. A post curing step forms a siloxane polymer on the surface which at the same time immobilizes the quaternary nitrogen, which is the reactive site of the molecule.



Octadecylaminodimethyltrimethoxysilylpropylammonium chloride



Polyhexamethylene biguanide

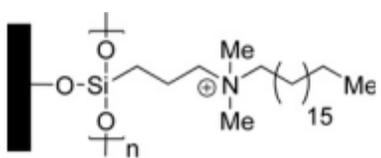
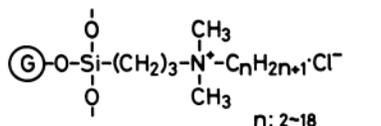
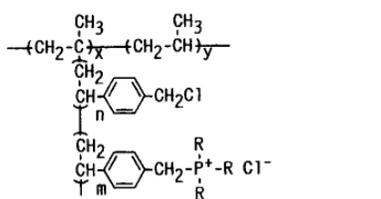
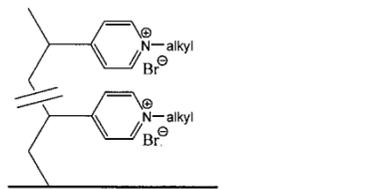
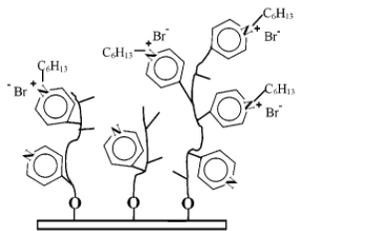
Figure 2-16 Bound antimicrobials [123]

Chitosan as a modified biopolymer regenerated from crustacean shells has also antimicrobial properties and can be applied to the substrate via microencapsulation or via covalent bond formation with cellulosic fabrics. The free amino groups developed during the alkaline treatment exhibits fungistatic and bacterostatic properties. Methylation of the amino group to quaternary trimethylammonium boosts the antibacterial effect [123].

In a study performed in 1973 on a bound antimicrobial at Dow Corning Co. [143,144], 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride was applied on 28 natural and synthetic substrates and the treatments were evaluated using twenty six

different microorganisms, and they were all reported to have antimicrobial properties with acceptable wash fastness. Some of examples of polycations with antibacterial properties immobilized on different surfaces are shown in Table 2-13. The activity of surface bound substances is limited by their molecular length and they can only penetrate the microbe cell membrane if they can extend far enough away from the surface. Beagheri et al. and Haynie et. al. reported that immobilization of the amphiphilic peptide through covalent bonds reduces the activity by two orders of magnitude [152,153]. Tiller et. al. [147] found that that shorter polymer chains of poly(vinyl- N-alkylpyridinium bromide) (PVP) immobilized on NH₂-glass slide are significantly less effective than those with higher molecular weight (62% as opposed to 94% for 60,000 and 160,000 g/mol respectively). He also demonstrated that the effectiveness of biocidal activity is significantly affected by the number of carbons in the fatty alkyl chain attached to the N atom in the pyridinium groups. Figure 2-17 shows that propylated (C₃), butylated (C₄), hexylated (C₆), and octylated (C₈) immobilized PVP chains were more effective in reducing the number of viable bacterial cells (*S. aureus*), with hexyl-PVP being the most effective. This is why immobilized PVP N-alkylated by decyl (C₁₀) through hexadecyl (C₁₆) bromides, as well as the non-alkylated chains, were ineffective.

Table 2-13 Various antimicrobial polycations immobilized on different surfaces

Item	Chemical Structure	Substrate	Method of Immobilization	Microorganism	Refs. Year
1	 <p>3-(trimethoxysilyl)-propyldimethyl-octadecyl ammonium chloride</p>	28 different substrate	Wet chemical. Glass surfaces and cotton cloth were immersed at room temperature in 0.1% Si-QAC for 10 min and then dried at 70° C for 30 min.	26 different microorganisms	143,144 1972
2	 <p>Quaternary ammonium of 3-chloropropyltrimethoxysilane</p>	Porous glass	Wet chemical. Porous glass was reacted with 3-chloropropyltrimethoxysilane under toluene refluxing at 110° C and then quaternized with N,N-dimethyl-n-alkylamines	E. coli	145 1984
3	 <p>Phosphonium salt</p>	Polypropylene film	Radiation grafting by light (photografting). PP was photografted with 4-chloromethylstyrene and then reacted with trialkylphosphine in n-hexane	E. coli	146 1993
4	 <p>Poly(4-vinyl-N-alkylpyridinium bromide)</p>	Glass	Surface graft copolymerization with 4VP, quaternized with alkyl bromide.	S. aureus, S. epidermidis, P. aeruginosa, E. coli	146 2001
5	 <p>N-hexyl bromide poly(4-vinylpyridine)</p>	PET film, Paper	Plasma treatment with argon –exposed to air – UV irradiated in 4VP – quaternization with hexyl bromide.	E. coli	148 2003

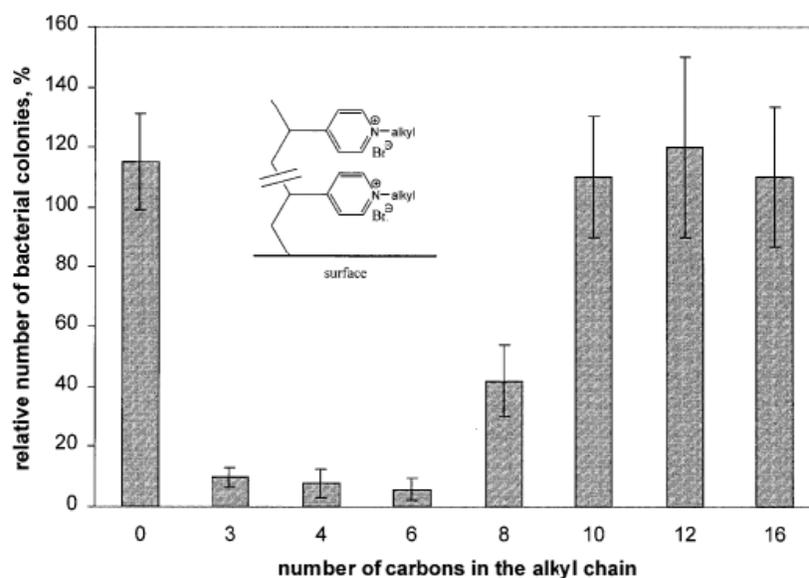


Figure 2-17 Effect of N-alkylation to antimicrobial activity of polyvinyl pyridine against *S. aureus* (106 cells/mL) [151]

2.8.3. Antimicrobial plasma treatment on polymeric substrates

Over the last ten years, plasma treatments of textiles were extensively studied. A very large number of papers were published and patents were registered on this subject, all focusing on different aspects of plasma processing such as gas composition, types of textiles, plasma treatments for textile finishing and product innovation.

Applications of plasma processes in imparting antimicrobial properties on textile surfaces through chemically bonded antimicrobial received significant interest in the last decade. However the majority of the reported processes were performed using vacuum plasma [44,45,46,48]. Atmospheric pressure plasma technique was used recently for antimicrobial treatment on textile substrates [49, 50]. Morent's review paper [43] provided an exhaustive discussion on the use of plasma to impart different functionalities and surface modifications for textiles. Table 2-14 lists the activities in the development of antimicrobial polymers and textiles aided by non-thermal plasma, which was used either to create functional groups or active sites for grafting on the substrate surface. Although the APP system has existed since late 1990's, all the studies cited above are dominated by low-

pressure plasmas. However, studies reported on the use of atmospheric plasma started to appear in the second half of the period. In all cases, plasma had been utilized to create reactive sites, in the form of oxygen functionalities or radical sites, for graft-polymerization to take place via either grafting-from or grafting-to method. However, none of them used plasma to induce the grafting reaction; plasma was employed as a means for surface activation only. Graft polymerization, on the other hand, was carried out by the conventional wet chemical reaction [43, 44, 49,50] pad-cure[158] or UV irradiation [46,148] which is illustrated as an example in Figure 2-18. In this case, plasma-aided or plasma-assisted graft-polymerization would be the more appropriate term. Mittal's [159] research is an example for plasma induced graft polymerization in which the substrate is pre-activated by plasma and then the monomer was vapor deposited on the substrate surface. Following the deposition of the monomer, the substrate was exposed to a second plasma treatment to ensure complete polymerization of the monomer.

Table 2-14 Antimicrobial plasma treatment of polymers and textiles in chronological order.

Item	Substrate	Plasma System	Plasma Medium	Antimicrobial Agent	Year	Authors	Refs.
1	PE, PP, PET, PU, PTFE	Low-pressure	CO ₂ +C ₂ H ₄ , CO ₂ +C ₄ F ₈ (plasma polym.); O ₂ (PIGP)	Acrylic acid, butyl acrylate, methyl vinyl acetamide. AgNO ₃	1995	Jansen & Kohnen	160
2	PET nonwoven	Low-pressure	Ar	Acrylamide, itaconic acid. AgNO ₃ , chitosan, VQAS	2002	Yang et al.	161
3	PE film	Low-pressure	He/Air	DADMAC	2003	Thome et al.	44
4	PET film, cellulose nonwoven	Low-pressure	Ar/Air	4-vinylpyridine	2003	Cen et al.	148
5	PA fabric	Low-pressure	O ₂	AgNO ₃	2003	Yuranova et al.	48
6	PET film	Low-pressure	Ar/Air	Viologen	2005	Shi et al.	162
7	PVDF mesh	Low-pressure	Ar	Acrylic acid, Gentamicin	2005	Junge et al.	163
8	Cellulose nonwoven	Low-pressure	O ₂	Acrylic acid, Gentamicin	2006	Jampala et al.	164
9	PET nonwoven	Low-pressure	Ar	N-vinyl-2-pyrrolidone	2006	Chen et al.	46
10	Cotton fabric	Low-pressure	O ₂	Neem extract (Azadirachtin)	2007	Vaideki et al.	47
11	PP nonwoven	APP	He	GMA, chitosan	2007	Gawish et al.	49
12	PP nonwoven	APP	He+O ₂	GMA, chitosan	2007	Wafa et al.	50
13	Wool	Low-pressure	Ar	SiO ₂ (Ag)-NH ₂	2007	Wang et al.	167
14	PET,PA fabric	Corona	Air	Nano silver	2008	Radetic et al.	169
15	PET fabric	APP	Ar+O ₂ /Air	Chitosan	2008	Change et al.	158
16	Nylon fabric	APP	Air	Chitosan	2009	Tseng et al.	165

Table 2-15 Continued

Item	Substrate	Plasma System	Plasma Medium	Antimicrobial Agent	Year	Authors	Refs.
17	Polyimide	Low pressure	Ar/Air	Vinyl-viologen, AgNO ₃	2009	Cui et al.	166
18	PET,PA fabric	Corona	Air	Nano silver	2009	Ilic et al.	170
19	PET fabric	Corona	Air	Nano silver	2010	Gorensek et al.	171

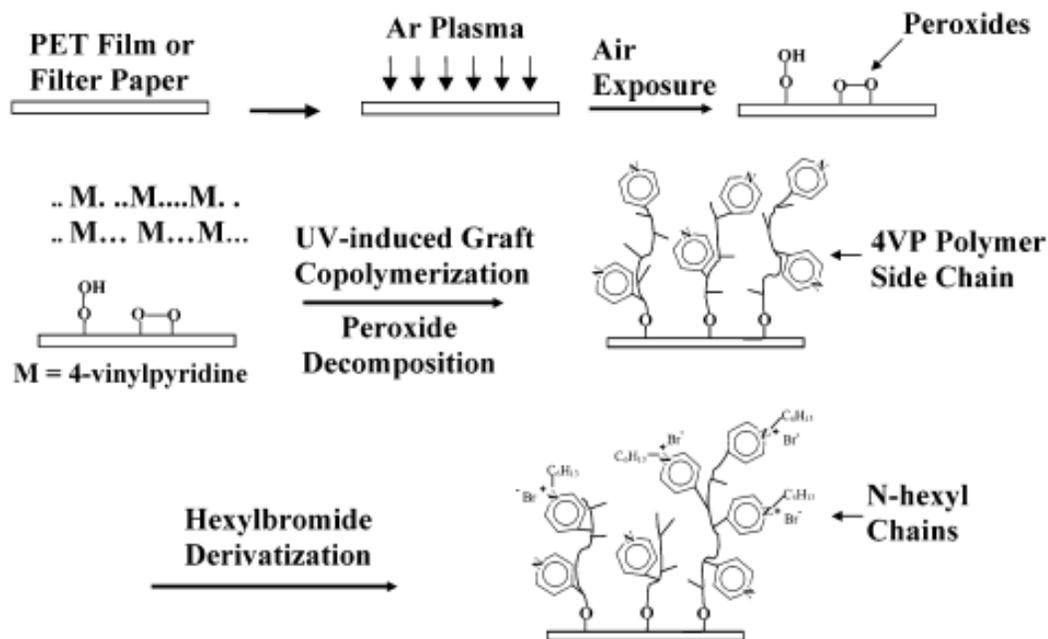


Figure 2-18 Plasma-assisted UV-induced graft-polymerization for antimicrobial functionality on PET film and cellulose nonwoven surface using 4-vinylpyridine. Substrates were activated by Ar plasma, and then exposed to ambient air to generate surface peroxides, which decomposed into free radicals during the subsequent UV-irradiation. The formed radicals were used as the reaction sites and to initiate the graft-polymerization of monomers from the surface.

2.8.4 Evaluation of antimicrobial treatment

There are several standard test methods to evaluate the antimicrobial finish on textiles. Table 2-15 lists the AATCC Test Methods for antimicrobials evaluations. AATCC - 147 is a qualitative test and AATCC-100 is considered as a quantitative one. The agar-based

zone of inhibition tests and the bacteria counting tests are more common than the other methods.

Table 2-16 AATCC antimicrobial evaluation test methods [123]

AATCC test method	Comments
147- Agar plate test	Rapid and qualitative , applicable for both Gram-positive and Gram-negative bacteria. Treated material is placed in nutrient agar that is (agar plate test) streaked with test bacteria. Bacterial growth is determined visually after incubation. Antibacterial activity is demonstrated by zones of inhibition on and around the textile. (Figure 20)
100- Antibacterial finish assessment	Quantitative method, applicable for both Gram-positive and Gram-negative bacteria. The amount of bacterial growth in inoculated and incubated textiles is determined through serial dilutions and subsequent inoculations of sterile agar.
30- Antifungal activity assessment	Include Four methods for determining the antifungal properties of treated textiles[123]
174 -Antimicrobial activity assessment for carpets	Have procedures and materials similar to those in the above test methods.

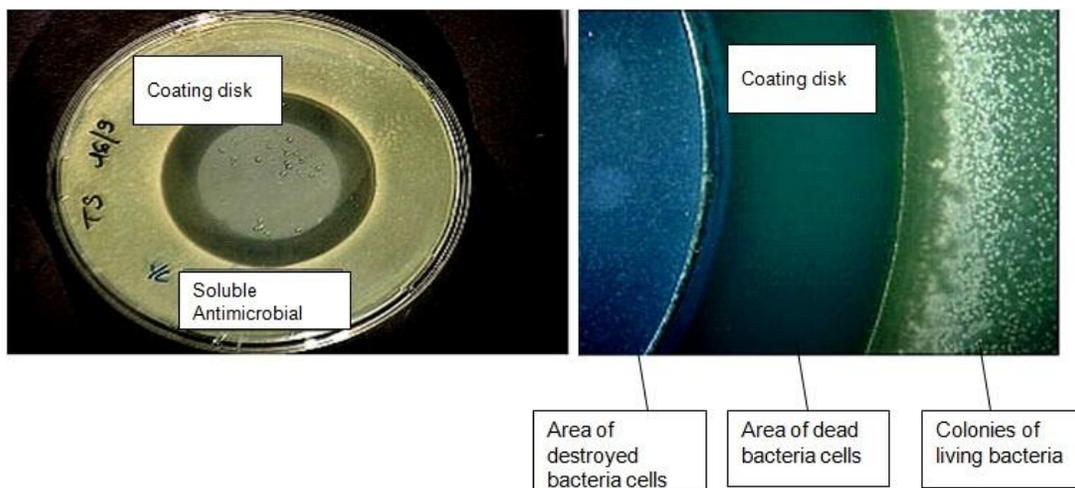


Figure 2-19 AATCC-147; Qualitative zone of inhibition testing (Courtesy of Anovotek, LLC)

New York State method 1241 and ASTM-2149 are quantitative methods. The former was developed for purchasing specifications and has been under review by AATCC. The latter originated at Dow Chemical in the need to proof the effectiveness of quaternary silane based product and then was adopted by ASTM.

AATCC-100 is a relatively dry test method (1 ml solution in large sample container) in which the surface area can vary. It works best for highly soluble products and fabric with high moisture regain. This test is also more suitable for leaching and non-durable antimicrobials.

NYS-1241 has a fixed area of sample and is relatively a humidity test (10 ml water reservoir in the small volume of a closed petri dish). It works best for low solubility, moisture activated products and for fabric with lower inherent moisture regain. The samples are static after inoculation and the method is good for low solubility antimicrobials with high durability. ASTM-2149 has also fixed sample size and works well for both soluble and insoluble chemistries, the samples are continuously shaken during the test.

The choice of test condition within a particular antimicrobial test depends on several parameters such as:

- Organism type: Some species behave more reproducibly than others on specific fabrics
- Nutrient: The higher the nutrient, the stronger the antimicrobial must be to overcome the organisms
- Cell concentration: The higher the cell concentration, the stronger the antimicrobial must be to overcome the organisms
- Moisture content in environment
- Number of swatches used in the AATCC 100
- Fabric characteristics: Fabric type, wettability, chemical/physical properties of the antimicrobial treatment, laundering conditions, temperature, detergent and detergent residual
- Analyst-dependent operations: Fabric inoculation, recovery are manual techniques that vary from person to person and must be closely controlled to ensure reproducibility

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Chapter 3 Hydrophobic/Oleophobic Properties Imparted by Plasma

Induced Graft Polymerization on Nonwoven Substrate

3.1 Abstract

Hydrophobic/Oleophobic properties were achieved on nonwoven polyester (PET) via vapor deposition of different non C8-perfluorcarbon monomers including perfluorohexylethylmethacrylate, perfluorohexylethylacrylate, allylpentafluorobenzene, pentafluorostyrene or 1,3-divinyltetramethyldisiloxane followed by induced graft polymerization using high density atmospheric pressure plasma. Different nanolayer thicknesses (80-180nm) of the grafted polymer were furnished to generate surfaces with different level of wettabilities for medical applications and and water/fuel separation. The effect of different monomer chemistries, different plasma conditions, and plasma device parameters including plasma power and plasma exposure time were studied and the performance was characterized by measuring the contact angle and the wettability rating against liquids with broad range of surface tensions ranged from 59.0 to 20.0 mN/m. The surface chemistry and morphology of the treated samples were characterized using XPS TOF-SIMS and SEM techniques.

3.2 Introduction

Plasma technology has received enormous attention as a solution for environmental problems in textiles [1,2]. Moreover, low-temperature plasma or so called cold plasma has been proven to be suitable for textile applications because of its high electron energy and low thermal capacity which changes only the surface chemistry of the substrates while maintaining the bulk intact [3-5]. The main processes in plasma are etching, activation, and graft-induced polymerization. In grafting, the accelerated electrons and ions from the plasma have sufficient energy to homolytically break the chemical bonds in the polymeric structure of the fabric and generate kinetically reactive radical macromolecule on the substrate surface,

which subsequently initiate graft-induced polymerization of the introduced monomer [6,7]. Figure 3-1 shows a typical grafting process of vinyl monomer on a polymeric surface containing kinetically reactive radicals generated using cold plasma. Unlike conventional finishing methods in the textile industry, plasma treatment is a water free dry process because it uses monomers in the neat form, and therefore, it is considered a green chemistry technique for value added textiles. Atmospheric cold plasma treatment has been successfully used to create covalently-bonded finishes with excellent durability on different textile substrates for different applications [8-10]. Furthermore, surface functionalization with different hydrophobic monomers has been demonstrated to be a reliable approach to generate hydrophobic functionalities for water/fuel separation [11-13].

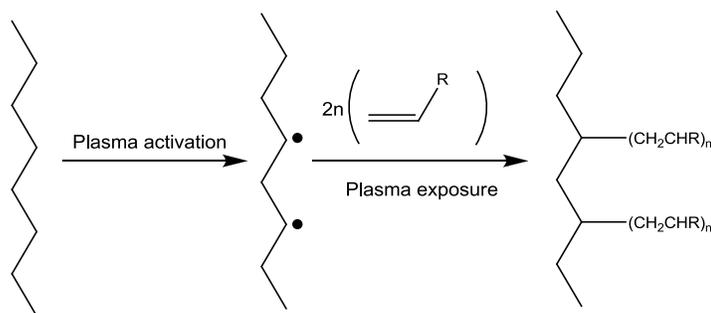


Figure 3-1 Plasma induced graft polymerization of vinyl monomer, where n is the number of repeating units and $\text{R} = \text{C}_n\text{F}_{2n+1}\text{CH}_2\text{CH}_2\text{OCO}$.

The EPA Stewardship Program 2010/2015 states that all companies should stop manufacturing, using and/or selling C8 fluorocarbons, e.g., perfluorooctylethylacrylate analogs, or any other fluorocarbons that would produce perfluorooctanoic acid (PFOA) as a byproduct [14]. To comply with the EPA Stewardship Program, only C6 fluorochemistry, has been used on nonwoven PET in the present work. Nonwoven PET has a wide range of applications, including hydrophobic pre-filter for air intakes, residential ventilation, surgical face masks, acoustic layers, depth filters and also as oleophobic screen for water/fuel separation or fuel filtration. The performance of the treated nonwovens was evaluated measuring the static and the rolling contact angles, AATCC water/alcohol and oil repellency ratings, XPS and TOF-SIMS techniques.

3.3 Experimental

3.3.1 Materials

An unfinished spunbond PET nonwoven supplied by the Nonwoven Cooperative Research Center (NCRC at NCSU) with the basis weight of approximately 50 g/m² and approximate thickness of 0.66 mm was used as the substrate. Two commercial monomers based on 2-(perfluorohexyl)ethyl methacrylate (TG-20) and perfluorohexylethyl acrylate (TG-30) were used as received from Daikin America, Inc. Pure monomers including pentafluorostyrene, allylpentafluorobenzene and 1,3 divinyldimethylsiloxane were used as received from Sigma-Aldrich, USA. The chemical structure of the monomers is shown in Figure 3-2. Industrial grade helium and ultrahigh pure argon grade 5.0 supplied by Machine and Welding Supplies Co., North Carolina, USA, were used for plasma process. The flow rate of the monomer was changed using a peristaltic pump assembly (0.6-35mL/min) from Cole-Parmer Instrument Company. The flow rates of helium and argon were controlled using flowmeters purchased from Thermo Fisher.

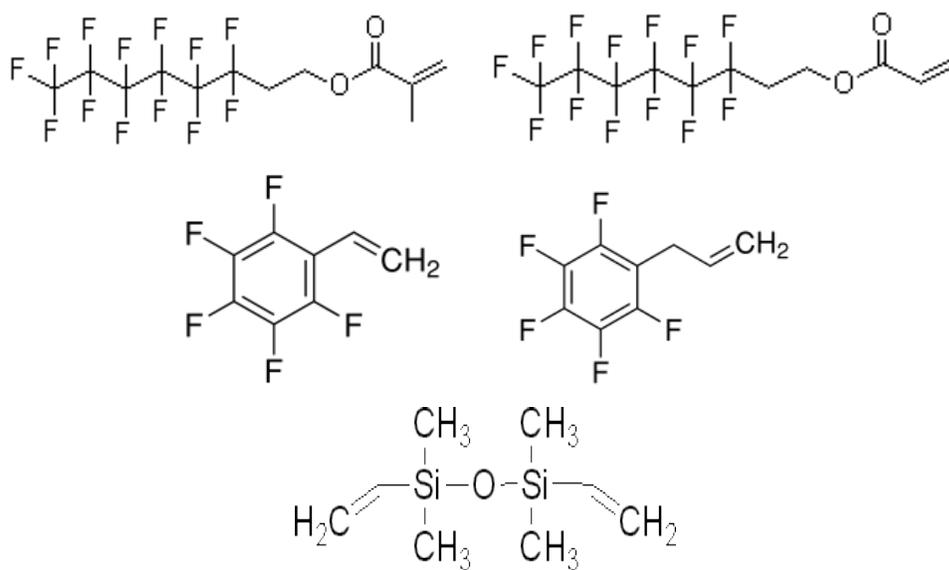


Figure 3-2 Chemical structure of the monomers

3.3.2 Apparatus: Atmospheric Pressure Plasma Reactor (APPR)

Plasma treatments were conducted with e-Rio™ Atmospheric Pressure Plasma System Model APPR-D300-13 (APJeT, Inc. Santa Fe, New Mexico) (Figure 3-3). It is a glow-discharge plasma reactor having dimensions of 33 cm by 12.5 cm powered by a RF (13.56 MHz) power supply and matching network. It can operate in in-situ or down-stream mode depending on the configuration of the electrodes. In in-situ mode of operation, the sample stage is grounded so that it becomes the ground electrode and forms parallel plate electrodes with the RF-powered electrode. The substrate, with maximum sample size of 31 cm by 31 cm, is passed through the plasma volume, which is generated and sustained between the two electrodes (Figure 3-4). In downstream mode, the substrate is passed under the plasma volume at a certain distance that can be adjusted externally with the use of a synchronized adjustment screw. The standard feed gas is helium, which can be mixed with a small amount of NH₃ gas (0.1-0.3%) to increase the lifetime of active species created in the plasma.

The plasma assembly consists of an evaporator and applicator. The evaporator is a heated assembly that operates at 10°C higher than the boiling point of the monomer to ensure complete conversion of the liquid monomer into vapor once it enters the evaporator. The temperature of the evaporator is regulated by a logic controller that is connected to a thermo-coupler attached to the evaporator. Similarly, the temperature of the applicator is regulated by a logic controller that is connected to a thermo-coupler attached to the applicator. The temperature of the applicator is usually set at 10°C higher than that of the evaporator to maintain the monomer in the vapor form, and the applicator acts as a heated nozzle to deliver the vaporized monomer onto the fabric sample through a narrow and uniform slit across the ground electrode. The hot monomer vapor condenses on the room temperature fabric surface, fastened to the ground electrode using a double-sided tape, forming a thin layer of monomer liquid in the nanolayer range (80-180nm), depending on the flow rate of the monomer. The monomer vapor is pushed from the evaporator into the applicator onto the fabric surface with the aid of argon gas. The feed gas, typically helium, flows at a particular rate to generate the plasma in the plasma chamber between the RF electrode and ground electrode, and the substrate loaded with a nanolayer of the monomer passes between the two electrodes. The

gap between the two electrodes is considered as one of the plasma variables that can be changed depending on the fabric thickness.

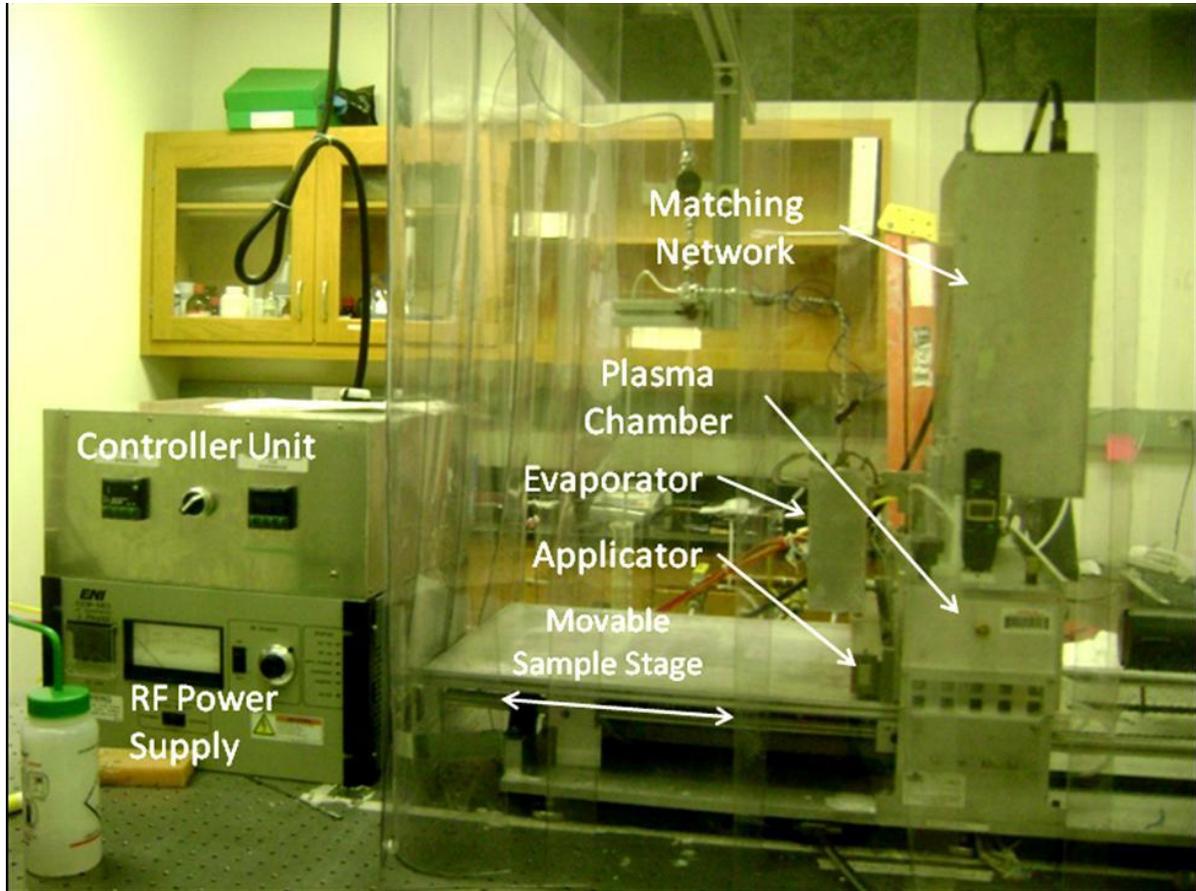


Figure 3-3 Atmospheric pressure plasma jet APPR-D300-13 at College of Textiles, NCSU.

3.3.3 Procedure

The nonwoven samples (15×25 cm) were placed on the moving stage of the device. The stage is equipped with a speed controller system which adjusts the time of plasma exposure and monomer deposition. The significance of plasma treatment and monomer deposition sequence was examined by following a process includes a surface pre-activation of the sample by passing the sample through the plasma volume, followed by vapor deposition of the monomer onto the nonwovens immediately after the plasma exposure, and

then the second plasma treatment to complete the graft polymerization reaction on the surface.

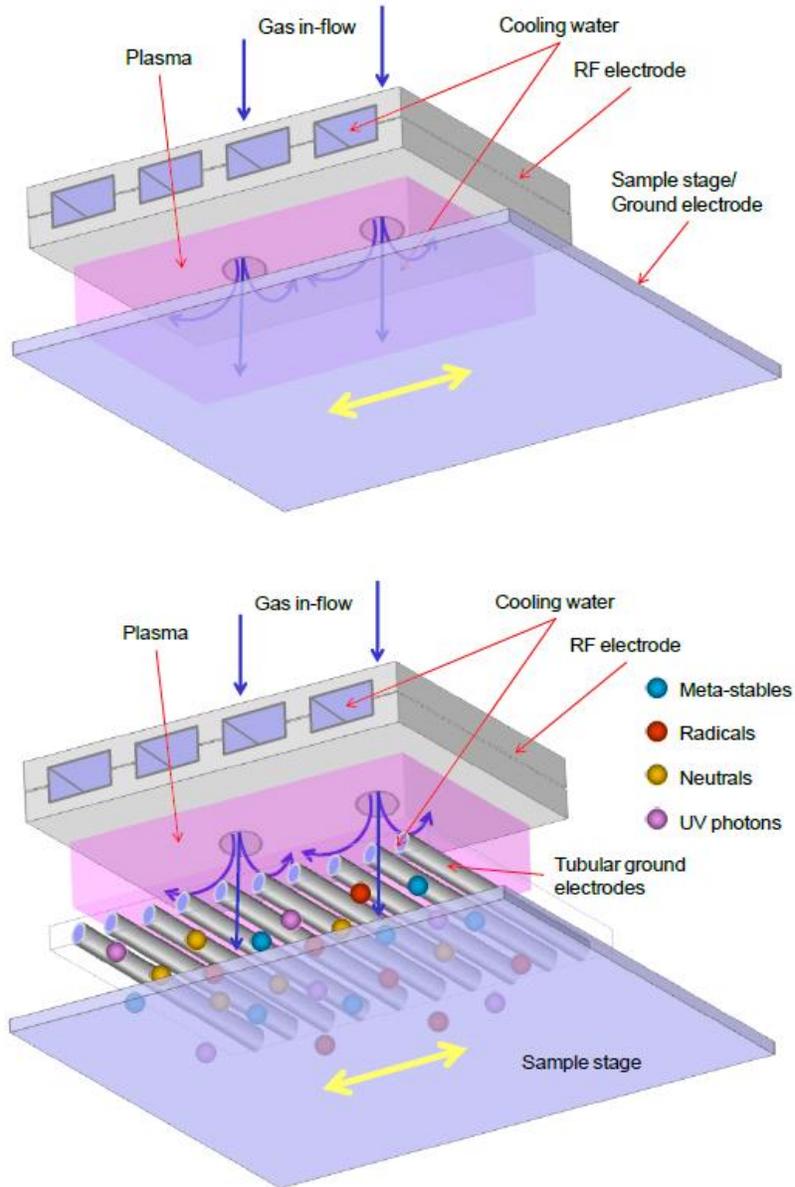


Figure 3-4 Schematic diagram of in-situ (top) configuration in APPR-D300-13 atmospheric pressure plasma jet viewed in perspective angle from below.

The experiments were carried out at constant flow rates of He (40 SLPM) and Ar (1 SLPM). The electrodes gap was kept constant (1.0 mm for in-situ mode and 3.0 mm for down-stream mode) while the other parameters including power of the plasma, time of exposure for both plasma pre-activation and post induced polymerization step and the monomer flow rate were varied for each individual monomer. All the results reported herein for perfluorohexylethyl methacrylate (TG-20) were collected when the device was operating in the in-situ mode. The rest of the monomers were investigated in the down-stream mode of the device. Table 3-1 to 3-5 shows the experimental parameters applied for each monomer.

Table 3-1 Experimental parameters for Perfluorohexylethyl methacrylate (TG-20)

Parameter	Value
Flow Rate of Monomer (ml/min)	0.6,0.8,1.00
Flow Rate of Helium (SLPM)	40
Flow Rate of Argon (SLPM)	1
Operating Plasma Power (Watt)	350,450,550,650
Gap Between Electrodes (mm)	1.0
Pre and Post Plasma Exposure Time (Sec)	30

Table 3-2 Experimental parameters for Perfluorohexylethyl acrylate (TG-30)

Parameter	Value
Flow Rate of Monomer (ml/min)	0.6,0.8,1.00
Flow Rate of Helium (SLPM)	40
Flow Rate of Argon (SLPM)	1
Operating Plasma Power (Watt)	300,450,600,750 W
Gap Between Electrodes (mm)	3.0
Pre and Post Plasma Exposure Time (Sec)	5,10,15,20,25,30

Table 3-3 Experimental parameters for Pentafluorostyrene

Parameter	Value
Flow Rate of Monomer (ml/min)	0.6,0.8,1.00,1.2,1.4
Flow Rate of Helium (SLPM)	40
Flow Rate of Argon (SLPM)	1
Operating Plasma Power (Watt)	750
Gap Between Electrodes (mm)	3.0
Pre and Post Plasma Exposure Time (Sec)	30

Table 3-4 Experimental parameters for allylpentafluorobenzene

Parameter	Value
Flow Rate of Monomer (ml/min)	0.6
Flow Rate of Helium (SLPM)	40
Flow Rate of Argon (SLPM)	1
Operating Plasma Power (Watt)	300,450,600,750 W
Gap Between Electrodes (mm)	3.0
Pre and Post Plasma Exposure Time (Sec)	30

Table 3-5 Experimental parameters for 1,3 Divinyltetramethyldisiloxane

Parameter	Value
Flow Rate of Monomer (ml/min)	0.6,0.8,1.0
Flow Rate of Helium (SLPM)	40
Flow Rate of Argon (SLPM)	1
Operating Plasma Power (Watt)	750
Gap Between Electrodes (mm)	1.0
Pre and Post Plasma Exposure Time (Sec)	30

3.4 Characterization Methods

3.4.1 Static and Rolling Contact Angle

Both static and roll-off contact angle measurements were measured on the control and plasma treated PET fabrics at room temperature using the sessile drop technique. The volume of distilled water droplets were 10 μ L. The static contact angle images were obtained with an

optical contact-angle measurer (VCA Optima, AST Products, Inc) .The rolling contact angles were measured by placing a specimen on a level platform mounted on a Newport 495 rotation stage and inclining the specimen. Water droplets were placed onto the surface, and the angle of the stage was recorded when the drops begins to roll off. Contact angles were measured at five different spots of the fabric surface and the mean values were calculated.

3.4.2 Water/Alcohol and Oil Repellency Rating

Water/Alcohol and oil repellent properties of the treated samples were also measured according to AATCC (American Association of Textile Chemists and Colorists) 193-2009 Test Method and AATCC 118-2009 Test Method respectively. AATCC 193 test method evaluates the treated fabric resistance to wetting by a series of 8 water/alcohol solutions with different surface tensions, while in AATCC 118 the treated surface is tested by a series of test liquids consisting of 8 selected hydrocarbons with varying surface tensions. In the case of studying the water/alcohol repellency, drops of standard test liquids are placed on the fabric surface and are observed for wetting and wicking. The aqueous repellency is graded according to the highest numbered test liquid from 1 to 8 that does not wet the fabric surface within 30 seconds. In the case of oil repellency, test drops of oils are placed on the fabric and observed-the oil repellency rating of the fabric is the highest-numbered test liquid that will not wet the fabric within a period of 10 seconds.

3.4.3 Field Emission SEM

FE-SEM images were collected by The JEOL 6400 at NC State which is a cold field emission scanning electron microscope that allows for high resolution (1.5nm at 30kV).

3.4.4 X-Ray Electron Spectroscopy (XPS)

Surface chemical changes of the PET nonwovens were analyzed by a Perkin Elmer PHI 5400 XPS (x-ray photoelectron spectroscopy) spectrophotometer. The x-ray source was MgO (1,253.6 eV) with a 45° take-off angle. The possible scanning area varied from 200 microns in diameter to 3 -10 mm, and the scanning depth was about 1–10 nm. The references of XPS spectra were 285 eV for C1s, observed in hydrocarbon polymers.

3.4.5 TOF-SIMS

Time-of-flight secondary ion mass spectrometry, the TOF-SIMS, experiments were performed on treated samples at the NCSU Analytical Instrumentation Facility (AIF) with a TOF-SIMS instrument using a ^{69}Bi liquid metal ion gun at 25 kV primary high voltage and 2 kV extraction voltage. TOF-SIMS analyses were conducted using a TOF-SIMS V (ION TOF, Inc. Chestnut Ridge, NY) instrument equipped with a Bi_n^{m+} ($n = 1 - 5$, $m = 1, 2$) liquid metal ion gun. TOF-SIMS is a highly sensitive surface analytical technique for acquisition of elemental and molecular information from the surface (top 10 to 20 Å) of a material with high spatial and mass resolution. This technique neatly characterized the fluorine fragments/groups incorporated onto the surface of the fiber via RF plasma treatment.

3.5 Results and Discussion

3.5.1 Plasma Induced Graft Polymerization of Perfluorohexylethyl methacrylate (TG-20) in the *in-Situ* mode

3.5.1.1 Static Contact Angle Measurement

3.5.1.1.1 Effect of Monomer Flow Rate at Constant Operating Power

Figure 3-5 shows the image of water droplet on the surface of a sample treated with TG-20. Figure 3-6a shows the effect of different monomer flow rates on the static contact angle of samples treated at the 350 Watt. It is observed that the static contact angle of treated PET fabric increased linearly as a function of the monomer flow rate. By applying the minimum amount of monomer deposition (0.6 ml/min) on the fabric, the contact angle increased from 93° to 131° . It is expected that as the flow rate of monomer increases, the thickness of the graft polymerized nanolayer on the fabric surface increases. The first plasma exposure generates free radicals on the substrate surface which attack the vinyl group in the monomer and initiates a free radical graft polymerization. The second plasma exposure ensures that the polymerization reaction reaches completion. Figure 3-6b shows the effect of increasing the monomer flow rate from 0.6 to 1.0 mL/min on the wettability of the fabric at 650 Watt. The contact angle of the treated sample (70°) at the lowest monomer flow rate (0.6 ml/min) is lower than the control sample (93°). One possible explanation for this behavior is that using plasma at higher power (650 Watt) at a low flow rate of the monomer (0.6 mL/min)

could lead to the etching of the nanolayer of the fluorocarbon followed by substrate etching, and the generation of free radical that can react with oxygen and moisture from air to form peroxides and hydroxyl groups on the substrate surface and makes it more wettable than the control. However, this behavior was not observed at higher monomer flow rates, i.e. thicker nanolayers requires more plasma exposure time to etch the surface, which confirms the above explanation.

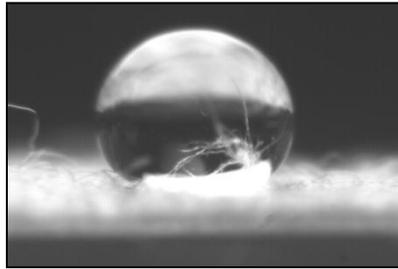


Figure 3-5 Image of water droplet on the surface of PET treated web

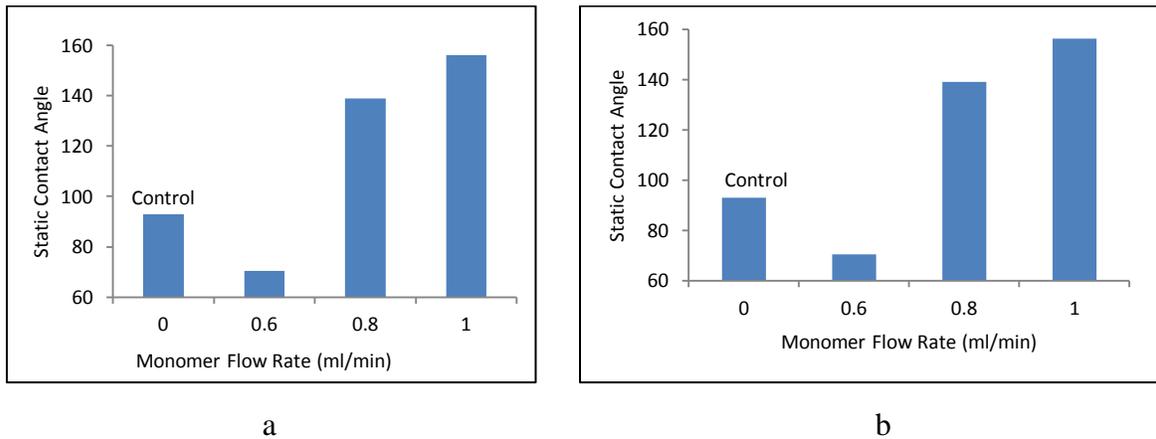


Figure 3-6 Effect of the monomer flow rate on the static contact angle at the operating power of a) 350 W and b) 650W.

3.5.1.1.2 Effect of Plasma Operating Power at Constant Monomer Flow Rate

Figure 3-7 shows the effect of different operating powers on the static contact angle at constant monomer flow rate (1.00 ml/min). It was found that increasing the plasma power at a constant monomer flow rate (1.00 ml/min) does not have a significant impact on the contact angles. The contact angle increased slowly from 152° to 156° as the plasma power increased

from 350 to 650W at 100 Watt intervals, which confirms that satisfactory contact angles can be achieved even at low operating power.

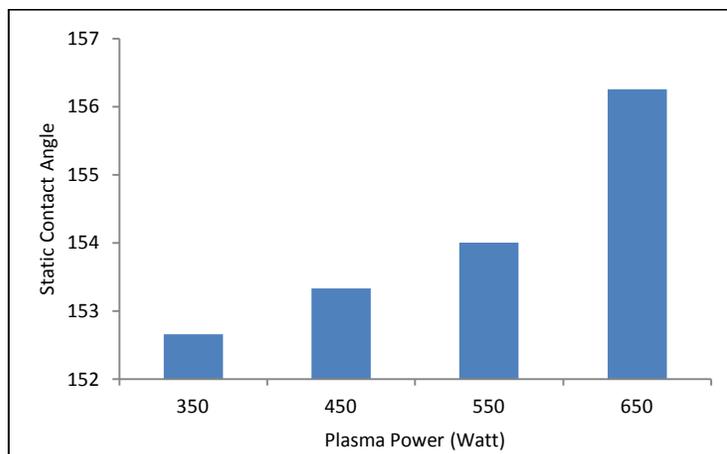


Figure 3-7 Effect of plasma operating power on static contact angle at constant monomer flow rate (1.00 ml/min).

3.5.1.2 Rolling Contact Angle Measurement

3.5.1.2.1 Effect of Monomer Flow Rate at Constant Operating Power

Figure 3-8 shows the steps of measuring rolling contact angles on the treated samples. The effect of monomer flow rate on rolling contact angle at two different operating powers is shown in Figure 3-9. It was observed that increasing the monomer flow rate increases the hydrophobic behavior of PET as the roll-off angle decreases, except for the samples treated at maximum plasma power with minimum monomer flow rate. The lower the dynamic contact angle, the more hydrophobic the surface is. The rolling contact angle of the samples decreased dramatically from 45° for the control to 27° after the plasma treatment at 350W. However, for the samples treated at 650W, the roll-off angle at 0.6mL/min flow rate was 44°, but it dropped off significantly when higher flow rates of the monomer were used, e.g., 24° at 1mL/min flow rate .

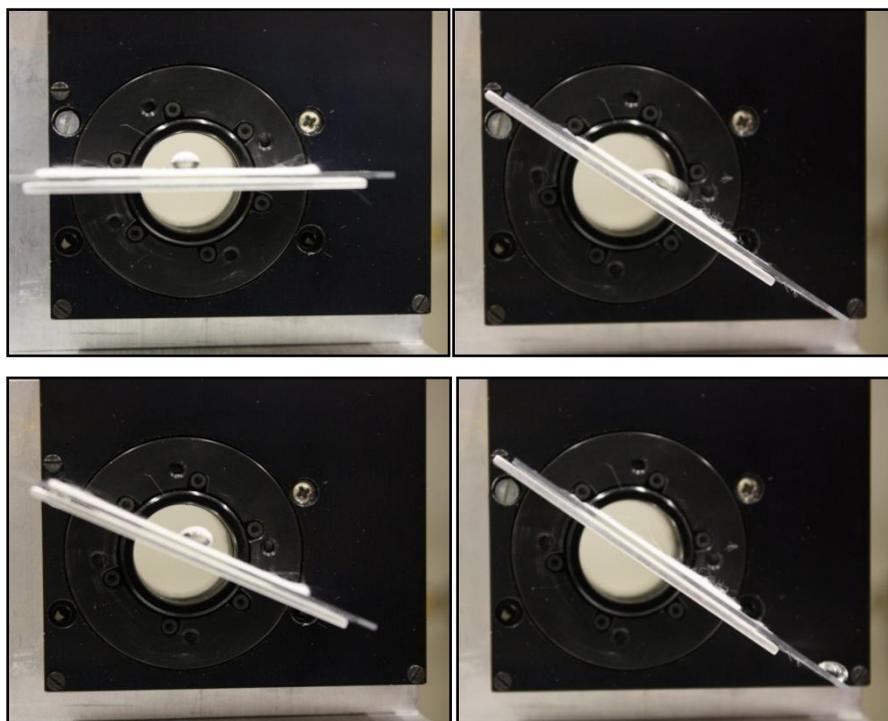


Figure 3-8 Rolling contact angle measurement on the PET samples.

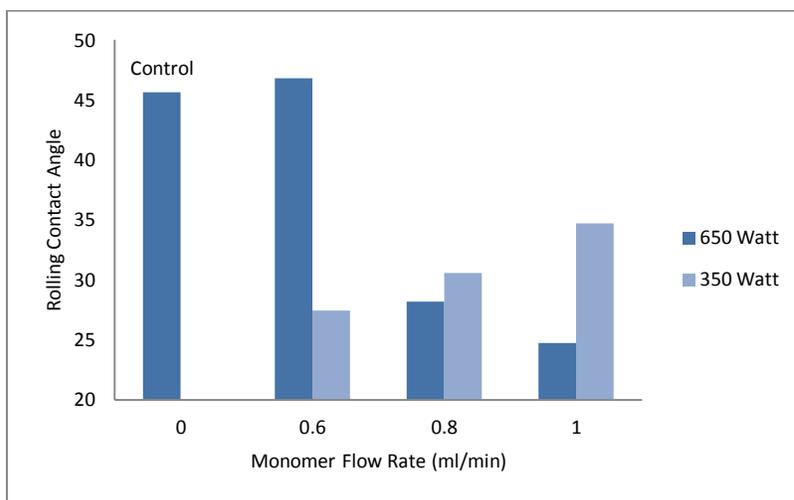


Figure 3-9 Effect of monomer flow rate on the rolling contact angle at the operating power of 350 and 650 W.

3.5.1.2.2 Effect of Plasma Power at Constant Monomer Flow Rate

The results of rolling contact angle measurements for samples treated at different plasma powers at the same flow rate of the monomer are depicted in Figure 3-10. The

dynamic contact angle at the maximum flow rate (1mL/min) was slightly reduced by increasing the plasma power.

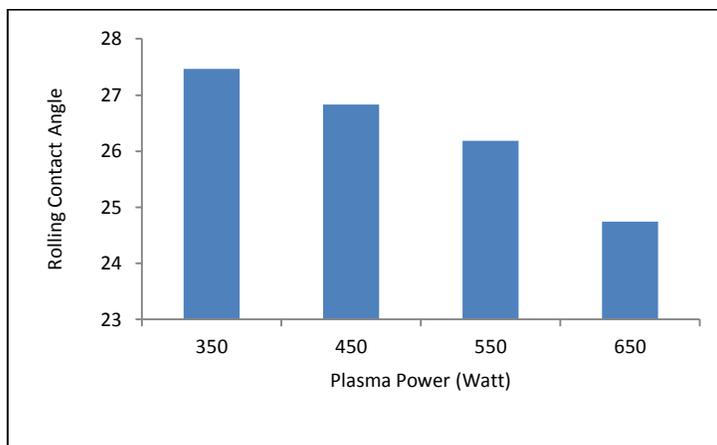


Figure 3-10 Effect of plasma operating power on the rolling contact angle at constant monomer flow rate (1.00 ml/min)

3.5.1.3 Surface Energy Rating /Wettability Analysis

3.5.1.3.1 Effect of Plasma Operating Power at Constant Monomer Flow Rate

Table 3-6 shows the combinations of the liquids and the corresponding surface tensions applied on the samples surfaces in both AATCC 118 and 193 Test Methods.

Table 3-6 Test liquids for water and oil repellency evaluation listed in AATCC TM 193 and 118.

Rating	Water/Alcohol repellency test liquids *	Surface Tension (mN/m)	Oil repellency test liquids	Surface Tension (mN/m)
1	2	59.0	Kaydol	31.5
2	5	50.0	65% kaydol **	28
3	10	42.0	n-hexadecane	27.6
4	20	33.0	n-tetradecane	26.7
5	30	27.0	n-dodecane	25.4
6	40	25.4	n-decane	23.9
7	50	24.5	n-octane	21.8
8	60	24.0	n-heptane	20.0

*Volume % Isopropanol in distilled water.; **Volume % in n-hexadecane.

Both PET control sample and TG-20 treated samples fails even the kaydol drop test (rated 1 in AATCC 118), which indicates that Tg-20 does not provide any oil repellency level on the surface.

Figure 3-11 shows the AATCC Test method 193 results comparing samples treated at two different powers with different monomer flow rates. Hydrophobic plasma treatment of the PET webs has significant effect on changing the fabric surface properties in a way that improves the water/alcohol repellency of the control sample from 2 for the control sample to 6 for the treated sample. Increasing the monomer flow rate at constant power slightly increases the repellency grade, while increasing the plasma power at the same monomer flow rate has stronger effect on changing the surface wettability behavior. Comparing the samples treated at the same monomer flow rate but different RF powers highlights the crucial role of plasma power on surface treatment. Higher amount of fluorocarbon monomer does not lead to the higher level of hydrophobicity. In fact, the ratio of monomer that undergoes free radical polymerization reaction on the surface is strongly tied to the amount of active species created so far on the surface via plasma pre-exposure and completing the reaction through the plasma post-exposure steps.

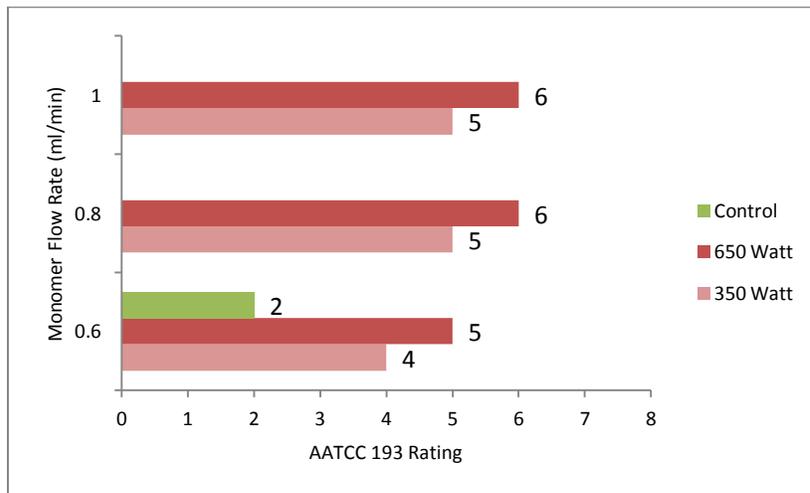


Figure 3-11 Effect of plasma operating power on the rolling contact angle at constant monomer flow rate (1.00 ml/min)

3.5.1.4 Surface Analysis

3.5.1.4.1 FE-SEM Imaging

Figure 3-12 shows the FESEM micrograph of PET control sample and TG20 plasma treated one in two magnifications. The surface of the control PET was very smooth while in the case of treated sample, a grafted monomer layer was clearly observed throughout the surface and fibers.

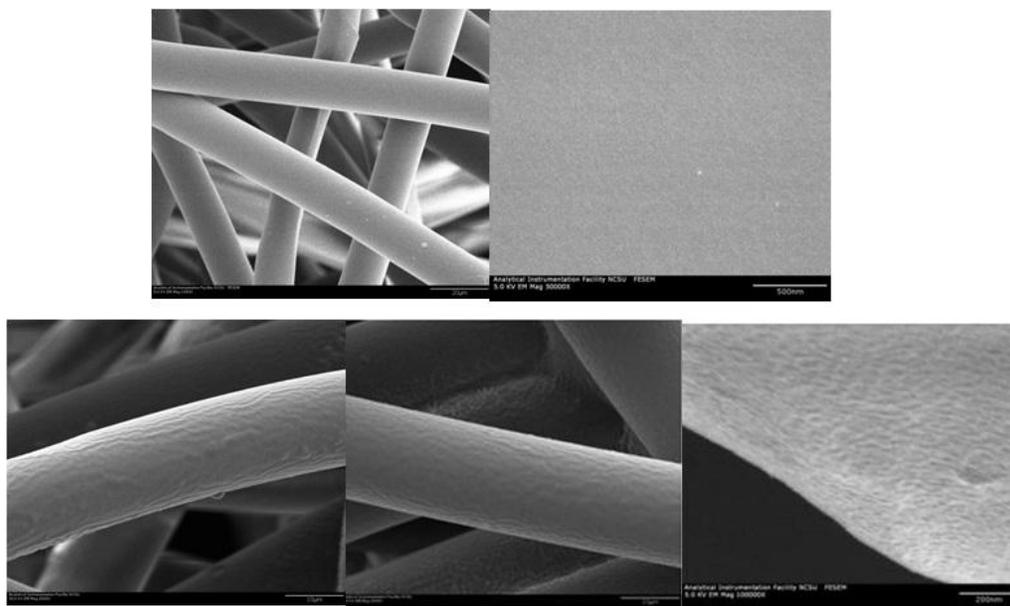


Figure 3-12 FESEM micrograph of control (top) and TG20 treated(bottom) PET samples

3.5.1.4.2 XPS

Figure 3-13 shows the XPS spectra of the untreated sample (a) versus the treated sample at two different powers of 350 and 650 W (b and c). The fluorine peak corresponding to the treated sample at 0.6 mL/min flow rate of the monomer at two different powers confirms the grafting of the monomer onto the surface. Furthermore, comparing the elemental percentage between two samples treated at the two different powers and same monomer flow rate, b and c spectra, indicates that the higher the power of the plasma, the greater the fluorine percentage on the surface is. In all samples, it was demonstrated that the carbon and oxygen content of the PET samples decreased after the plasma induced grafting

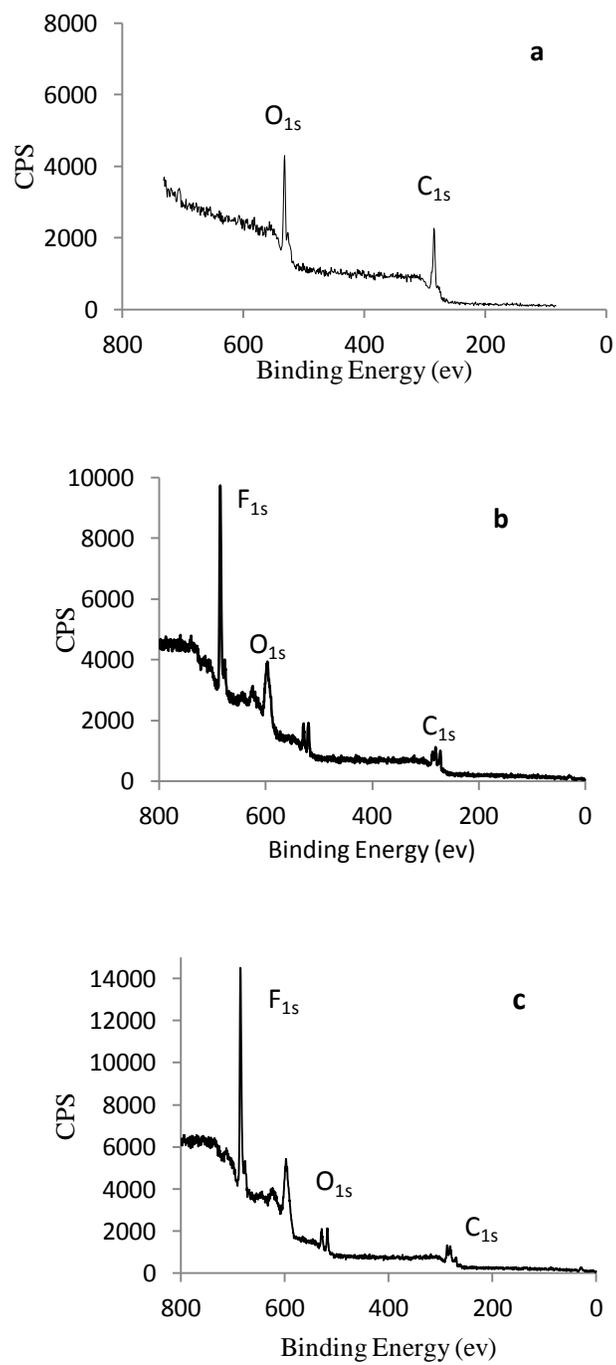
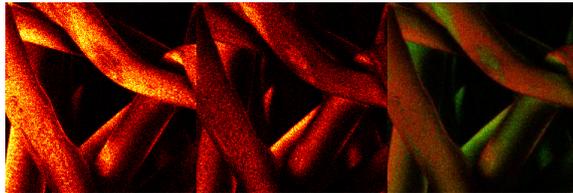
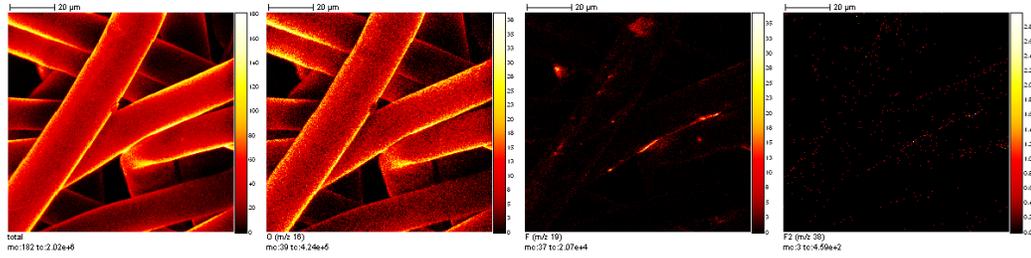


Figure 3-13 XPS survey scan of PET nonwoven fabrics; a) control, and b) treated sample in 350 W and c) treated sample in 650 W

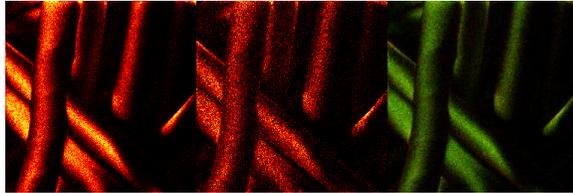
3.5.1.4.3 TOF-SIMS

In-situ grafting effects on the surface topo-chemistry were analyzed more through Time-of-flight secondary ion mass spectrometry technique. Samples treated at two different RF powers and same monomer flow were studied using TOF-SIMS on both top and bottom. Figures 3-14 and 3-15 show the qualitative data collected using TOF-SIMS for the control and the treated samples. Figure 3-16 shows the positive ion images while Figure 3-17 shows the negative ion images. Figure 3-14-a illustrates the positive ion images of top and bottom faces of the samples treated at 350 W and 0.6 ml/min monomer flow rate. The maximum threshold number for each image is the ion count per brightest pixel on that image. The highest maximum threshold numbers for the brightest colors on the first image represents $C_2F_5^+$ at m/z 119, $C_7H_4O^+$ at m/z 104 (PET substrate) in the second image and the overlaid of 119/104 in the last image. Part b shows the same sequence of the fragments for the top and bottom face of the sample treatment at 650 W of RF power and 0.6 ml/min monomer flow rate. Analyzing the TOF-SIMS results on both side of the fabric demonstrates how the plasma treatment acts on the very outer layer of the fiber and leave the other side of the fabric unchanged which is an advantage for applications focused on double side functional fabrics.

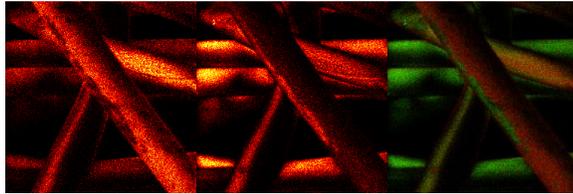
Figures 3-16 and 3-17 show the TOF-SIMS spectra for negative and positive modes on the samples treated at 350 and the minimum flow rate of the monomer (0.6ml/min). Both negative and positive spectra were normalized for $C_7H_5O_2^-$ (amu 121) and $C_7H_4O^+$ (amu 104) respectively, which are the peaks corresponding to PET. This normalization helps in comparing the different fluorine fragments created on the surface based on their peak heights. In the negative mode, fragments such as F_2, HF^-, CF_3^- and COF_3^- are observed while in the positive spectra, traces of $CF^+, CF_2^+, CF_3^+, C^2F_4^+$ and $C_2F_5^+$ were identified. After plasma induced grafting, both positive and negative TOF-SIMS spectra exhibit new peaks characterizing the presence of the functional species reported above.



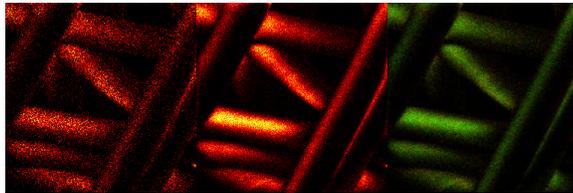
a (top face)



a (bottom face)

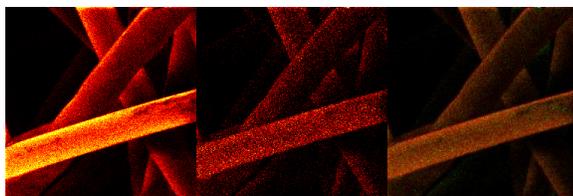


b (top face)

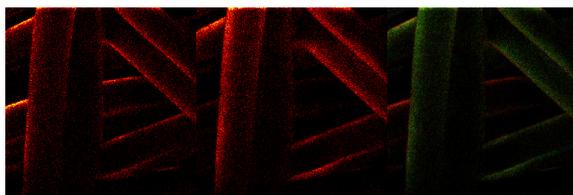


b (bottom face)

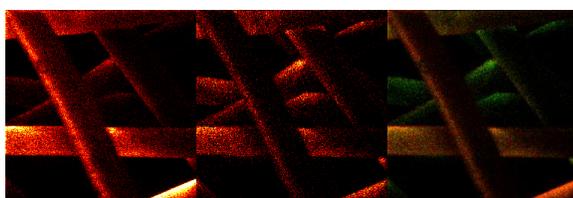
Figure 3-14 TOF-SIMS total Negative ion images of RF plasma treated sample with TG-20 incorporated onto the surface of the fiber, a) Top and bottom faces of 350 W treated samples, FC polymer $C_2F_5^+$ (m/z 119), PET substrate $C_7H_4O^+$ (m/z 104) and overlaid, from left to right. b) Top and bottom faces of 650 W treated samples, FC polymer $C_2F_5^+$ (m/z 119), PET substrate $C_7H_4O^+$ (m/z 104) and overlaid of both, from left to right.



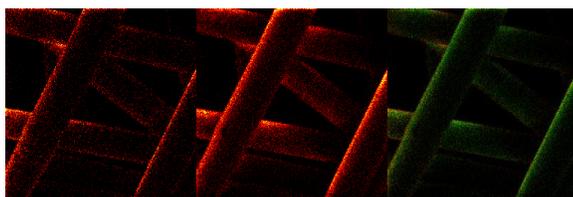
a (top)



a (bottom)



b (top)



b (bottom)

Figure 3-15 TOF-SIMS total Negative ion images of RF plasma treated sample with Fluorine monomer incorporated onto the surface of the fiber, a) Top and bottom faces of 350 W treated samples, FC polymer HF_2^- (m/z 39), PET substrate $\text{C}_7\text{H}_5\text{O}_2^-$ (m/z 121) and overlaid, from left to right. b) Top and bottom faces of 650 W treated samples, FC polymer HF_2^- (m/z 39), PET substrate $\text{C}_7\text{H}_5\text{O}_2^-$ (m/z 121) and overlaid, from left to right.

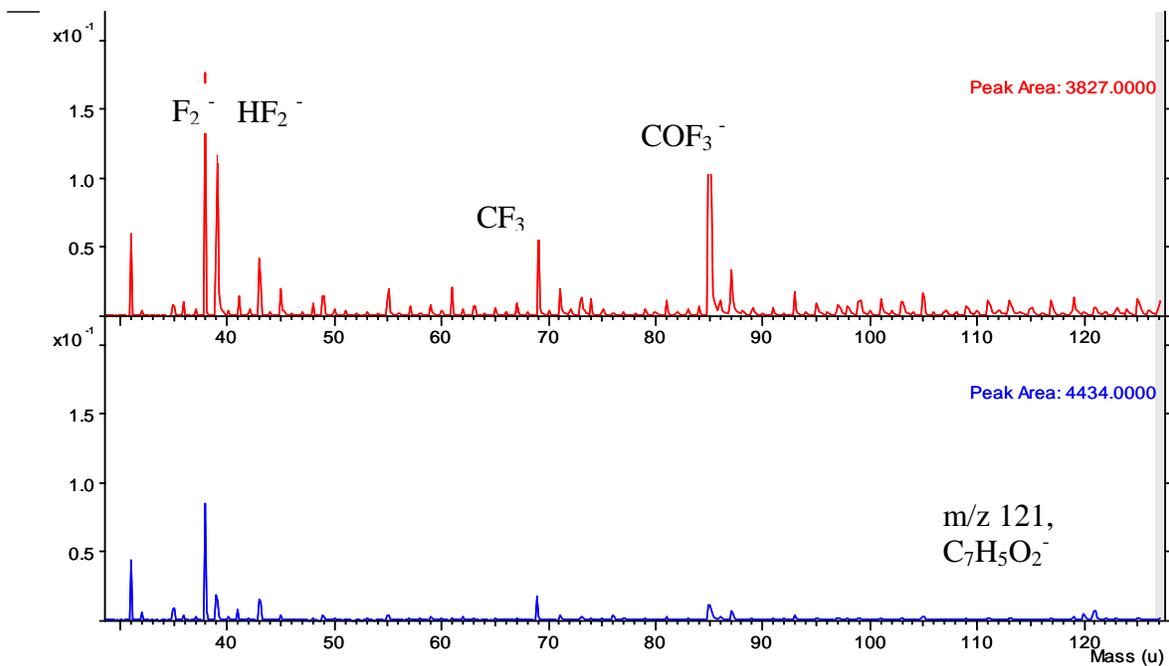


Figure 3-16 Total Negative TOF-SIMS spectrum of 350 W treated samples (350 W high mass Resolution Negative ion Spectra)

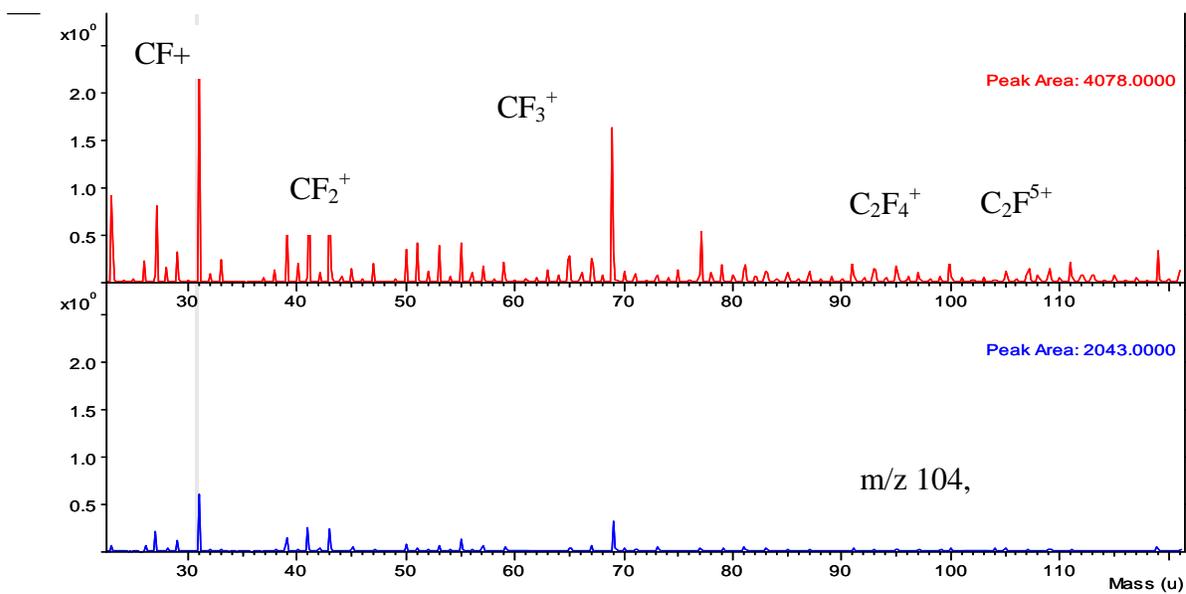


Figure 3-17 Total Positive TOF-SIMS spectrum of 350 W treated samples (350 W high mass Resolution Negative ion Spectra)

3.5.2 Plasma Induced Graft Polymerization of Perfluorohexylethyl acrylate (TG-30)

3.5.2.1 Effect of plasma exposure time at constant monomer flow rate

Figures 3-18 and 3-19 show the values of static contact angle and the AATCC 118 test rating measured on the samples treated for different plasma exposure times at constant flow rate of 0.6ml/min and power of 650 W. The AATCC 118 test rating was 5 for the samples treated for 10 seconds. However, it was demonstrated that increasing the exposure time decreases the oil repellency level of the sample. Figure 3-20 shows that the highest value of static contact angle was achieved for the samples that were plasma treated for 10 seconds. Increasing the exposure time did not follow a constant trend in static contact angle values, and this is mostly because longer plasma exposure times could introduce hydrophilic functional groups to the fabric surface.

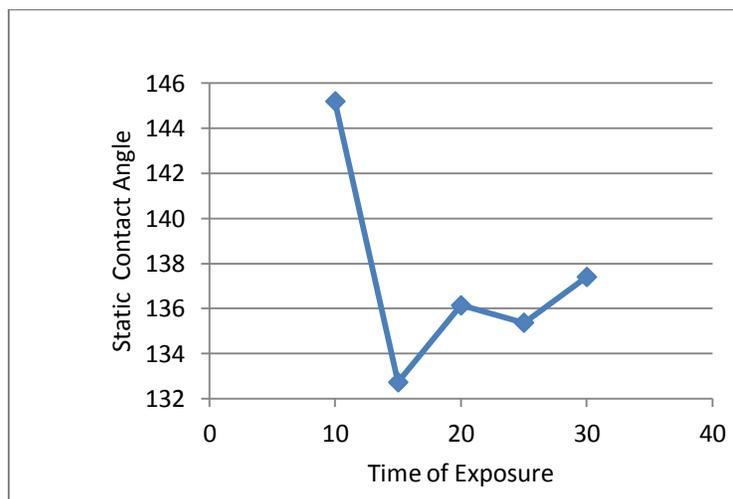


Figure 3-18 Effect of plasma exposure time on contact angle at constant monomer flow rate.

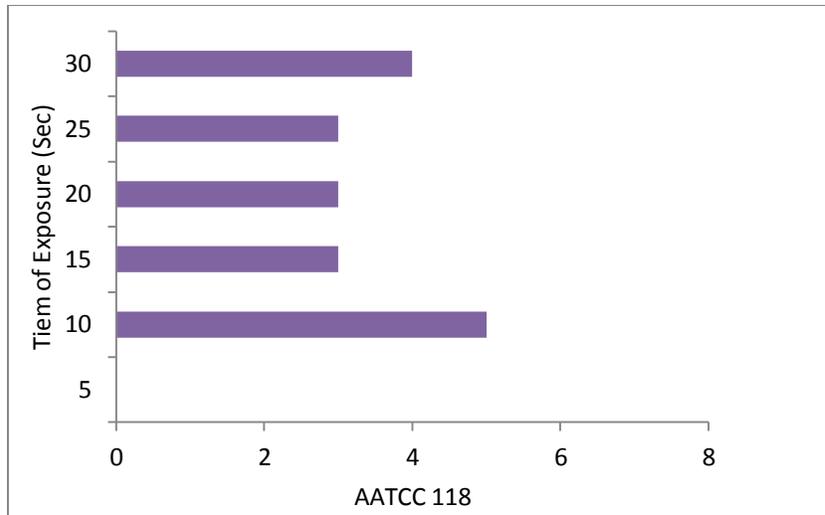


Figure 3-19 Effect of plasma exposure time on oil repellency rating at constant monomer flow rate.

3.5.2.2 Effect of plasma power at constant monomer flow rate

Figures 3-20 and 3-21 show the AATCC rating and the values of water contact angle measurements of the treated samples at 4 different treatment powers. Both characterization methods illustrate the good level of hydrophobicity on the webs treated with TG-30 and the best results achieved in the highest power (750 W).

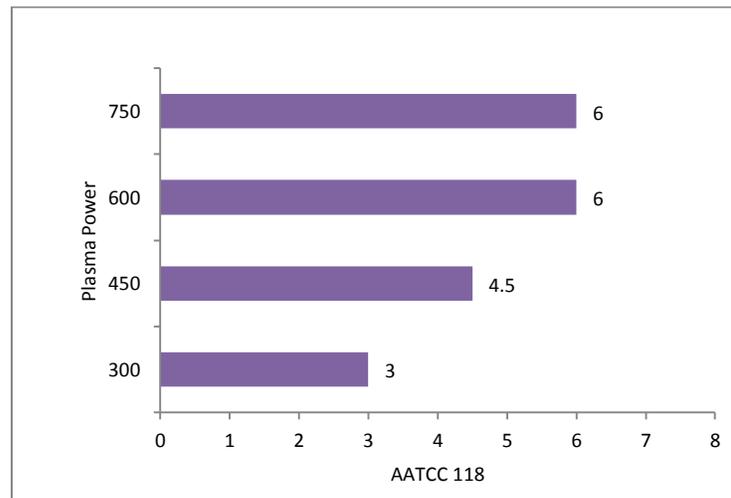


Figure 3-20 Effect of plasma operating power on oil repellency rating at constant monomer flow rate.

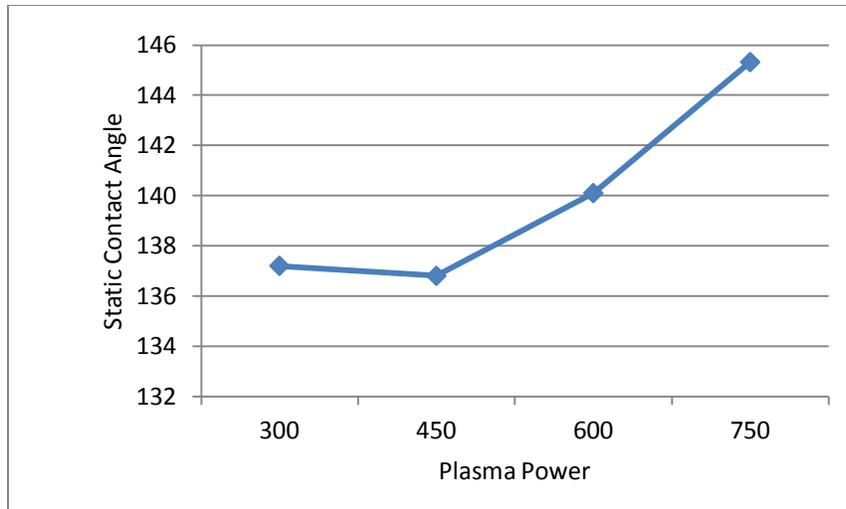


Figure 3-21 Effect of plasma power on water contact angle at constant monomer flow rate.

3.5.2.3 Effect of monomer flow rate at constant plasma power

Figure 3-22 shows the AATCC rating of the TG-30 treated samples at 3 different monomer flow rates at constant plasma power (750 W) and exposure time (10Sec.) The results shown in Figure 3-23 clearly demonstrates that increasing the monomer flow rate while keeping both plasma exposure time and power fixed furnished lower hydrocarbon resistance rating.

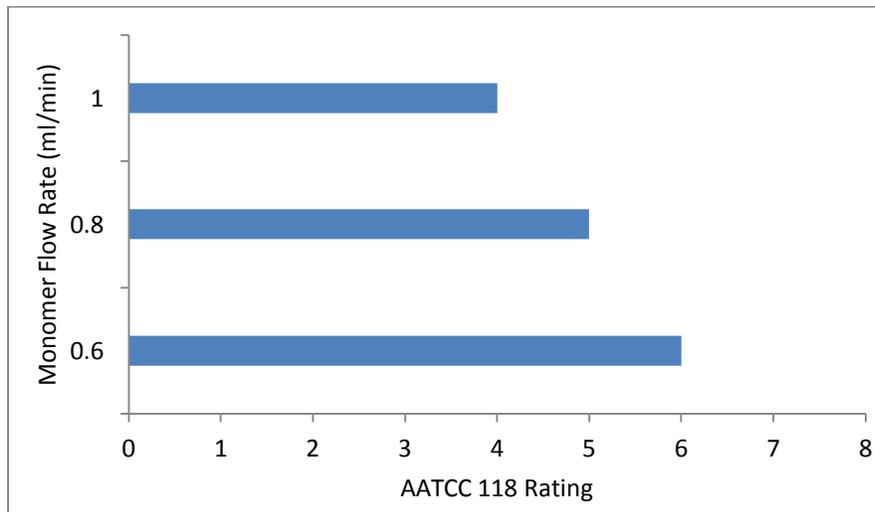


Figure 3-22 Effect of monomer flow rate on oil repellency rating at constant plasma power

3.5.3 Plasma Induced Graft Polymerization of Pentafluorostyrene

3.5.3.1 Effect of monomer flow rate at constant plasma power

Figures 3-23 and 3-24 show the AATCC 118 rating and the values of static contact angle measurements on the samples treated at 3 different monomer flow rates at constant plasma power (750) and time of exposure (10 Sec.). Both AATCC results and contact angle values indicate a high level of water and oil repellency on the fabric. The best results were achieved by treating the sample at 1.00 ml/min of monomer flow rate. Increasing the monomer flow rate to 1.2 or 1.4 ml/min while keeping both plasma power and exposure time fixed decreased the contact angle and AATCC 118 repellency rating which confirms that the excess amount of monomers does not necessarily translate into higher level of repellency unless the other parameters, especially the power of the plasma which directly determines the amount of active species on the surface for effective free radical polymerization, are optimized.

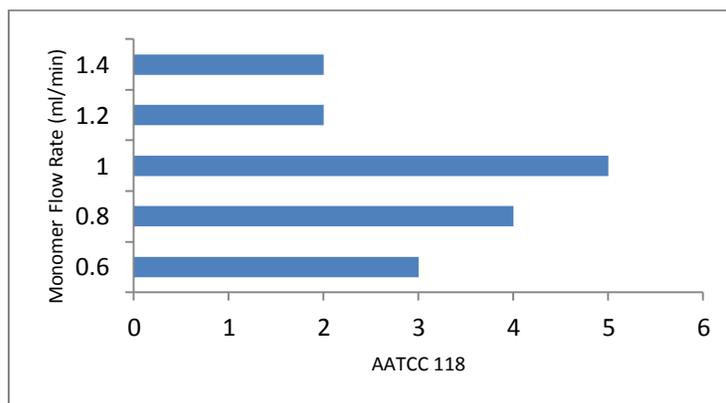


Figure 3-23 Effect of monomer flow rate on oil repellency rating at constant plasma power.

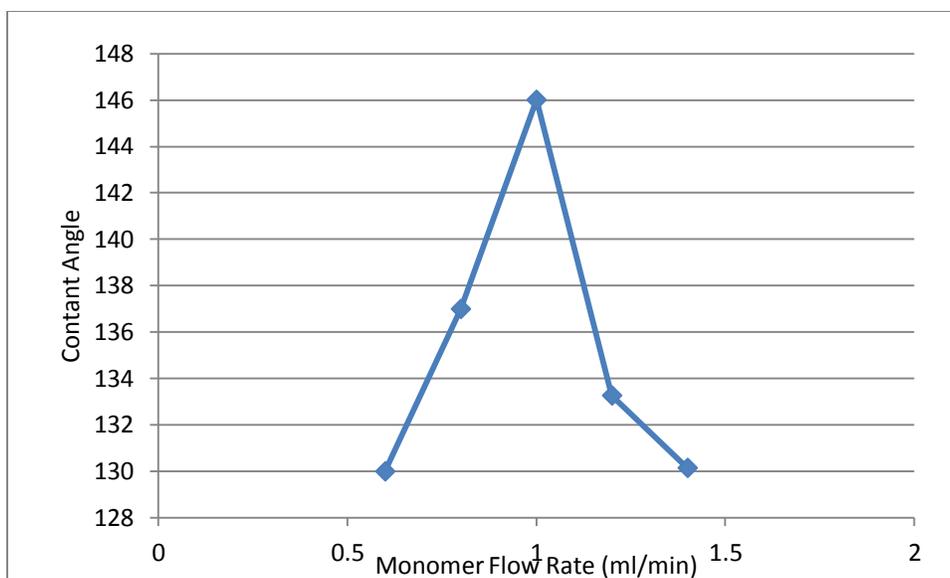


Figure 3-24 Effect of monomer flow rate static contact angle at constant plasma power

3.5.4 Plasma Induced Graft Polymerization of Allylpentafluorobenzene

3.5.4.1 Effect of plasma power in constant monomer flow rate

Figure 3-26 shows the AATCC 118 rating of the treated samples at 4 different powers. These results firstly demonstrate that allylpentafluorobenzene is a monomer with high hydrophobic effect. The highest grade was assigned to the samples treated at 750 W at constant monomer rate which confirms the effect of higher power in higher grafting rate on the surface.

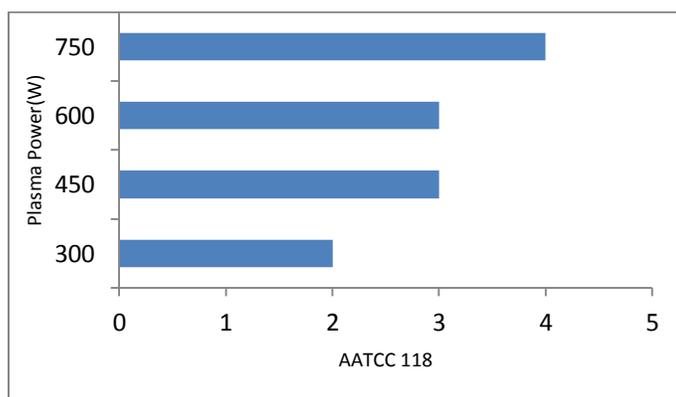


Figure 3-25 Effect of plasma power on oil repellency rating at constant monomer flow rate.

3.5.5 Plasma Induced Graft Polymerization of 1,3 Divinyltetramethyldisiloxane

The AATCC 118 oil repellency rating for all the PET samples treated with divinyltetramethyldisiloxane was zero, which indicates that the silicone chemistry does not provide oil repellency effect. Regarding to the fact that mineral oil (kaydol) has surface tension of 31.6 dynes/cm, it is expected that the silicon containing monomer cannot create the expected low surface energy on the surface. However considering the values of static contact angle shown in Figure 3-27, it provides good water repellency properties on PET webs.

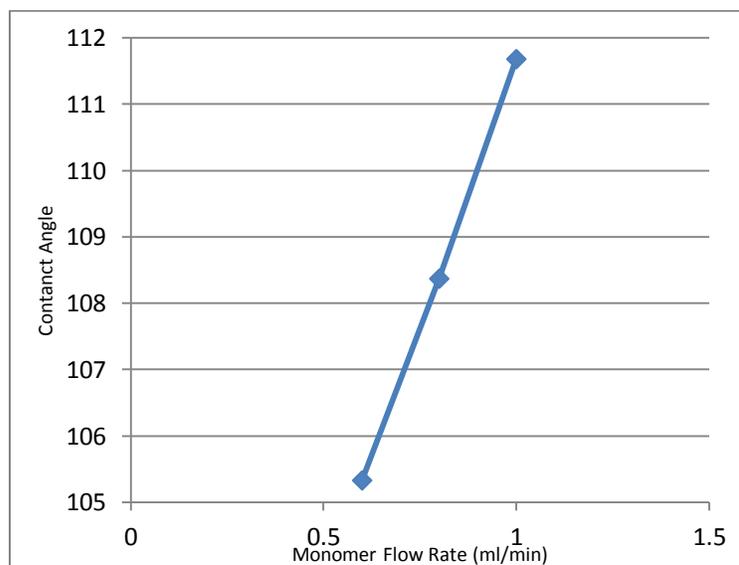


Figure 3-26 Effect of monomer flow rate on contact angle at constant monomer flow rate.

3.5.6 XPS

XPS survey scans showed apparent alteration in the chemical composition in the surface of polyester nonwoven webs after plasma treatment. Figure 3-28 shows an example spectrum of the TG-30 sample treated at power of 750 W and 1 ml/min of monomer flow rate.. The results of surface elemental analysis of PET webs treated with different monomers at minimum monomer flow rate for each sample are shown in Table 3-7.

Table 3-7 Relative chemical composition on PET measured using XPS

Plasma treatment	%C	%O	%F
Untreated	64.69	34.31	-
TG-30	40.90	15.47	41.86
TG-20	34.74	16.50	47.53
Pentafluorostyrene	25.58	17.18	53.90
Allylpentafluorobenzene	35.70	11.90	52.40

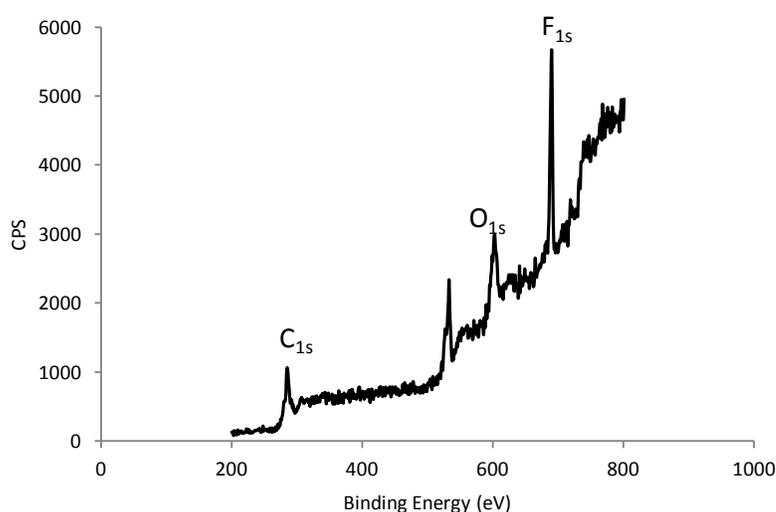


Figure 3-27 XPS survey scan of PET nonwoven fabric treated with Tg-30 at 0.6 ml/min and 750W.

3.6 Conclusions

This chapter was dedicated studying plasma induced graft polymerization of perfluorohexylethyl methacrylate (TG-20) onto the nonwoven fabric under the *in-situ* set up. Furthermore, the repellency performance of different monomers including perfluorohexylethyl acrylate (TG-30), pentafluorostyrene, allylpentafluorobenzene and 1,3 Divinyltetramethyldisiloxane which were graft polymerized on PET nonwoven in the *down-stream* mode, were investigate.

Static and roll-off contact angle measurements and water repellency rating confirmed that 2-(perfluorohexyl)ethyl methacrylate was graft polymerized on the substrate. Changing

the plasma parameters including plasma power and monomer flow rate, significantly change the hydrophobic properties of the substrate. Increasing the monomer flow rate at constant power was found to increase the static contact angles and decrease the dynamic contact angles, which confirms an increase in the hydrophobic properties of the substrate. Chemical compositions of the treated surfaces were also studied using XPS and TOF-SIMS which confirmed the presence of high levels of fluorine on the surface.

The down-stream results showed that perfluorohexylethyl acrylate TG-30 and pentafluorostyrene have the best performance in terms of water and oil repellency. Silicon monomer did not exhibit any level of oil repellency and can be a candidate to attain water repellency effect.

3.7 References

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Chapter 4 Nanolayer Plasma-Induced Graft Polymerization of C6-Fluorocarbon Monomer on Nonwoven Substrates for Water/Fuel Separation Applications

4.1 Abstract

High-performance water/fuel separator nonwoven substrates were developed via vapor deposition of 2-(perfluorohexyl)ethyl methacrylate and Pentafluorostyrene on nonwoven PET followed by induced graft polymerization using high density atmospheric plasma. Different nanolayer thicknesses (80-180nm) of the grafted polymer were furnished to generate surfaces with different wettabilities for water/fuel separation of different fuel compositions. The effect of different plasma conditions and device parameters including the flow rate of monomers, power of the device, and time of plasma exposure on the separation of different fuels was studied and characterized by measuring the surface energy of the treated substrates. The surface chemistry and morphology of the treated samples were characterized using XPS, SEM and TOF-SIMS techniques.

4.2 Introduction

Altering wettability characteristics of substrates by altering the surface energy is one of the most important applications of plasma treatment [1,2]. Plasma treatments can make textiles both hydrophilic and hydrophobic. Hydrophobic finishes reduce the surface energy of fabric surfaces. Surfaces that exhibit low interaction with liquids are referred to as low energy surfaces and their critical surface energy or surface tension must be lower than the surface tension of the liquid to be repelled [3].

The term water/fuel filtration/separation includes the filtration for vehicle engines and fuel transportation system. The former is related to the engines powered by gasoline or diesel fuel and the latter is for a number of distribution systems that mainly distribute oil and fuel to various locations through pipeline or different motor-vehicles. The issue of filtration in fuel transportation systems is more challenging since oil/fuel is exposed to different contaminations between the source and the destination [4]. Fuel contamination and the

contaminants are important topics in the field of fuel mixing, storage and transportation systems, aviation fuel industry and engines efficiency [4]. Most common fuel contaminants, except for commingling of different fuels, include particulate matters and moisture. Moisture could be present in the form of free or dissolved water. Free water can be seen in the fuel as a form of cloud, emulsion, droplets, or in large amounts at the bottom of a tank, sample container, or filter/separator reservoir. Dissolved water is the water that has been absorbed by the fuel. It cannot be seen and cannot be separated out from the fuel by filtration or mechanical means. Fuel surfactants are also considered as interference since they inhibit the water droplet coalescence in the separation processes [5,6]. Presence of water is more treacherous than solid particles mostly because its presence in fuel, even in small amount, is considered as the main source of many significant problems that can easily alter the fuel and the engine function. As ethanol blended fuel usage is increasing, the problem of water contamination issues exacerbate in a similar trend [7]. Water is the main reason for pipelines and instruments corrosion when the oil or fuel is in contact with them. It can either contain corrosive material such as chloride or easily dissolve polar corrosive compounds such as sulfuric acid and cause big damages over time. Water reacts with some anti-wear additives in fuel to produce hydrogen sulfide, sulphuric acid, and precipitate sludges. In addition to promoting corrosion due to increased oxidation, water reacts with antioxidants and rust inhibitors to forms precipitates.

Water contamination is the first contributor to tank and reservoir bottom corrosion, and it also provides the ideal condition for flourishing of micro-organisms such as bacteria and fungi in the fuel which gradually forms solid particulate that can plug the engine and influence the filtration effectiveness by plugging the filter media. Microbiological growth in the fuel could either be an indicator for water presence, since microbes cannot grow in the absence of water [8]. Water contamination is much more critical in aviation fueling. Very small free water droplets in the fuel may freeze at high altitudes or in very cold weather and plug the fuel screens, causing the engine to cease operation/flare out. For this reason, the most important component in any aircraft refueling facility is the separation system which provides the report of water contamination check based on the allowable water in parts per million (ppm). The danger of dissolved water in

aviation fuel is that it settles out as free water when the fuel is cooled to a temperature lower than that at which the water dissolved, and such fuel cooling is likely at high altitudes. [6, 9].

A fuel separation/filtration media should provide the required function in three steps; primary separation of the solid particles followed by the water coalescence and finally, precise water separation. In the first step a pre-filtration is carried out to separate the solid particles. In the coalescence process liquid droplets, usually water, existing in the immiscible mixture clot together and fall down due to their density differences [10, 11]. There are some techniques such as accelerating the rate of coalescence [12-15], and one of the most common methods is to pass the fluid through a treated resin medium. Phenolic resins are found to be good media since they provide the right surface tension value which makes the media hydrophilic and increasing the attraction of water droplets and holding them close together to eventually form larger droplets with faster settling rates. However, for the last step of filtration, the surface of the filtering media should be completely hydrophobic so as to be wettable by fuel and absolutely unwettable by water. This treated surface requires a specific low surface tension which repels every small droplet in the fluid and passes the pure fuel mixture. Hydrophobic woven meshes, commonly made from polyethylene terephthalate (PET) or polyamide (PA), are coated with a hydrophobic finish to effectively separate water from fuel. The surface of the mesh can be made hydrophobic using a hydrophobic coating which could be silicone based or fluorine based [17, 18].

Changing the surface properties of the filter media can be achieved via surface functionalization on the substrates via plasma induced graft polymerization of fluorocarbons or silicones monomers. Depending on the composition of the fuel, the surface energy of the filtration medium can be optimized, using the right hydrophobic monomer, so that the medium passes only the fuel and repels any hydrophilic components.

Plasma technology has received enormous attention as a solution for environmental problems in textiles [19]. Moreover, low-temperature plasma or cold plasma has been proven to be suitable for textile applications because of its high electron energy and low thermal capacity which changes only the surface chemistry of the substrates while maintaining the bulk properties [20-22]. The main processes in plasma are etching, activation, and graft-induced polymerization. In grafting, the accelerated electrons and ions from the plasma have

sufficient energy to carry out hemolytic scission of chemical bonds in the polymeric structure of the fabric and generate kinetically reactive radical macromolecules on the substrate surface, which subsequently initiate graft-induced polymerization of the introduced monomer [23, 24]. Figure 4-1 shows a typical grafting process of vinyl monomer on a polymeric surface containing kinetically reactive radicals generated using cold plasma.

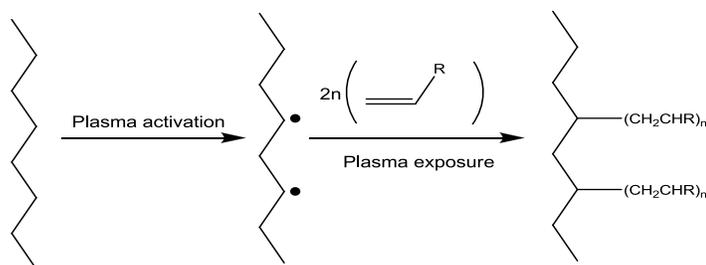


Figure 4-1: Plasma induced graft polymerization of vinyl monomer, where n is the number of repeating units and $R = C_nF_{2n+1}CH_2CH_2OCO$.

In the present study, plasma-induced graft polymerization of 2-(perfluorohexyl)ethyl methacrylate (TG-30) and pentafluorostyrene were performed on PET spunbond nonwovens with the ultimate goal of developing nonwoven filters for water/fuel separation. The hydrophobic properties of the treated nonwovens were evaluated by measuring the water/alcohol and oil repellency levels and also static and dynamic (advancing) contact angles measurements were performed on the treated samples. XPS, SEM and TOF-SIMS techniques were applied for surface characterizations. Nonwoven PET has a wide range of applications, including hydrophobic pre-filter for air intakes, residential ventilation, surgical face masks, acoustic layers, depth filters and also as oleophobic screen for water/fuel separation or fuel filtration. The chemical structures of TG-30 and pentafluorostyrene are shown in Figure 4-2.

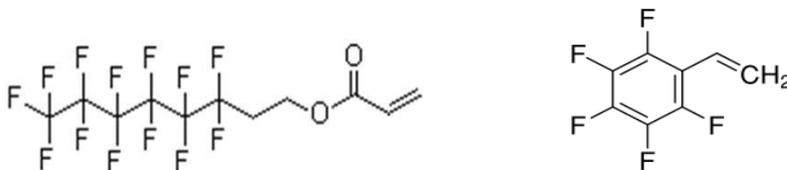


Figure 4-2 Chemical structure of 2-(perfluorohexyl)ethyl acrylate and Pentafluorostyrene

4.3 Experimental

4.3.1 Materials

Spunbond PET nonwoven was supplied by the Nonwovens Institute (NWI at NCSU) with approximate basis weight and thickness of 50 g/m² and 0.66 mm respectively was used as the substrate. The hydrophobic monomer 2-(perfluorohexyl)ethyl acrylate (Hereafter, TG-30) was obtained from Daikin America Inc., and used as received. Pentafluorostyrene was purchased from Sigma-Aldrich and was used as received. Industrial grade helium (99.99% pure) and ultrahigh pure argon grade 5.0 supplied by Machine and Welding Supplies Co., North Carolina, USA, were used for plasma process.

4.3.2 Atmospheric Pressure Plasma Reactor (APPR)

The atmospheric pressure plasma Reactor (APPR, fabricated by APJeT, Inc.), at the College of Textiles, North Carolina State University was used for plasma treatments of the nonwoven PET. The Atmospheric Pressure Plasma Reactor (APPR) provides a non-thermal, glow-discharge plasma operating at atmospheric pressure.

4.3.3 Procedure

For plasma treatment, the nonwoven samples (15 × 25 cm) were placed on the moving stage of the device. The stage was equipped with a speed controller system which controls the time of plasma exposure and the time of monomer deposition as well. A two level factorial design (2^k design), with 4 major plasma parameters – plasma power, plasma pre and post exposure time, and monomer flow rate (monomer %add-on), was applied for investigating the aforementioned process parameters. The information of the factor levels for the DOE is tabulated in Table 4-1 and 4-2. A set of experiment also was run at constant monomer %add-on and other parameters as variable for better understanding of factors implication.

Table 4-1 Factors and values of DOE for TG-30 and PFS

Factors Level						
	Low (-)		High(+)		Center Point (0)	
Monomer	<u>TG-30</u>	<u>PFS</u>	<u>TG-30</u>	<u>PFS</u>	<u>TG-30</u>	<u>PFS</u>
Monomer % add-on	4%		6%		8%	
Plasma Pre- exposure Time	0		60		30	
Plasma Post-exposure Time	15		60		35	
Plasma Power	400		800		600	

Table 4-2 2³ fractional factorial design with 3 center points for fluorocarbon monomer percent add-on and plasma exposure time

Run Order	Pattern	Parameters			
		Plasma Pre-exposure(Sec)	Plasma Power (W)	Plasma Post-exposure (Sec)	Monomer % add-on
1	0000	30	600	35	6
2	---+	0	400	60	8
3	+--+	60	400	60	4
4	----	0	400	15	4
5	-++-	0	800	60	4
6	++--	60	800	15	4
7	0000	30	600	35	6
8	-+++	0	800	15	8
9	++++	60	800	60	8
10	+---	60	400	15	8
11	0000	30	600	35	6

AATCC TM-118 (oil repellency rating) test method was selected as the primary response variable. The results were analyzed with JMP 9® statistical software by SAS Institute Inc. to determine the best processing parameters and develop a regression model for the applied monomers. The sample with the highest predicted rating of both tests was then selected to be characterized in the subsequent steps.

4.4 Characterization Methods

4.4.1 Goniometry - Static Contact Angle Measurement

Static contact angle was measured on plasma treated PET fabrics for surface wettability at 20 °C using the sessile drop technique. The volume of the applied droplets of distilled water was 10 µL. The static contact angle images were obtained with an optical goniometer (OCA20, Future Digital Scientific Corp.). Contact angles were measured at five

different spots of the fabric surface and the average values were calculated. Figure 4-3 shows the goniometer instrument.

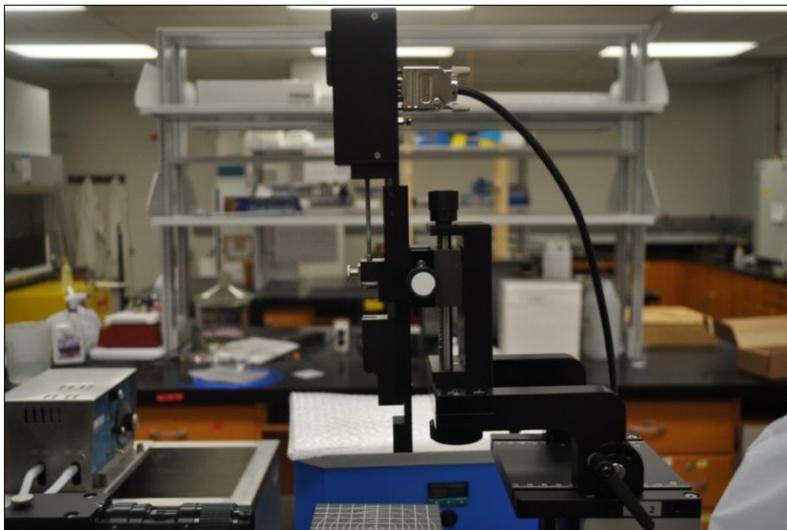


Figure 4-3 OCA (goniometer) instrument @ College of Textiles

4.4.2 Water/Alcohol and Oil Repellency

The water and oil repellent properties of the treated samples were also measured according to AATCC (American Association of Textile Chemists and Colorists) 193-2009 Test Method and AATCC 118-2009 Test Method. AATCC 193 test method evaluate the treated fabric resistance to wetting by a series of 8 water/alcohol solutions with different surface tensions, while in AATCC 118 the treated surface is rated by a series of test liquids consisting of 8 selected hydrocarbons with varying surface tensions. To investigate the water/alcohol repellency, drops of standard test liquids are placed on the fabric surface and observed for wetting and wicking. The aqueous repellency is graded according to highest numbered test liquid from 1 to 8 that does not wet the fabric surface within 30 seconds. In oil repellency, test drops of oils are placed on the fabric and observed. The oil repellency rating of the fabric is the highest-numbered test liquid that will not wet the fabric within a period of 10 seconds.

4.4.3 Dynamic Contact Angle /Modified Wilhelmy Method

In general, contact angle measurements serve as a good initial technique to characterize the surface energy and to evaluate the wettability of a solid by a liquid. However two different approaches are commonly used to measure contact angles of nonporous solids like fabrics and nonwovens: goniometry and tensiometry. Tensiometry including the Wilhelmy method or Washburn method and involves measuring the forces of interaction as a solid is brought into contact with a test liquid (Figure 4-4). When the fabric surface contacts the liquid, a change in weight is detected because of buoyancy and the apparatus registers this as zero depth of immersion. As the solid is pushed into the liquid, the forces on the balance are recorded. These forces are the net of the actual wetting force, the weight of the probe and the effect of the buoyancy of the sample. The apparatus is tared to offset the influence of the weight of the probe and also to remove the effect of the buoyancy force by extrapolating the graph back to zero depth of immersion. The remaining force is the wetting force F which is defined as: $F = \gamma L \nu P \cos \theta$, in which $\gamma L \nu$ is the surface tension of the test liquid, P is the perimeter of the cross-section of the sample at the height of the water surface and θ represents the contact angle between the solid test piece and the test fluid. Thus at any depth, data is received which can be used to calculate the contact angle. This contact angle which is obtained from data generated as the sample advances into the liquid is called the advancing contact angle (AA).

Advancing contact angle was measured on the control and treated samples using the modified Wilhelmy method. A number of solutions which cover the useful range of surface tensions for water/fuel separation, including surface tension values of about 72 to 19 mN/m were selected; a series of hydrocarbons (non-polar) and water/alcohol (polar) solutions were applied to characterize the surface wettability through AATCC Test Method 193 and 118. The surface tension of each solution was also measured using the Wilhelmy plate method via tensiometer instrument (DCAT11) from Future Digital Scientific Corp (figure 4-5) equipped with SCAT11 software. Then the advancing contact angle was measured on the rectangular samples with the following settings:

- Sample size: 5×15 mm

- Detection speed: 1.0 mm/s
- Detection threshold: 8.0 mg
- Measurement speed: 0.2 mm/s
- Penetration depth: 5mm

The sample is immersed to a pre-defined depth and then the process is reversed. As the probe retreats from the liquid data collected is used to calculate a receding contact angle (RA). The difference between these two values is known as the contact angle hysteresis. For each test solution, contact angle was measured more than three times on every treated sample and the advancing contact angles here reported were the average values of 3 measurements.

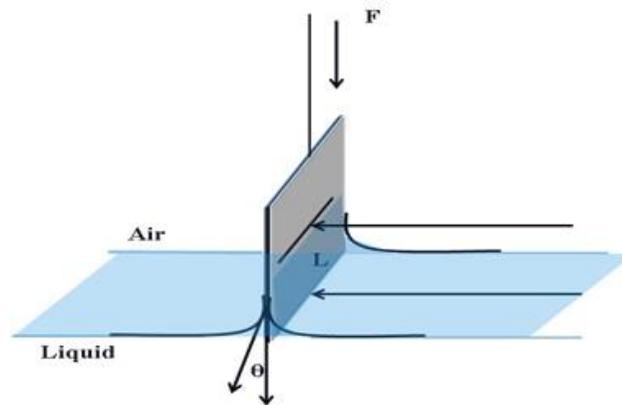
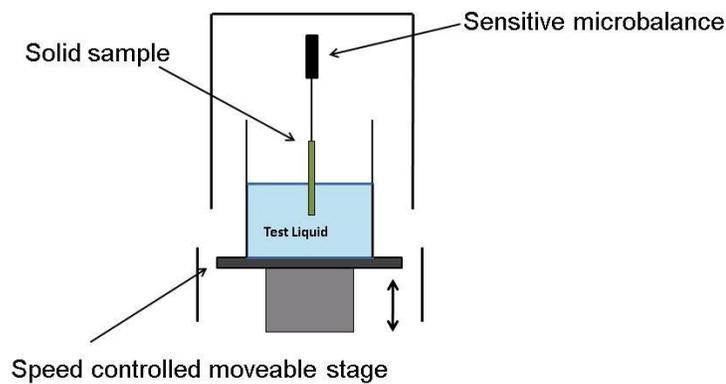


Figure 4-4 Wilhelmy method illustrator in two profiles



Figure 4-5 Tensiometer instrument @ College of Textiles

4.4.4 Water Resistance: Hydrostatic Pressure Test

Another method to evaluate hydrophobic performances of technical textile is the water resistance test by measuring the hydrostatic pressure based on the AATCC Test Method 127-2009. This test method measures the resistance of a fabric to the penetration of water under hydrostatic pressure. It is applicable to all types of fabrics, including those treated with a water resistant or water repellent finish. A min 225 cm² (6"x6") sample, initially dry, is subjected to an increasing pressure (3mbar/min) of water on one face, until penetration occurs in three parts of the mesh. The measures obtained with this method often show a certain correlation with contact angle values. The pressure reading is done at first and, where possible, third droplet intrusion. For every different plasma treatment, WIP data here reported are the average values of measurements performed on three samples.

4.4.5 X-ray Photoelectron Spectroscopy

Surface chemical changes of the PET nonwovens were analyzed by a Perkin Elmer PHI 5400 XPS (x-ray photoelectron spectroscopy) spectrophotometer. The x-ray source was MgO (1,253.6 eV) with a 45° take-off angle. The possible scanning area varied from 200

microns in diameter to 3 -10 mm, and the scanning depth was about 1–10 nm. The references of XPS spectra were 285 eV for C1s, observed in hydrocarbon polymers.

4.4.6 Time-of-flight Secondary Ion Mass Spectrometry

TOF-SIMS method were performed on treated samples at the NCSU Analytical Instrumentation Facility (AIF) with a TOF-SIMS 5 instrument using a ⁶⁹Bi liquid metal ion gun at 25 kV primary high voltage and 2 kV extraction voltage. TOF-SIMS analyses were conducted using a TOF-SIMS V (ION TOF, Inc. Chestnut Ridge, NY) instrument equipped with a Binm+ (n = 1 - 5, m = 1, 2) liquid metal ion gun.

4.4.7 Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR was conducted on the synthesized HTCC samples using a Nexus®470 FT-IR in conjunction with a Nicolet® Omnisampler.

4.5 Results and Discussion

This part of the research was dedicated to imparting hydrophobic/partially oleophobic properties to the nonwoven PET that can be utilized in water/fuel separation applications. To achieve this level of repellency, plasma-induced graft polymerization of fluorocarbon monomers was attempted, and the level of oil and water repellency was tested using the standard AATCC Test Methods 118 and 193.

After analyzing all experimental data and investigating the performance of the treatment on many treated samples at different plasma sequences, the following conclusions were drawn:

1- Plasma pre-exposure: both statistical analysis and oil repellency visual assessment showed that the plasma pre-exposure does not have a significant role in increasing the performance of the treatment or providing more repellency on the PET surface. Samples treated with zero pre-exposure time or high exposure time do not show much difference in water/alcohol repellency, contact angle and oil repellency values. Therefore this step parameter seems negligible to the researcher and can be dropped off in the procedure specially in industrial scaling of plasma sequences.

2- Optimized monomer flow rate: a concept named “monomer percent add-on” was defined in this stage of the research which includes several important parameters such as monomer flow rate, monomer density, and monomer exposure time and fabric dimension in order to employ in rough estimation of the amount of monomer deposited on the fabric via the applicator. The calculation of monomer percent add-on in was explained in Appendix A. Performance investigation showed that the optimized monomer percent add-on depends mainly on the monomer type and its chemical structure, excluding the effect of plasma post exposure. For TG-30, lower levels of add-on (4%) provide better results than the higher levels (8%) and for PFS, higher values of add-on (8%) were required to reach higher oil repellency rating. TG-30 (fluoroacrylate monomer) was considered a more efficient monomer than PFS (fluorostyrene monomer), and this was attributed to the higher fluorine content of the TG-30 ($C_{11}H_7F_{13}O_2$: 59.06% vs. $C_6F_5C_2H_3$: 48.94%).

3- Plasma induced grafting step (post-exposure): Plasma post exposure step had the most significant effect on the treatment performance. The longer the plasma post exposure time, the higher the oil repellency rating is and the better the repellency performance in term of the droplet shape on the surface. The lowest values of AATCC 118 were observed on the samples treated at the lowest plasma post exposure time. Longer plasma post exposure provides more direct and more available free radical for monomer on the surface to go through free radical polymerization and grafting onto the surface. Higher exposure time in a multi-pass fashion gave the best results for both monomers specifically for TG-30 at lower monomer flow rate, which means that the higher exposure time with lower percent add-on (thinner layer) on the surface was the best combination for achieving higher repellency levels.

4- Plasma Power: The results clearly confirmed that higher plasma power was needed to achieve higher repellency levels on the fabrics. The performance of the samples treated at the same values of monomer %add-on and post exposure time improved as the plasma operating power increased from 400 to 800. Higher plasma power volume consists of more free radicals which generated more unsaturated functionalities on the monomers and led to more growth of polymer chain and rapid grafting, which furnished higher % yield of the grafted polymer.

4.5.1 Static Contact Angle

Figure 4-6 shows the actual water droplets on the treated surface in the goniometer set up. Figure 4-7 shows the average values of five measurements of static contact angle on TG-30 and PFS treated samples at the optimized parameters of plasma conditions (plasma power: 800 W, monomer add-on: 4% for TG-30 and 8% for PFS and plasma exposure time: 60 seconds) compared with the untreated nonwoven PET samples. The static contact angle of the water droplet increased from 93° for the untreated sample to 149.32° and 139.66° for TG-30 and PFS treated samples, respectively. Nanolayer graft polymerization of the two fluorocarbon monomers on the surface of the nonwoven fabric significantly increased the static contact angle and resulted in a very hydrophobic surface, specifically for TG-30 with the contact angle of 149 which could be improved to more than 150° , furnishing a super hydrophobic surface.

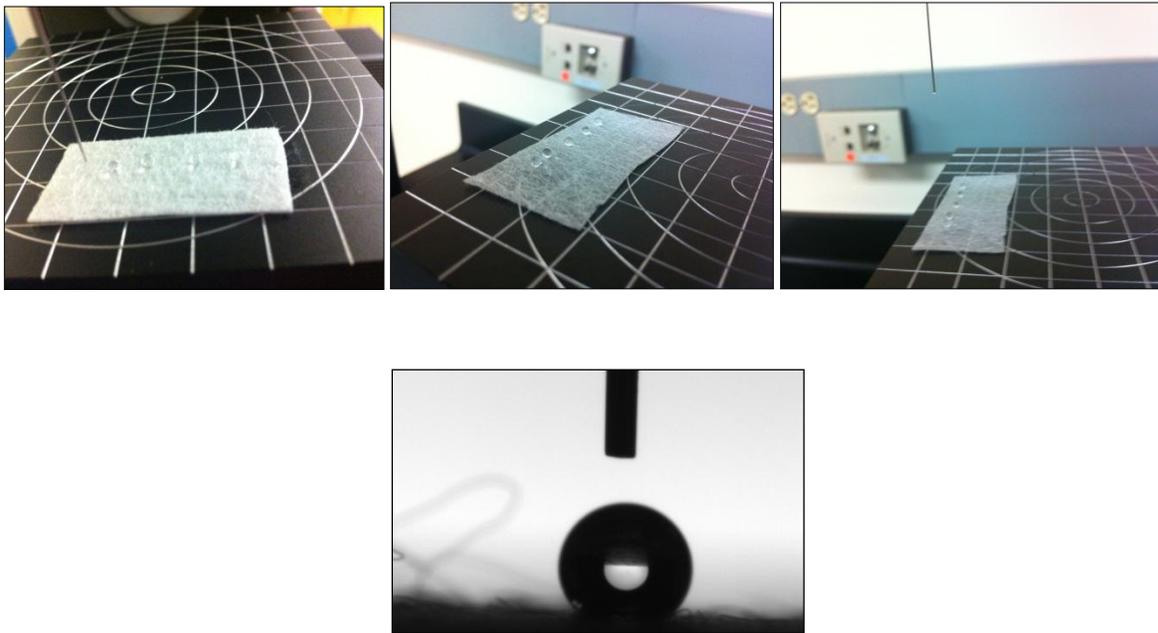


Figure 4-6 Static contact angle image on TG-30 treated sample

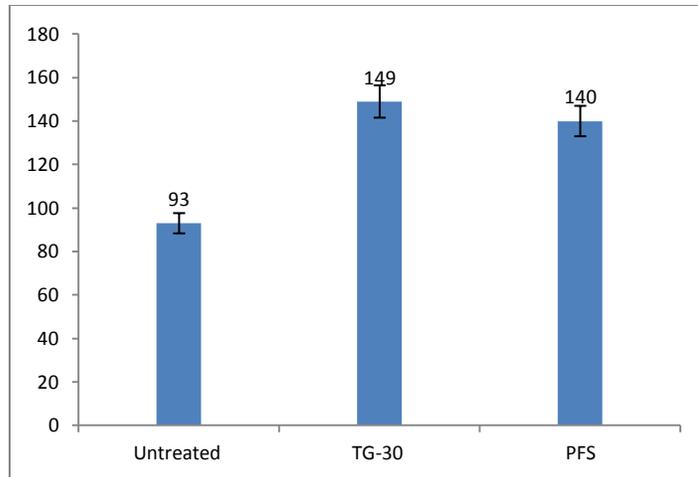


Figure 4-7 Wettability of plasma-treated PET nonwoven fabric surface with different monomers

4.5.2 Wettability Analysis / Surface Energy Estimation

Applying the AATCC water/alcohol and oil repellency test methods provided valuable information pertaining to the performance of the treated samples in real world application as a fuel filter media, mostly for the reason that the selected liquids in both AATCC Test Methods cover a wide range of surface tensions which covers the real world fuels such as gasoline or jet fuel or any aqueous contaminant with different surface tension are involved in them. Table 4-3 shows the combination and surface tensions of the applied liquids in both tests. Table 4-4 gives an overview of the typical oil repellency levels that can be obtained with a variety of perfluoro groups [30].

Table 4-3 Test liquids for water and oil repellency evaluation listed in AATCC TM193 and 118

Rating	Water/Alcohol repellency test liquids *	Surface Tension (mN/m)	Oil repellency test liquids	SurfaceTension (mN/m)
1	2	59.0	Kaydol	31.5
2	5	50.0	65% kaydol **	28
3	10	42.0	n-hexadecane	27.6
4	20	33.0	n-tetradecane	26.7
5	30	27.0	n-dodecane	25.4
6	40	25.4	n-decane	23.9
7	50	24.5	n-octane	21.8
8	60	24.0	n-heptane	20.0

*Volume % Isopropanol in distilled water. **Volume % in n-hexadecane.

Table 4-4 Perfluoro groups and the typical oil repellency level that can be reached with them.

Perfluoro Group	Oil Repellency Level
-CF ₃	0
-CF ₂ -CF ₃	3-4
-(CF ₂) ₂ -CF ₃	6-7
-(CF ₂) ₄ -CF ₃	7-8
-(CF ₂) ₆ -CF ₃	7-8
-(CF ₂) ₈ -CF ₃	8

Figure 4-8 shows the AATCC Test method 118 and 193 results comparing the control and the treated samples. PET control sample was rated 3 for water/alcohol test and failed the kaydol drop tests. However, after plasma-induced graft polymerization treatment, the water/alcohol repellency increased to 11 in the case of TG-30 and to 7 in the case PFS. Using ATTCC Test Method 118, the oil repellency improved from zero to 7, and from zero to 4 for TG-30 and PFS samples, respectively. The data indicate that hydrophobic plasma treatment of the PET webs had significant effect on changing the fabric surface wettability properties in a way that considerably enhanced both aqueous and oil repellency levels of the fabric. However TG-30 treatment showed better performance than PFS.

Figure 4-9 shows the actual oil droplets on the full size surface of a treated sample, which also confirms the uniformity of the treatment throughout the sample surface dimension. Oil repellency rating of 8 was even recorded for several samples treated with TG-30 and has been plasma exposed for multi passes up to 180 seconds which matches the surface energy of 20 erg/cm².

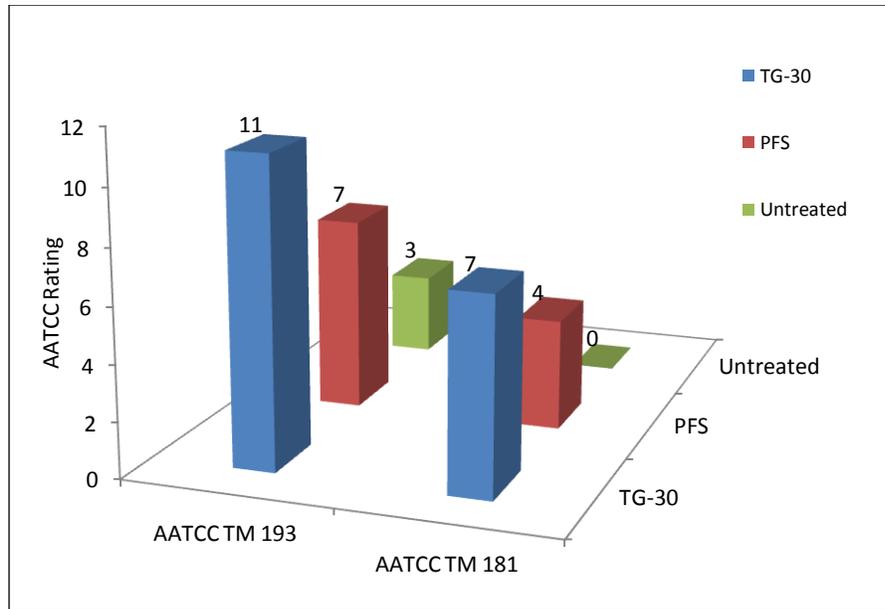


Figure 4-8 Effect of plasma treatment with different monomers on the water/alcohol and oil repellency of the nonwoven fabrics



Figure 4-9 Actual drop test evaluation on treated samples

4.5.3 Advancing Contact Angle/ Surface Energy Rating

Table 4-5 lists the liquid mixtures used for measuring the advancing contact angle and their corresponding surface tensions. Figure 4-10 shows the trend of measured surface tensions of the 10 liquids. The maximum surface tension is for water (72.75 Nm/m) and the minimum is for n-heptane (19.46 Nm/m). These numbers of liquids fully cover the range of surface tension for different fuels in real world applications and evaluate the wettability of treated fabric against both polar and non-polar liquids, which subsequently could be used to calculate the solid surface energy of the fabric through Young equation or Equation of State [28]. Table 4-6 shows the surface tension range of different fuels in the real world.

Table 4-5 Surface tension values of water/Alcohol and hydrocarbon solutions used for measuring dynamic contact angles measurements

Liquid	Surface Tension(mN/m)
Water	72.75
Water/Alcohol :98/2	58.75
Water/Alcohol :95/5	53.05
Water/Alcohol :90/10	40.22
Kaydol	33.04
Kaydol/ n-hexadecane :65/35	29.55
n-hexadecane	27.27
n-dodecane	25.08
n-octane	21.42
n-heptane	19.46

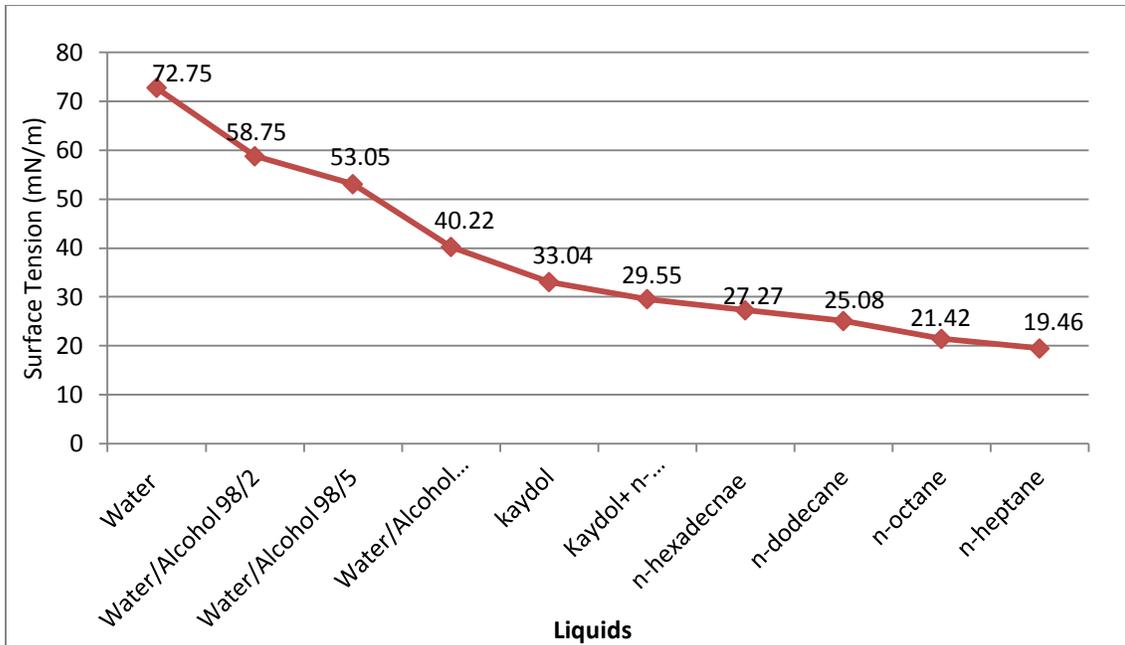


Figure 4-10 Values of surface tensions measured on wetting liquids

Table 4-6 Different fuels surface tension

Fuel	Surface Tension (mN/m)
Gasoline	20-23
Jet fuel	25-26
Diesel	27-29
Oil	Figure 4-11

Figure 4-11 to 4-14 shows the actual measurement curves of the weight change (weight/g on vertical axis) versus the depth of immersion (position/mm on horizontal axis) reported for several different measurements of water and n-hexadecane on the control and TG-30 treated samples. The following can be concluded from the curves of both control and treated samples:

- The weight increase on the treated samples in contact with water and other wetting liquids was smaller than the control sample, which confirm the hydrophobic character of the treatment (less steep slope was observed) .

- As the surface tension of the liquids decreased (more wetting liquids), for example from water to n-hexadecane, more variation was observed between the contact angles of the control and the treated samples since the liquid wetted the untreated sample more. The graphs did not show a linear behavior, this is mostly because of the porous structure of the material which is not a homogenous network or a solid smooth surface like polymeric films.

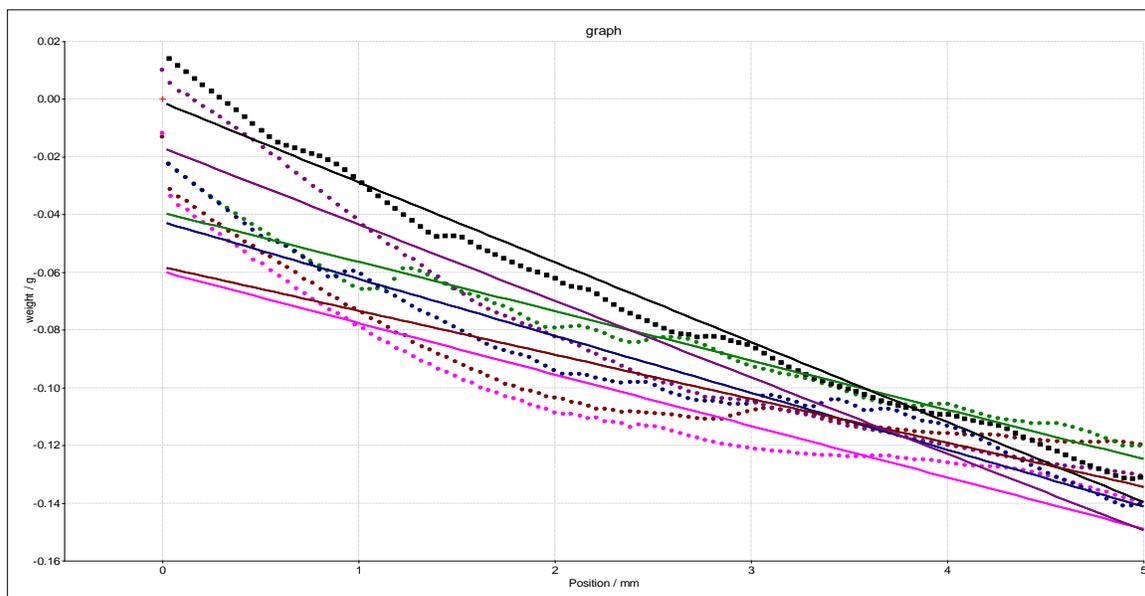


Figure 4-11 Plot of the weight change versus the liquid front position as measured for water on the control sample

Figure 4-15 shows the advancing contact angle values measured on the untreated, TG-30 treated and PFS treated samples as a function of the surface tension of the reference wetting liquids.

The advancing contact angle measured on both TG-30 and PFS treated samples were much higher than that measured on the untreated PET for every tested solution. Untreated sample curve is laid below the wettable/unwetable transition, with the contact angle measured with pure water of 89° . The plasma treatment of nonwoven PET and grafting of the fluorocarbon monomers on the surface of the substrate significantly altered the wetting behavior of the fabric against both polar and non-polar liquids.

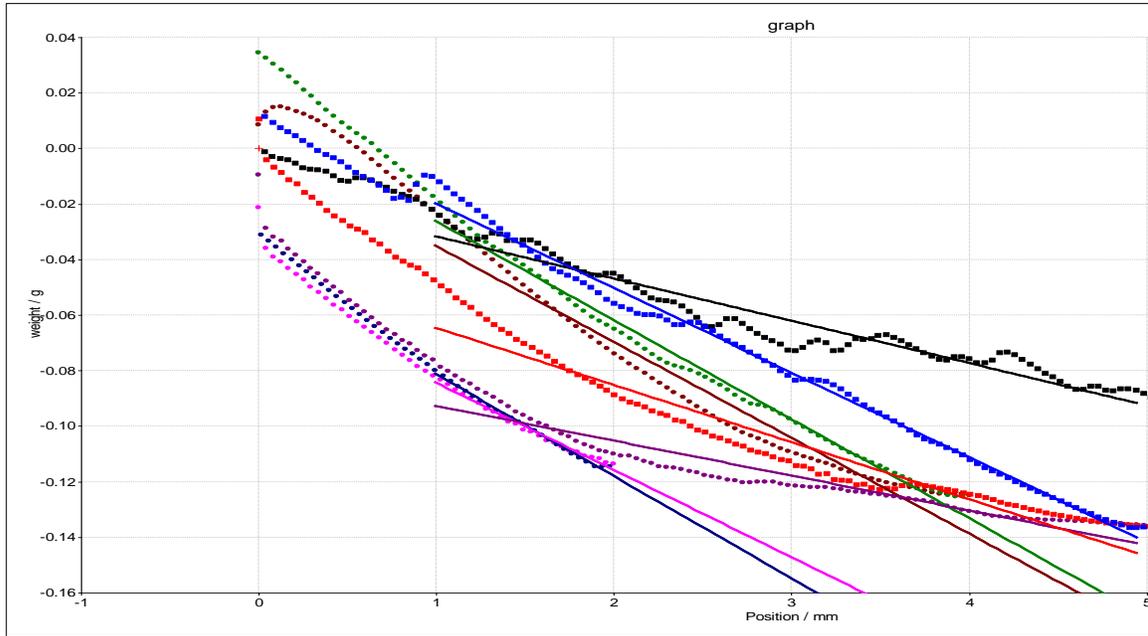


Figure 4-12 Plot of the weight change versus the liquid front position as measured for water on TG-30 treated sample

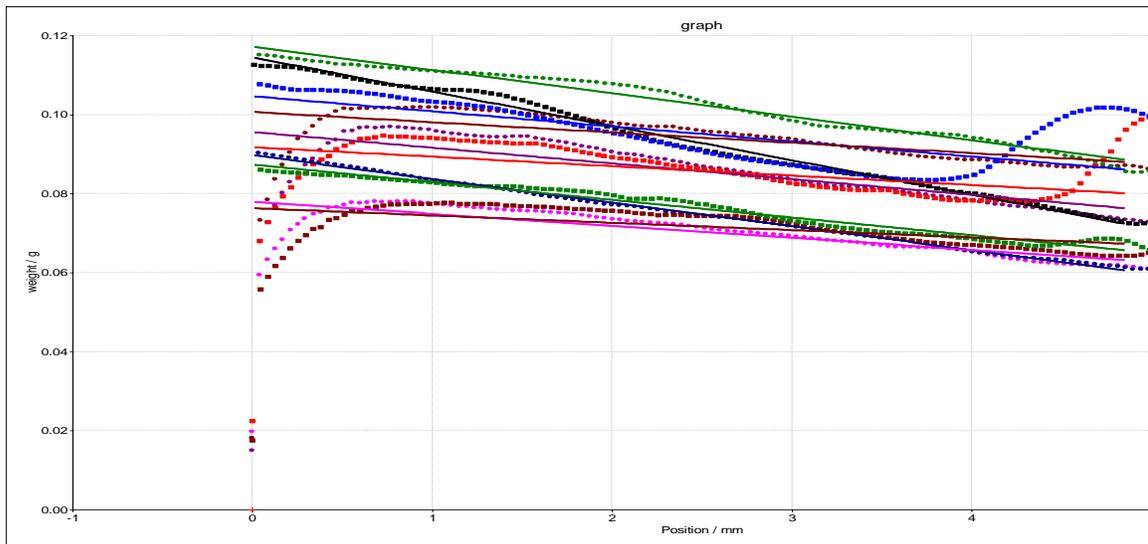


Figure 4-13 Plot of the weight change versus the liquid front position as measured for n-hexadecane on the control

PFS treatment decreased the surface energy of nonwoven PET and lowered the wettable/unwettable transition to 50 mN/m (the point where the PFS curve crosses the transition line) and increased the average advancing contact angle of water to 101 °. The

lowest dynamic contact angle was observed for the liquid with the lowest surface tension (n-heptane $\sim 19.47\text{mN/m}$) which is the most wetting liquid. The wicking of liquid into the fabric structure was not observed for solutions such as water/alcohol combinations with higher surface tensions.

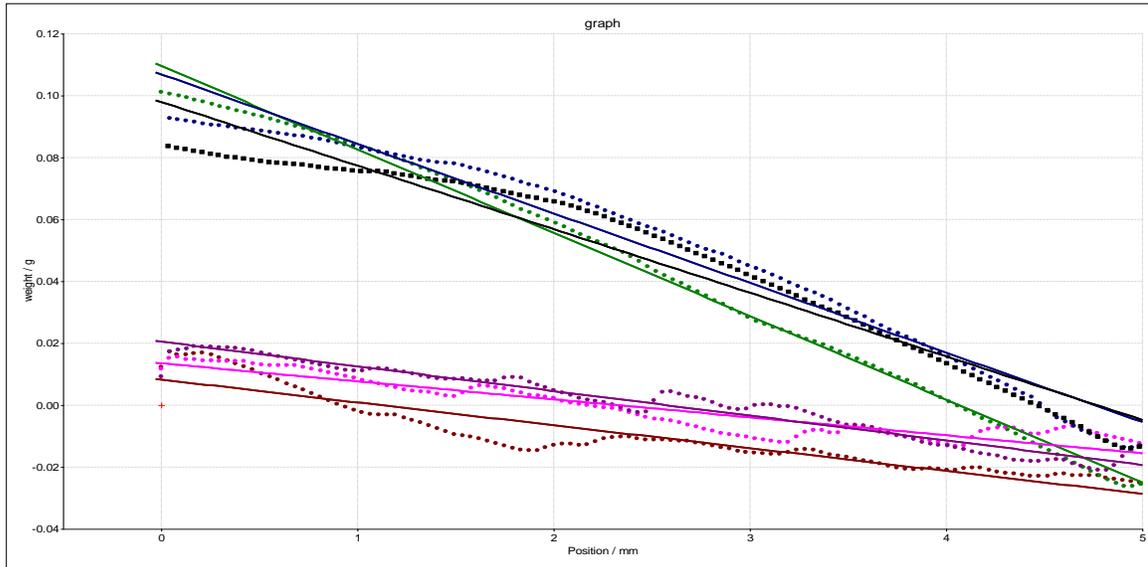


Figure 4-14 Plot of the weight change versus the liquid front position as measured for n-hexadecane on TG-30 treated sample.

The nonwoven PET fabrics treated with TG-30 were also completely hydrophobic in a way that reduced the wettable/unwettable transition to 30 mN/m (point where TG-30 curve crosses the transition line). Translating this wettability behavior into fuel separation field, the TG-30 treated nonwoven can stop every liquid with surface tension higher than 30mN/ while the fuel with lower surface tension can easily pass through it. The dynamic contact angle recorded on this sample with pure water was 110° indicating a very hydrophobic surface. On the other hand, PFS fabric can separate every liquid with a surface tension higher than 50 mN/m from fuel combinations.

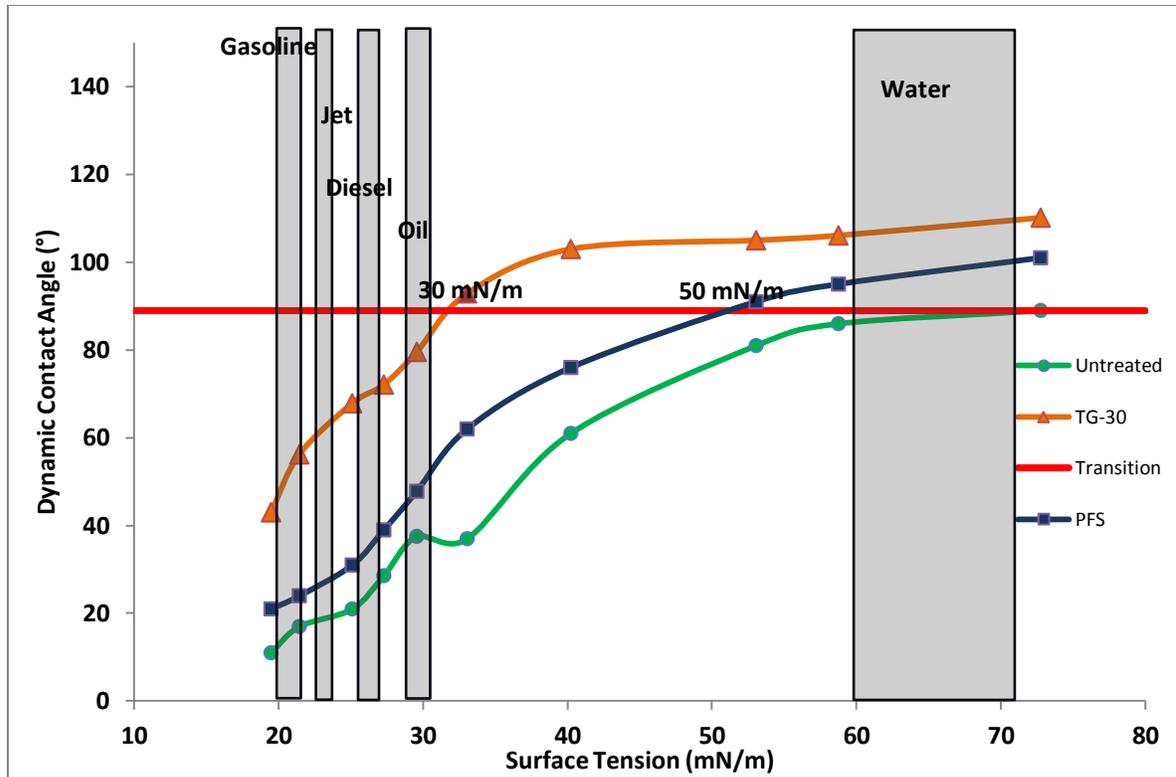


Figure 4-15 Dynamic Contact Angles measured on PET webs for different liquid surface tension

Discussion: Three major methods were applied for the assessment of the wetting behavior and hydrophobic/oleophobic properties of the plasma surface treated samples including:

- 1- Goniometry: involves the observation of sessile drop of the test liquid on the substrate.
- 2- Water/alcohol and oil repellency (AATCC 193 and 118): normalized methods to assess the surface energy of the treated samples in a range between 59 mN/m to 20 mN/m .
- 3- Tensiometry: Involves measuring the forces of interaction of the solid with the liquid.

Goniometry method was found to be a useful method for liquids such as water with high surface tension that provide good shape of the droplet on the hydrophobic surface and easy to judge visually-to measure the contact angle in a reasonable time interval. Otherwise, for liquid with low surface tensions due to the open structure of the fabric once a droplet was placed on the fabric it was absorbed into the fabric within tenths of a second.

AATCC test methods were quick and an easy way to report the surface energy of the sample using numbers (rating) that corresponds to a certain range of surface energy values. Since the results were reported based on the measurement and visual observation on 3-5 spots of the sample, the researcher found a good potential in this method to investigate the uniformity of the plasma treatment throughout the surface (large dimensions of the sample) and to confirm the reproducibility of the results.

Wilhelmy method using the aforementioned settings produced very good uniformity in the measurement and a consistent behavior was observed on samples from liquids with high surface tension to liquids with low surface tension. Due to its dynamic nature, the method gave a clear understanding of the liquid movement on the treated surface and clear vision of how surfaces with different levels of hydrophobicity react against liquid with different wetting ability. However, the method was challenging because of the uni-surface treatment of the plasma since highly wetting liquids with low surface tension start penetrating the bulk of the substrate and interferes with the surface movement of the liquid front and advancing angle measurements. A drawback was that Wilhelmy method actually measures $\text{Cos}\theta$ and not θ directly. For low $\text{Cos}\theta$ values a small variation in $\text{Cos}\theta$ resulted in very large variations in θ . Another challenge was to ensure that each tested sample had the same shape and size specifically on the edge where they are touching the liquids.

4.5.4 Hydrostatic Pressure Test

Figure 4-16 illustrates the increased hydrophobic properties in an increasing water intrusion pressure value. The 50 gsm untreated spunbond PET has the average water intrusion pressure of 6 mbar. Treating the fabric with fluorine monomers considerably increased the hydrophobic performance of the fabric resulting in higher values for water intrusion pressure. The PFS treated samples showed lower average values (9 mbar) of hydrostatic pressure comparing for TG-30 treated samples with the intrusion pressure of 12.6 mbar which evidence a more hydrophobic surface comparing to PFS.

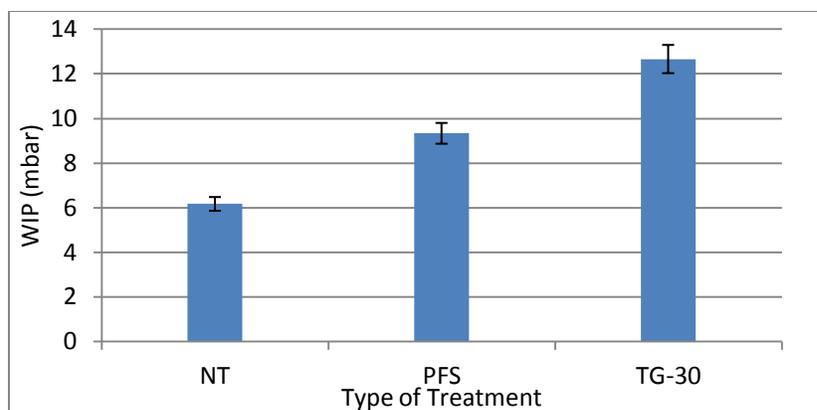


Figure 4-16 Water intrusion pressures measured on untreated and differently plasma.

4.5.5 FE-SEM Imaging

The performance discussion was backed up with further details collected from high resolution Field Emission SEM. Figure 4-17 demonstrates the FE-SEM images on the control and TG-30 and pentafluorostyrene treated samples. The images showed that the aliphatic monomer (TG-30) provided different shapes and orientation of polymeric layer than the flat aromatic monomer (PFS) on the surface. A variety of random rod, needle and global shapes of polymeric layer was observed on the surface of TG-30 treated sample while the pentafluorostyrene nanolayer was almost a uniform layer stretching along the fibers.

4.5.6 SEM-EDX

Scanning electron microscopy (SEM) images and EDX (energy dispersive X-ray spectroscopy) spectra of TG-30 treated fabric are shown in Figure 4-18. Compared to the smooth image of the control PET, the treated sample showed obvious changes in the surface texture and the presence of a polymer layer on the surface throughout the fibers, which was attributed to a nanolayer of grafted TG-30 on the surface. The non-uniform scratched appearance of the polymer film was mostly attributed to the deposition of the monomer in the vapor phase onto the fabric surface. The EDS spectrum showed the fluorine peak on the surface.

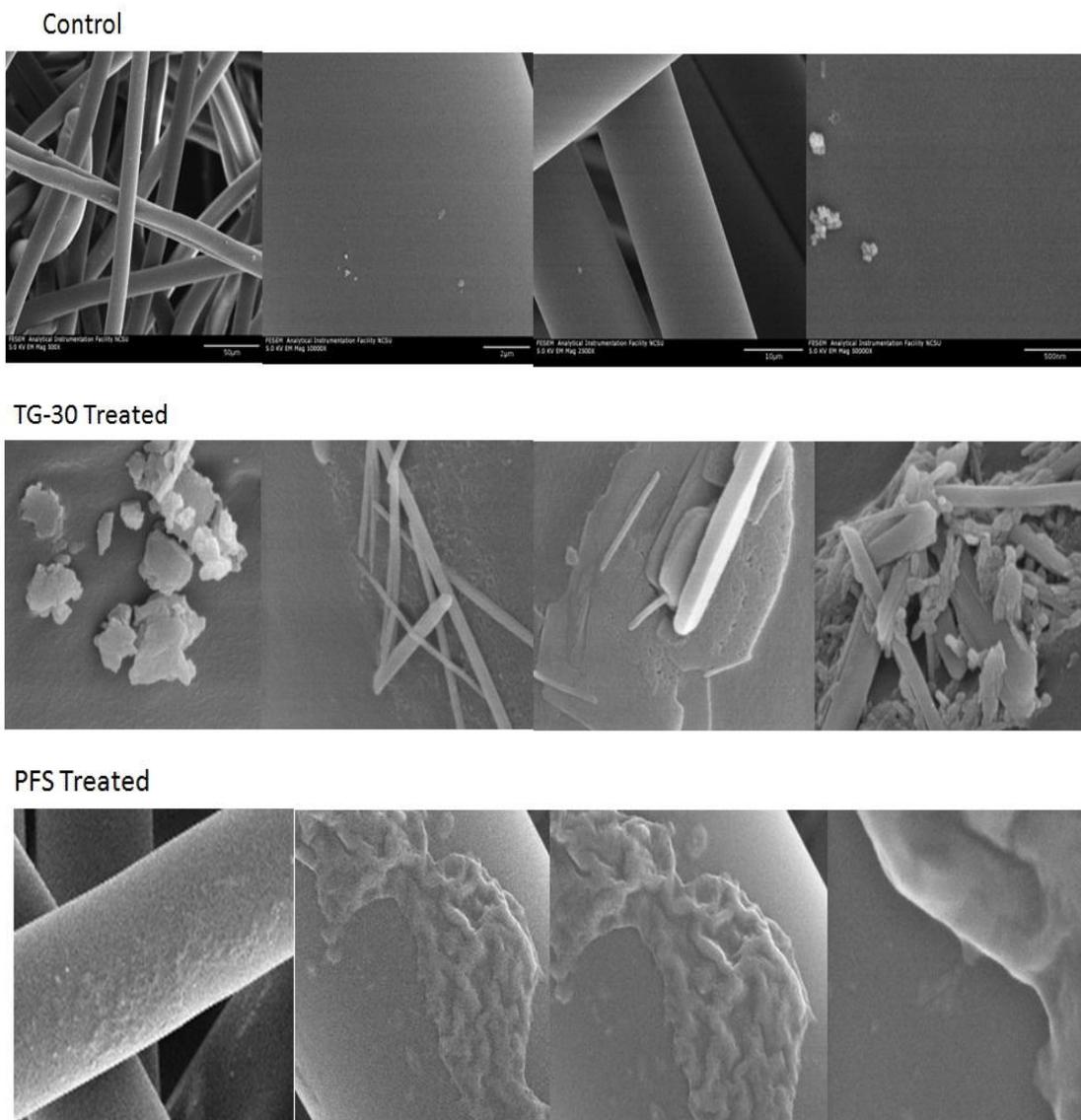


Figure 4-17 FESEM photographs of detected polymeric structures on TG-30 treated samples and pentafluorostyrene treated samples.

4.5.7 XPS

The chemical compositions on the surface of the treated samples were studied using XPS (X-ray photoelectron spectroscopy) technique. Figure 4-19 shows the XPS spectra of the untreated PET sample versus the TG-30 treated sample at the plasma power of 750 and 4% monomer add-on. The results showed obvious alteration of the chemical composition on the PET substrate. The sharp fluorine peak revealed that there was a chemical reaction

involving the generation of new functional groups on the surface. The fluorine percentage in the surface chemical composition not only depends on the amount of monomer applied but also on the chemical structure of the monomer and also on the applied plasma power.

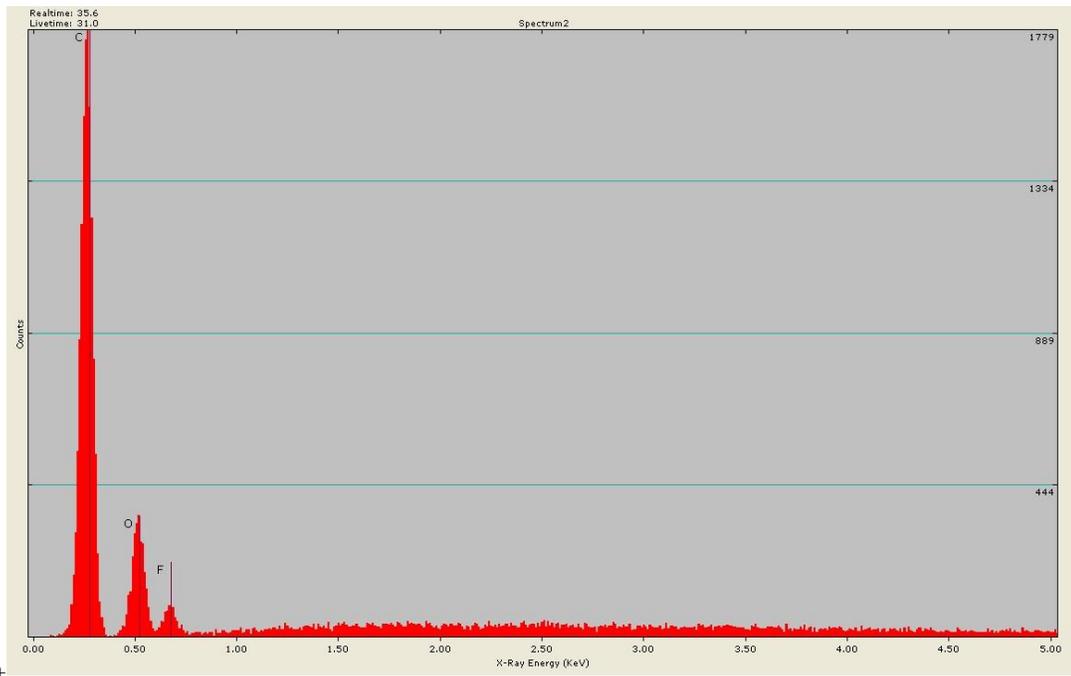
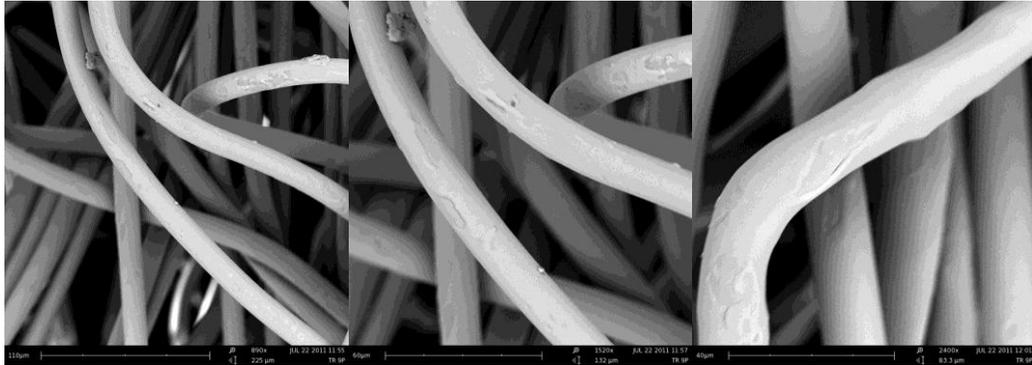


Figure 4-18 Tabletop SEM micrographs and EDX spectra for TG-30 treated sample

Figure 4-20 shows the XPS results on the samples treated with identical monomer add-on of the TG-30 but at different plasma powers. The graph showed that the fluorine percentage increased from 29.10% for the samples treated at 300 Watt to 59.83% for the sample treated at 750 Watt which emphasizes the significance of the effect of the plasma

power and the level of surface functionalities that can be achieved on the surface at different powers. Table 4-7 also shows the results of surface elemental analysis on the PET.

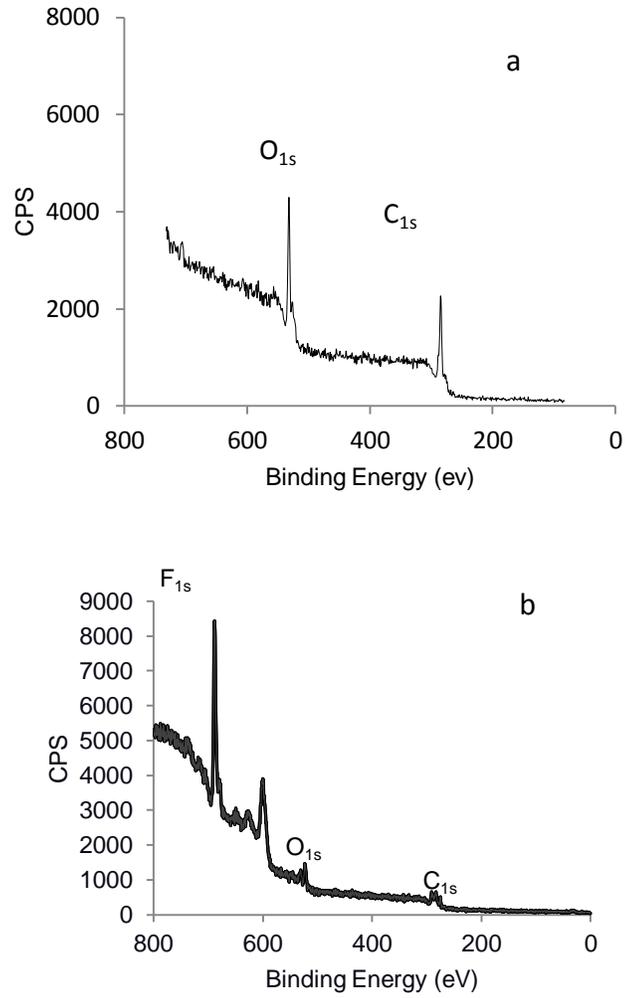


Figure 4-19 XPS survey scan of PET nonwoven fabrics; a) control, and b) TG-30 treated sample

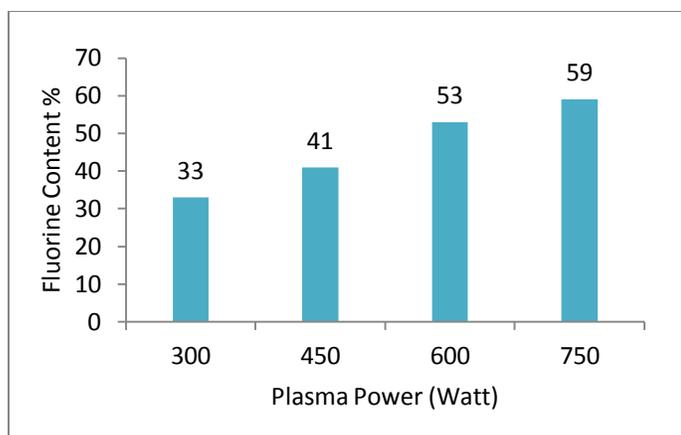


Figure 4-20 Fluorine content of the samples treated at same monomer flow rate and different plasma power

Table 4-7 Relative chemical composition on PET measured using XPS

Treatment	Chemical Composition, %			Atomic Ratio, %		
	C1s	O1s	F1s	F/C	O/C	(F+O)/C
Control	66.39	33.61	0	0	0.5	0.5
TG-30	30.19	9.99	59.83	1.98	0.33	2.31
PFS	25.58	17.18	53.90	2.1	0.67	2.7

4.5.8 TOF-SIMS

This technique neatly characterized the fluorine fragments/groups incorporated onto the surface of the fiber via RF plasma treatment. Figure 4-21 shows the TOF-SIMS Spectra for negative and positive modes on the samples treated with TG-30 at 750 W. Both negative and positive spectra were normalized to $C_7H_5O_2^-$ (amu 121) and $C_7H_4O^+$ (amu 104) peaks respectively, which correspond to PET. This normalization helped us directly compare the fluorine fragments created on the surface according to their peak heights.

Both TOF-SIMS spectra exhibited new peaks characterizing the presence of new functional species including fluorine. In the negative mode fragments such as F_2^- , HF^- , CF_3^- and COF_3^- were observed while in the positive spectra, traces of CF^+ , CF_2^+ , CF_3^+ , $C_2F_4^+$ and $C_2F_5^+$ were identified.

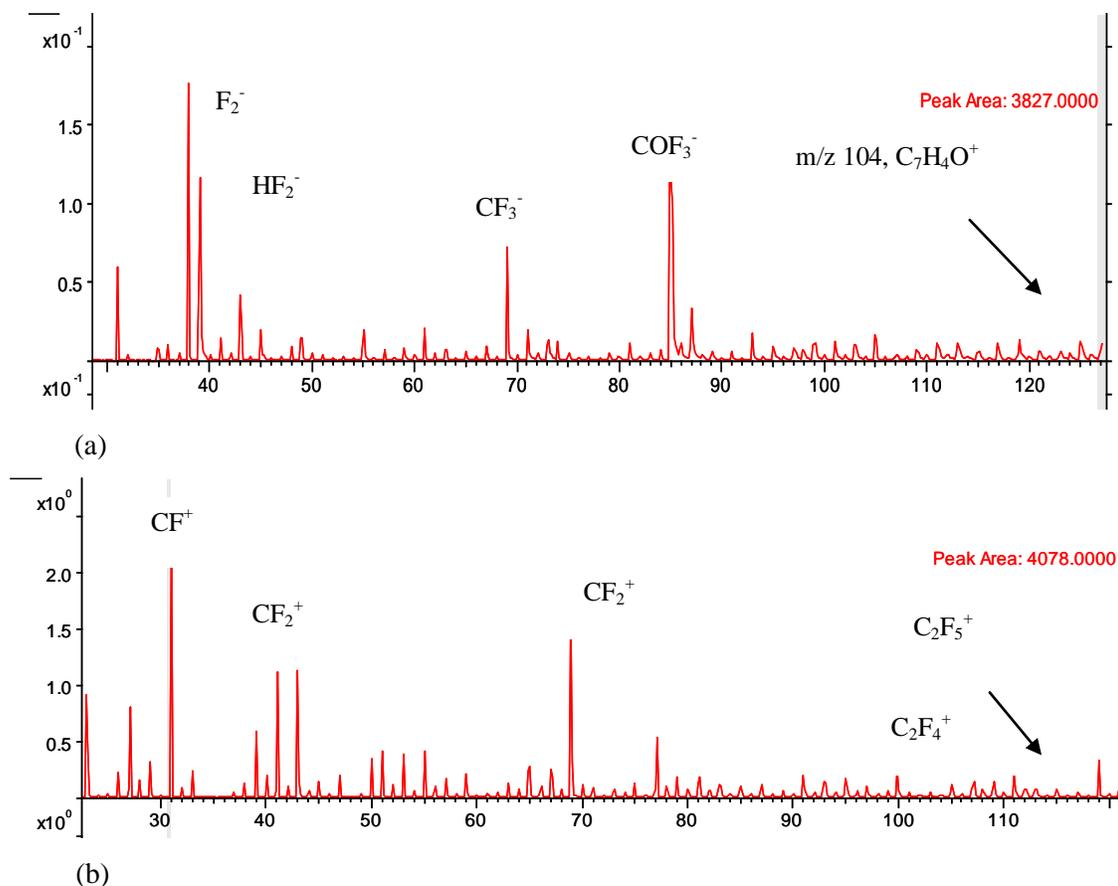


Figure 4-21 Total (a) negative, and (b) positive TOF-SIMS spectra of TG-30 treated sample.

Figure 4-22 shows the TOF-SIMS images on untreated PET sample and TG-30 treated samples at different plasma powers (300,450,600 and 750 Watts) at the same monomer percent add-on (4%). The brilliant yellow color corresponds to fluorine element (M=19) on the samples. The level of brightness of the yellow color demonstrates the qualitative aspect of the effect of plasma power on the percent fluorine on the surface.

Employing the TOF-SIMS on both sides of the fabric also verified that how the plasma treatment acts on the very outer layer of the fiber surface and leaves the other side of the fabric unchanged, which is a great advantage for applications focused on double side functional fabrics. Figure 4-23 illustrates the face and back sides of the nonwoven PET treated with TG-30 at 4% monomer add-on.

The right side images are the TOF-SIMS overlaid image of the same samples on the back side which has no trace of yellow or red colors as the indicator of fluorine.

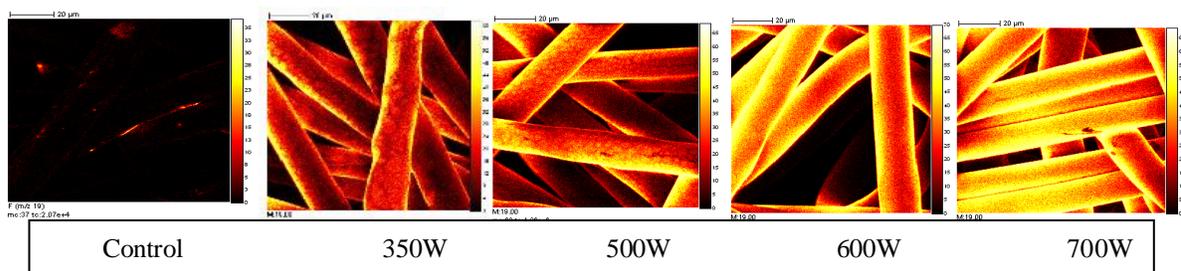


Figure 4-22 From left to right, ToF-SIMS total Negative ion images of untreated PET web, TG-30 plasma grafted web on its treated side and bottom side.

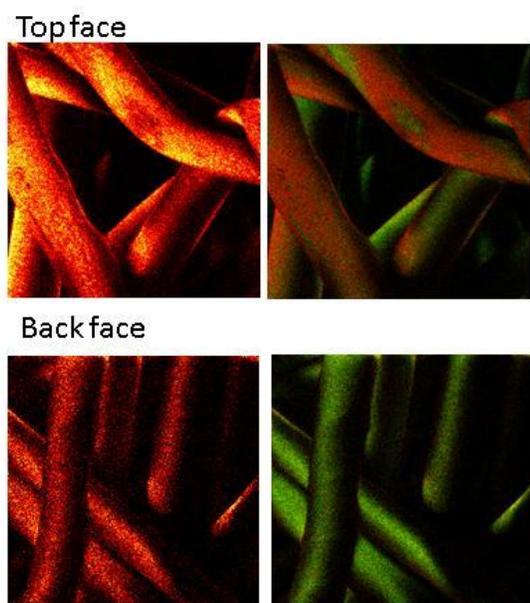


Figure 4-23 ToF-SIMS total Negative ion images of RF plasma treated sample on top and bottom face of the fabric.

4.5.9 FTIR

Figure 4-24 shows the FT-IR spectra on PET control sample and sample treated at 4% monomer add-on of TG-30 at 800 W. The peak in the range $1100\text{-}1200\text{ cm}^{-1}$ (1147 , 1123 and 1216 cm^{-1}) corresponds to C-F stretching, which confirms the presence of TG-30 grafted onto the PET surface.

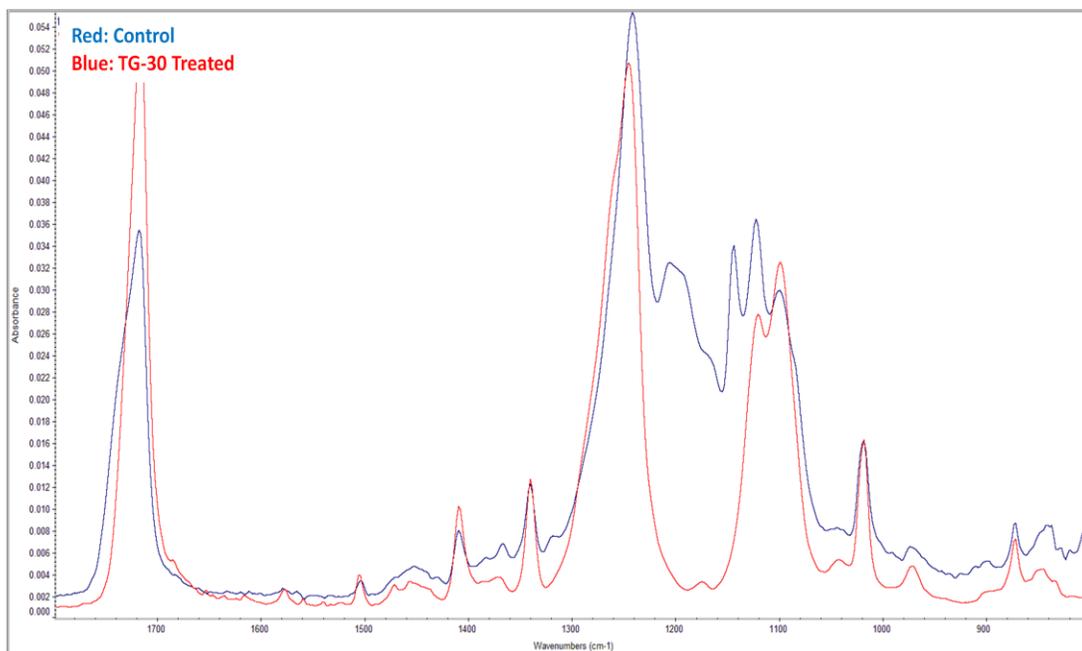


Figure 4-24 FTIR spectra of PET control and TG-30 treated samples

4.6 Reaction Chemistry

TG-30 reacts through a chain-growth free radical polymerization of the vinyl group of the monomer with PET substrate. The π bond of the vinyl breaks homolytically via free radical initiators, which is supplied by the plasma treatment, and generate free radicals on the surface. Once the double bond breaks homolytically, the free radical graft chain polymerization ensues. As seen in Figure 4-25, the graft polymerization occurs when the monomer reacts with a free radical of the surface of the fabric. The free radical attacks the double bond of the monomer, opening the double bond, and a new covalent bond was formed between the fabric and the monomer. This leaves a free radical on the monomer, which may undergo different reaction pathways. Two plausible reaction pathways are depicted in Figure 4-23. In the propagation pathway, the free radical left on the monomer, which is covalently bonded to the fabric, attack an unreacted monomer, which will continue the free radical chain polymerization until the propagating species are terminated. In the termination pathway, the polymerization reaction may terminate by abstracting a hydrogen atom. The propagation pathway will lead to a polymer or an oligomer grafted to the surface of the substrate, while termination will lead to monomer grafted to the surface of the substrate. As both paths

furnish a fluorocarbon chain oriented vertically on the substrate, both are expected to provide durable water repellent properties.

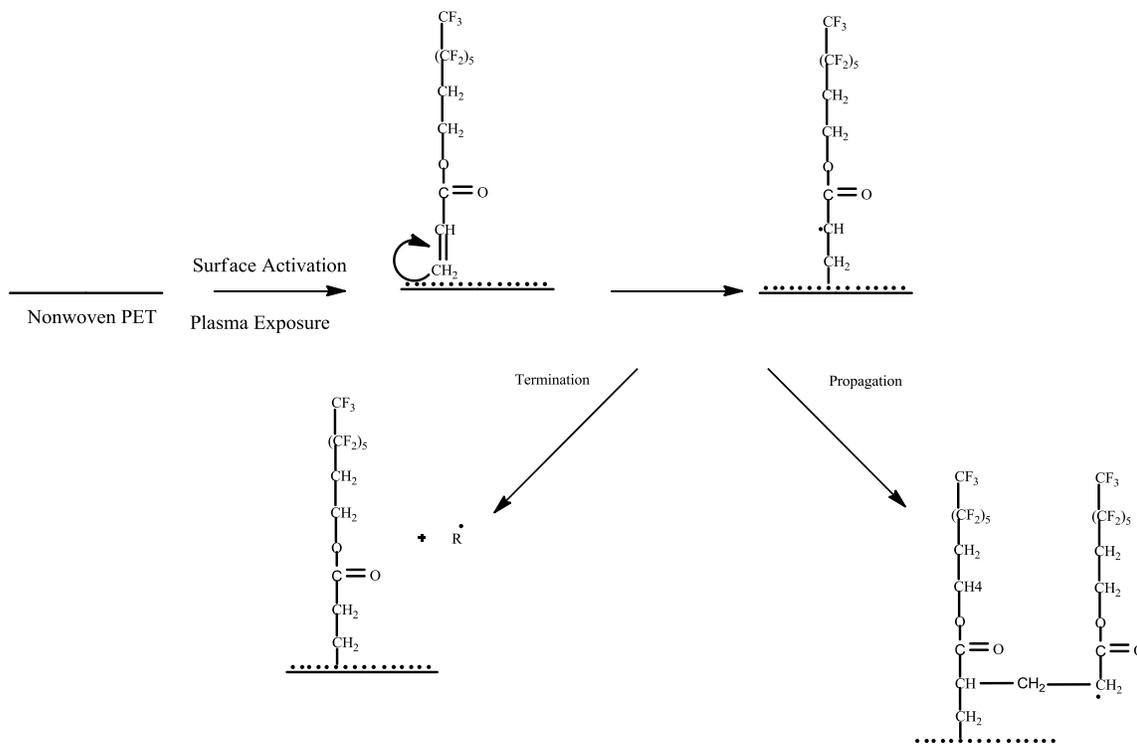


Figure 4-25 Proposed reaction mechanisms and polymerization for TG-30

4.7 Treatment Durability

The hydrophobic treatment durability was examined through soxhlet extraction of the treated samples for 2 hours with acetone as the solvent. TG-30 treated samples showed identical oil repellency rating (7) before and after soxhlet extraction which means that the monomer is grafted to the surface and is durable.

4.8 Ageing of the samples

The ageing behavior of the treatment was briefly investigated by comparing the values of oil repellency and contact angle data on the treated samples after one day, one month, and six months. The results confirmed that for all the treated samples, the oil repellency rates and the contact angle values remained unaltered throughout the entire six months.

4.9 Challenges for Plasma in Industrial Processes

The researcher concluded that the experiments performed in this section of the project provided more insights and better understanding of the influence of each parameter on the final oil/water repellency performance. These findings can be used to scale up the laboratory work to an industrial scale. The followings are recommendations for future work:

- The atmospheric set up of the plasma device and the fact that all the procedures were done at atmospheric pressure and at ambient condition makes it feasible to scale these processes to a production scale.
- Shorter time of plasma exposure can be achieved in industrial devices with much higher powers , which will save time and makes the plasma treatment of textiles more compatible with the line speed of the conventional textile wet processes.
- Identifying different monomer chemistries that can be applied via vapor deposition system or spraying equipments will provide large variety of performance on the textile substrate with much lower lowest chemical consumption, compared to conventional textile processes.
- The researcher found the following aspects challenging and influential in plasma treatment efficiency and results reproducibility:
 1. 3D structure of the fabric
 2. Large surface area of the substrate
 3. Moisture (both absorbed by sample or in the ambient around the device)
 4. Air interference
 5. Cleanness of the substrate surface
 6. Switching from very hydrophilic materials (like cotton) to very hydrophobic one (like polypropylene)
 7. The performance of the monomer deposition system (applicator/evaporator)
 - The rate of the pumped monomer, the lost monomer through vaporization and the depositing amount onto the surface should definitely optimize.
 - The applicator temperature compatibility for thermoplastic and thermoset polymeric substrates should take into account in case sensitive materials are passing beneath the very hot applicator.

- The argon gas flow rate and its role in changing the depth of penetration of monomers vapor into substrates should be investigated.

8. The thickness of the material; since the plasma has a limited penetration into the textile structure. This effect can only be avoided by having plasma with higher intensity or by increasing the contact time in plasma volume.

9. The highly significant effect of the post exposure time which requires either longer time of exposure or several passes which is time consuming and lowers the treatment speed.

10. Thick high loft fabrics showed less uniform results throughout the samples with lower reproducibility rather than thin low loft samples.

What can be concluded in overall is that non-woven fabrics with relatively light weight and pretty open structures were good candidates for plasma processes rather than the woven fabrics. In the meantime non-woven fabrics benefits from more diverse and novel end-user applications in the commercial world which makes them more compatible with plasma treatment requirements.

4.10 Conclusion

Modifying the surface characteristics of the nonwoven PET for creating a media able to separate water from fuels was investigated. Wetting properties and the performance were investigated by means of measuring static contact angle, water/alcohol and oil repellency grad and Wilhelmy dynamic contact angle. Moreover, the water intrusion pressure was measured on the treated samples. Surface chemistry changes on the plasma treated samples were investigated by means of XPS and TOF-SIMS analysis.

Advancing contact angle measured on both TG-30 and PFS treated samples were higher than those measured on the untreated PET, for every tested solution. Untreated sample curve laid always below the wettable/unwettable transition, with a contact angle measured with pure water of 89°. TG-30 treatment lowered the surface energy of nonwoven PET so the wettable/unwettable transition moved to 30 mN/m, and the dynamic contact angle measured with water rose to 110°. PFS treatment decreased the transition to 50 mN/m, and increased the water dynamic contact angle upto 101°. XPS and TOF-SIMS results confirmed the presence of different fluorine fragments and the extensive chemical changes that took place on the surfaces by grafting the fluorocarbon monomer onto it.

4.11 References

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Chapter 5 Atmospheric Pressure Plasma Grafting of DADMAC To Nonwoven Polypropylene

5.1 Abstract

Spunbond nonwoven polypropylene fabric (Sb-PP), commonly used for hygienic products was treated with diallyldimethylammonium chloride (DADMAC). Atmospheric pressure glow discharge plasma was used to induce free radical chain growth polymerization of the DADMAC monomer on the Sb-PP, which furnished a graft polymerized network on the fabric with durable antimicrobial properties. The effect of different DADMAC concentrations, and plasma conditions including the RF power (400-800 W) and the time of plasma exposure (0-120 sec) were studied and the optimum treatment conditions were identified by calculating the surface charge density on the treated fabrics. The presence of poly-DADMAC on the polypropylene surface was confirmed using SEM, FT-IR and TOF-SIMS. Antibacterial performance was investigated using the Standard Test Method AATCC TM 100 for both gram positive and gram negative bacteria. The antimicrobial test results show 6 log reductions in the bacterial activities of *K. pneumoniae* and *S.aureus* on the SB-PP samples.

5.2 Introduction

With the threat of emerging new bacteria and old bacteria capable of reinventing themselves by changing their DNA to surpass different antimicrobial agents and the threat of blood-borne pathogens [1,2] such as HIV [3] and hepatitis [4], and air-borne viruses such as SARS, the need for garments that can disinfect wide spectra of bacteria and viruses is highly desirable [5,6].

Plasma-induced graft polymerization is the use of the plasma to covalently bond a chemical to the surface of a substrate. Chemicals that are grafted to a polymer may form either a monolayer or may subsequently undergo polymerization and form a finite thickness. Chemicals with a vinyl group or capable of ring opening may undergo polymerization, whereas chemicals with a hydroxyl or amine group are restricted to monolayer formation

(reaction between substrate and the functional group) [7]. Atmospheric pressure plasma is an alternative to conventional wet chemical grafting. Plasma has been shown to form free radicals on a substrate's surface; subsequently, these radicals are available for reaction with a monomer to form a permanent finish [8] (Figure 5-1). The plasma approach has the advantage of reducing water consumption and reaction time over conventional processes.

Diallyldimethylammonium chloride (DADMAC), a quaternary ammonium salt has vinyl group as a functional group. Several studies reported diallyldimethylammonium chloride (DADMAC) as a strong antimicrobial agent over the past few years. DADMAC is a quaternary ammonium compound (Figure 5-2) manufactured by reaction of allylchloride with dimethyl amine in a closed system [9]. Quaternary ammonium compounds bind to microorganisms via reacting with the cell membrane and disrupting the lipo polysaccharide structure resulting in the breakdown of the cell [10].

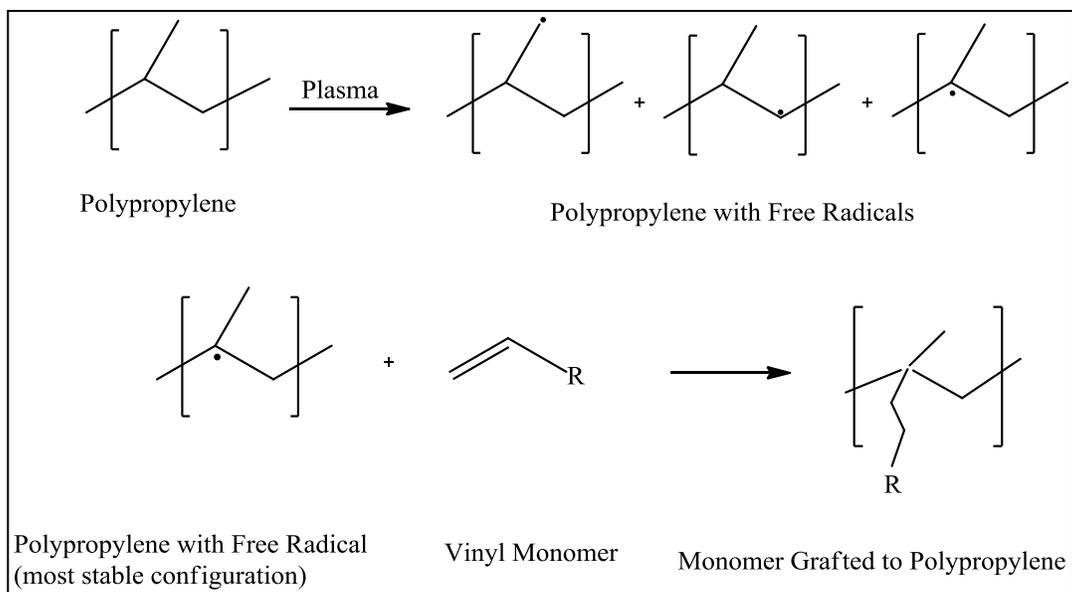


Figure 5-1 Grafting of a vinyl monomer to polypropylene using plasma

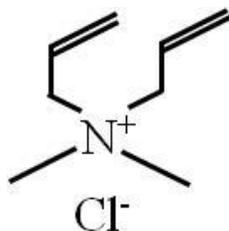


Figure 5-2 Chemical structure of diallyldimethylammonium chloride (DADMAC)

Thorne et al [11] developed antimicrobial coatings from DADMAC onto PE by graft polymerizing DADMAC on a plasma activated surface.. The coating was reported to be as thin as 2-3 nm and could reduce the settlement of *M. luteus* colonies by a factor of $10^5 - 10^6$. A copolymer of poly DADMAC and konjac glucamannan (KGM) was also reported to be highly effective against *B. subtilis* and *S. aureus* but not against *E.coli* or *P. aeruginosa* [12]. However, a polyDADMAC coating on glass indicated strong contact with bacteria killing *B. diminuta*, *E. Coli* and *R. terrigena* in a study by van der Mei et al [13]. PolyDADMAC was also used as the active ingredient in Derma Science's Bioguard® Barrier Dressings. It is bound to the barrier dressing without leaching, and has a very fast action with $> 5 \log$ (99.999%) reduction in activities of *E.coli*, *P.aeruginosa*, *M. luteus* and *S. aureus* [14,15]. This Chapter is focused on plasma grafting of DADMAC onto polypropylene nonwoven fabrics which can find applications in disposable hospital gowns, bedding covers and pillow cases, patient robes and other possible hospital situations. Different treatment strategies have been examined. The experimental work discussed here was designed to investigate the role of plasma in achieving higher grafting yield with and without cross-linker and heat to ascertain if a direct plasma grafting was possible and whether the grafted polymer will be durable.

5.3 Experimental

5.3.1 Materials

Fabric: Nonwoven polypropylene was provided by NCRC (Nonwovens Cooperative Research Center at NCSU). The fabric was produced by calendaring and with weight of 50 g/m^2 . Samples were cut into 15 x 25 cm swatches.

Chemicals: All chemicals were purchased from Sigma Aldrich, including Diallyl Dimethyl Ammonium Chloride (DADMAC) solution (65 wt. % in H₂O), pentaerythritol triacrylate (cross-linker) and ammonium persulfate (thermal initiator). Chemical structures used in this study are shown in Figure 5-3.

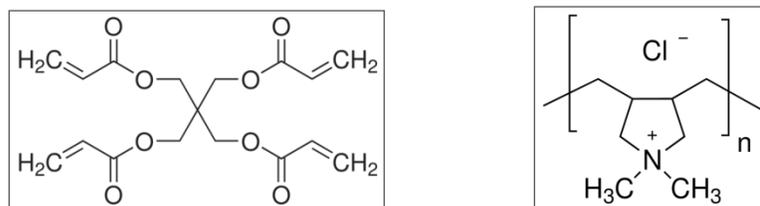


Figure 5-3 Chemical structure of pentaerythritol triacrylate and Diallyl Dimethyl Ammonium Chloride (DADMAC)

5.3.2 Plasma Device

Atmospheric pressure plasma treatment was performed on the APJet Rio® device. To generate a discharge, helium and oxygen gases were introduced into the plasma chamber at the rate of 40 SLPM and 0.04 SLPM, respectively. Helium gas was used as a feed gas to initiate the discharge due to its low ionization potential and then 0.1% oxygen was introduced into the helium stream and was ionized by the collision process. Increasing the percent oxygen dilutes the plasma and quenches the plasma instantaneously. The electrode gap was fixed at 2 mm, the exposure time varied in the range 0-120 Sec. and the plasma power changed in the range of 400-800 W.

5.4 Characterization Techniques

5.4.1 % Change in Mass

Each sample was weighed (W_0) before chemical/plasma treatment. Polypropylene fabrics are hydrophobic and there is no need for conditioning before monitoring the weight change. The average weight per sample was approximately 2 g, and treated samples were Soxhlet extracted in water for +8 hours to remove any un-reacted DADAMC. After extraction, the samples were dried at room temperature and re-weighed (W_f) using a microbalance with an accuracy of ± 100 micrograms.

$$\text{Weight Change (\%)} = 100\left(\frac{W_f - W_0}{W_0}\right)$$

5.4.2 Acid Dye Testing- Surface charge density calculation

Acid dyeing test results and calculation of surface charge density was used as the key process output variable for optimizing the experimental parameters. Polypropylene is a polymeric compound consisting exclusively of carbon and hydrogen groups (Figure 5-4) and contains no positive moieties to react with acid dye. Hence, the acid dye will exclusively react with the quaternary groups of DADMAC created after grafting on the polypropylene surface. Since dye will adhere to the polypropylene only if DADMAC is present (attaching to the quaternary group of DADMAC), fabric staining is an indicative of successful grafting. The calculation details for dye baths and surface charge density are provided in Appendix 1. The output variable for optimization process is the calculated values of surface charge density on the treated samples. The minimum number of dye molecules absorbed on the substrate surface is directly proportional to the number of positive charges created by DADMAC grafting onto the surface. Instead of measuring the concentration of dye extracted from the substrate surface, the measurement in this experiment was conducted directly on the concentration of dye solution mixed with the washing effluent at the end of dyeing experiment. The number of surface charges was calculated based on the difference between the initial and final concentration of dye solution (Appendix B).

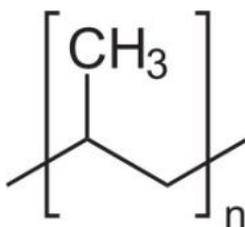


Figure 5-4 Polypropylene molecular structure

5.5.3 UV Spectrophotometry

To evaluate acid staining of DADMAC-grafted polypropylene, dye concentrations were measured in the dye baths using UV Spectrophotometry. UV spectrophotometry was

conducted on a Cary 3E UV-Visible Spectrophotometer using Varian Scan Software. Four standards of known dye concentrations were used to generate a calibration curve for the acid dye (Acid Sirius Red FB3). The conversion of the absorbance to concentration was based on Beer's Lambert Law, which states: $A = \epsilon bc$, where A =absorbance, b =path length, and ϵ =extinction coefficient $\text{Lmol}^{-1}\text{cm}^{-1}$). UV-VIS spectrophotometric analysis was performed on a Cary 300 UV-VIS spectrophotometer and the accompanying software Cary Win UV v.3.00 (182).

5.5.4 FTIR

Nexus 470 ESP FT-IR (Thermo Scientific), which is equipped with an Avatar Omni sampler, was used for infrared spectroscopy. A germanium crystal (single bounce internal reflection element) was used with a 45° incidence angle. The instrument uses DTGS (deuterated triglycine sulfate) detector, KBr beamsplitter ($375 - 7000 \text{ cm}^{-1}$), and Global source of radiation with a frequency range of $400 - 5000 \text{ cm}^{-1}$.

5.5.5 XPS (X-ray photoelectron spectroscopy)

XPS analyses were obtained with the Riber LAS-300 system at the Analytical Instrument Facilities (AIF) at NCSU. The system uses non-monochromatic Mg K- X-rays with excitation energy of 1253.6 eV. Energy calibration was established by referencing to adventitious carbon (C1s line at 284.5 eV binding energy). The takeoff angle was 75° from the surface with X-ray incidence angle at 20° , while the angle of X-ray source to the analysis was 55° . The base pressure in the analysis chamber was in 10^{-10} Torr range. Percent atom concentrations of surface elements in the survey scan were determined by using CASA XPS software.

5.5.6 SEM

Surface morphology of fibers was examined on a PhenomTM scanning electron microscope (SEM), which is equipped with an optical microscope for ease of navigation across the sample surface. It has a magnification range of 120 – 24,000 with lateral resolution

of up to 30 nm and allows for a sample size of up to 25 mm in diameter and 30 mm in height. Image processing was performed by Image J. V.1.43 (Wayne Rasband, NIH, USA) 264 for better visualization and analysis.

5.5.7 TOF-SIMS

TOF-SIMS analysis was performed on treated samples at the NCSU Analytical Instrumentation Facility (AIF) with a TOF-SIMS 5 instrument using a ^{69}Bi liquid metal ion gun at 25 kV primary high voltage and 2 kV extraction voltage. TOF-SIMS analyses were conducted using a TOF-SIMS V (ION TOF, Inc. Chestnut Ridge, NY) instrument equipped with Bi_n^{m+} ($n = 1 - 5, m = 1, 2$) liquid metal ion gun.

5.5.8 Focused Ion Beam (FIB)

A FEI Quanta 200 3D Dual Beam FIB system (FEI Company, Hillsboro, OR) was used for all FIB cross sectioning and imaging. All FIB nano-machining and imaging was done using 30 kV Ga^+ . Prior to FIB nano-machining, all fibers were coated with approximately 20 nm of gold-palladium using a Denton Desk II (Denton Vacuum, Moorestown, NJ) sputter coater to protect the surface of the fiber from Ga^+ induced ion beam damage and erosion during the subsequent Pt protective layer deposition.

5.5.9 AATCC 100 Antimicrobial Testing

Antimicrobial assays of the DADMAC grafted on polypropylene samples were conducted following the test method of AATCC (American Association of Textile Chemist and Colorist) Test Method 100-2004; Assessment of Antimicrobial Finishes on Textiles Materials. The test was performed by the Antimicrobial Test Laboratories in Texas. The test microorganism was grown in a liquid culture and the concentration of the test microorganism was standardized. The microbial culture was diluted in a sterile nutritive solution. Then the control and test fabric swatches were inoculated with microorganisms. The inoculation was performed such that the microbial suspension touches only the fabric. Bacteria levels on both control and test fabrics were determined at "time zero" by elution in a large volume of neutralizing broth, followed by dilution and plating. A control was run to verify that the

neutralization/elution method effectively neutralized the antimicrobial agent in the fabric. Additional inoculated control and test fabrics were allowed to incubate, undisturbed in sealed jars, for 24 hours. Figure 5-5 shows images of the actual test performed on the polypropylene sample.

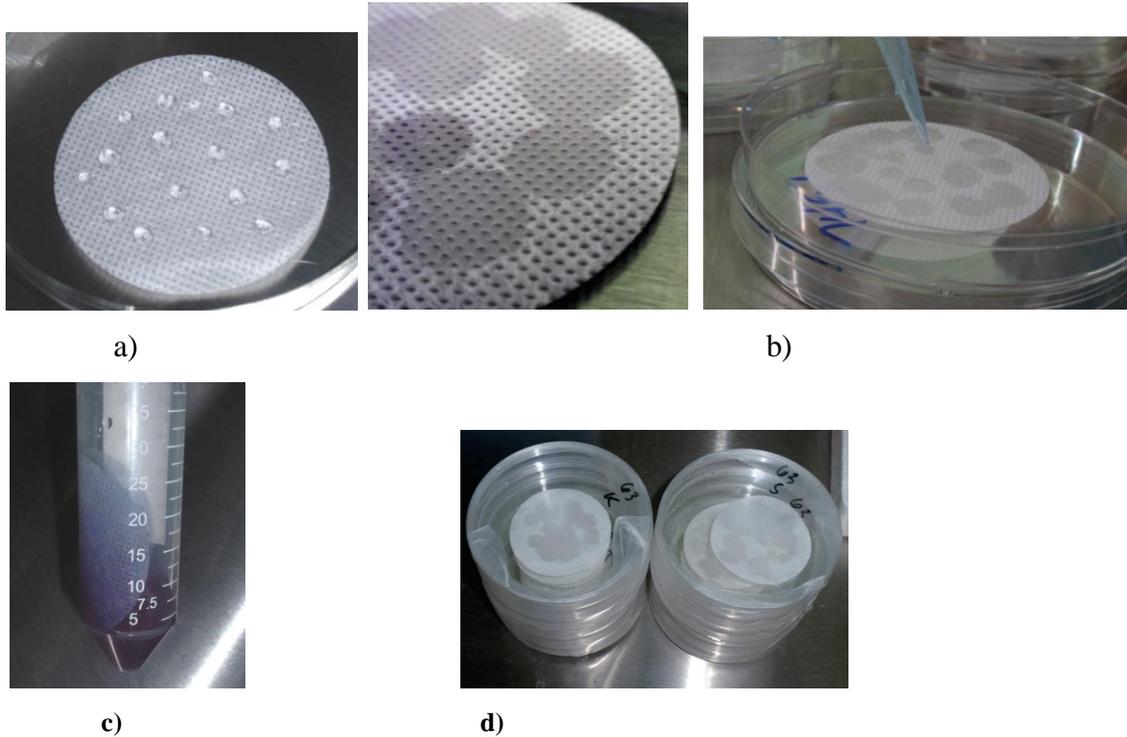


Figure 5-5 Antimicrobial test procedure: a) Inoculum right after inoculation prior to being absorbed by sample, b) Close-up of absorbed inoculum, c) Sample neutralized in D/E broth for enumeration, d) Inoculated samples sealed with parafilm prior to placing in incubator.

After incubation, microbial concentrations were determined. The reduction in numbers of bacteria was calculated using the following equation:

$$\text{Reduction Rate (\%)} = (A-B) / A \times 100$$

Where A = the number of bacterial colonies from untreated fabrics and B = the numbers of bacterial colonies from treated fabrics. One log reduction indicates that finished fabrics were able to kill 90% of the bacteria and so on for higher log reductions. The samples were tested against two different microorganisms, *Staphylococcus aureus* which is a facultative

anaerobic Gram-positive coccal bacterium and *Klebsiella pneumoniae* , a Gram-negative, non-motile, rod shaped bacterium.

5.6 Experimental

5.6.1 General Procedure: Grafting of DADMAC to Polypropylene Samples

Achieving the optimum conditions for antimicrobial finish, a design of experiment strategy with two different approaches was developed:

I) Plasma induced graft polymerization: the significance of plasma and non-thermal treatment was examined by introducing polypropylene, DADMAC, cross-linker and plasma in different sequences as shown below:

- a. Fabric surface was activated using Plasma -----> DADMAC was deposited ---->> 2nd post-plasma exposure
- b. DADMAC deposited on the fabric-----> Plasma exposure
- c. Fabric surface was activated using Plasma -----> activated fabric dipped in a solution containing DADMAC+ cross Linker -----> Plasma exposure
- d. Fabric was dipped in solution of DADMAC+ crosslinker -----> Plasma exposure

II) Plasma assisted graft polymerization: The significance of plasma and thermal treatment was examined by introducing polypropylene, DADMAC, cross-linker, thermal initiator and plasma in different sequences:

- a. Plasma -----> DADMAC+ thermal initiator -----> thermal curing
- b. DADMAC+ thermal initiator -----> thermal curing
- c. Plasma -----> DADMAC+ thermal initiator+ linker -----> thermal curing
- d. DADMAC+ thermal initiator+ linker -----> thermal curing

DADMAC solutions were prepared in different concentrations and were applied on polypropylene fabric at 100% wet pick up. Plasma exposure times were in the range of 0-120 Sec. and the composition of the plasma was a mixture of 99% helium and 0.1% oxygen

gases. After the samples were fully treated, they were soxhlet extracted for +8 hours in water to remove all un-reacted DADMAC.

5.6.2 Customized Procedure: Plasma Induced Grafting Polymerization Approach

5.6.2.1 1st DOE: Screening for DADMAC applied add-on % and Significance of He/O₂ Plasma Treatment on DADMAC grafting onto the Polypropylene

Table 5-1 shows the first DOE of parameters and their values designed based on the fractional factorial method. The purpose of this experiment was to: 1) investigate how plasma contributes to the formation of surface free radicals on an inert surface such as polypropylene, 2) how strong the plasma in generating enough free radicals for the initiation and propagation reactions to furnish high grafting yield, and 3) how the surface radical formation may correlate with surface charge density and grafting yield.

Radio frequency power was varied in from 400 to 800 W with 200 increments. The time of plasma pre-exposure was 0, 30 or 60 seconds, and the plasma post-exposure time was 30 to 45 or 60 seconds. The DADMAC concentration varied between 6 to 10 percent add-on. Swatches of 15x25 cm of nonwoven polypropylene fabric were weighed precisely, marked and then placed and secured on the device by using double side tape. The flow rate of Helium was set at 40 SLPM and oxygen was mixed at a rate of 0.04 SLPM. The gap between the electrodes was set at 2 mm, and the plasma exposure was done on both sides of the fabric. The solutions of DADMAC with different concentrations were applied on the both plasma treated and untreated polypropylene fabrics at 100% wet pick up. The samples were dried at 70°C for 2 minutes, and then plasma exposed for the second time on both sides of the samples to make sure that the graft polymerization reaction reached completion. Figure 5-6 illustrates the sequence of treatment. Soxhlet water extraction was run on all samples for +8 hours to remove all the un-reacted chemicals. After Soxhlet extractions, samples were rinsed with running cold water, dried at room temperature, then reweighed to determine the weight change as an evidence for DADMAC grafting onto the polypropylene surface. Acid dye staining and surface charge density calculation were also carried out on all samples.

Table 5-1 2³ Fractional design with 3 center points for DADMAC applied add-on % and plasma exposure sequences

Run Order	Pattern	Parameters			
		Plasma Pre-exposure(Sec)	Plasma Power (W)	Plasma Post-exposure (Sec)	DADMAC add-on %
1	0000	30	600	45	8
2	--++	0	400	60	10
3	+--+	60	400	60	6
4	----	0	400	30	6
5	-++-	0	800	60	6
6	++--	60	800	30	6
7	0000	30	600	45	8
8	-+++	0	800	30	10
9	++++	60	800	60	10
10	+--+	60	400	30	10
11	0000	30	600	45	8

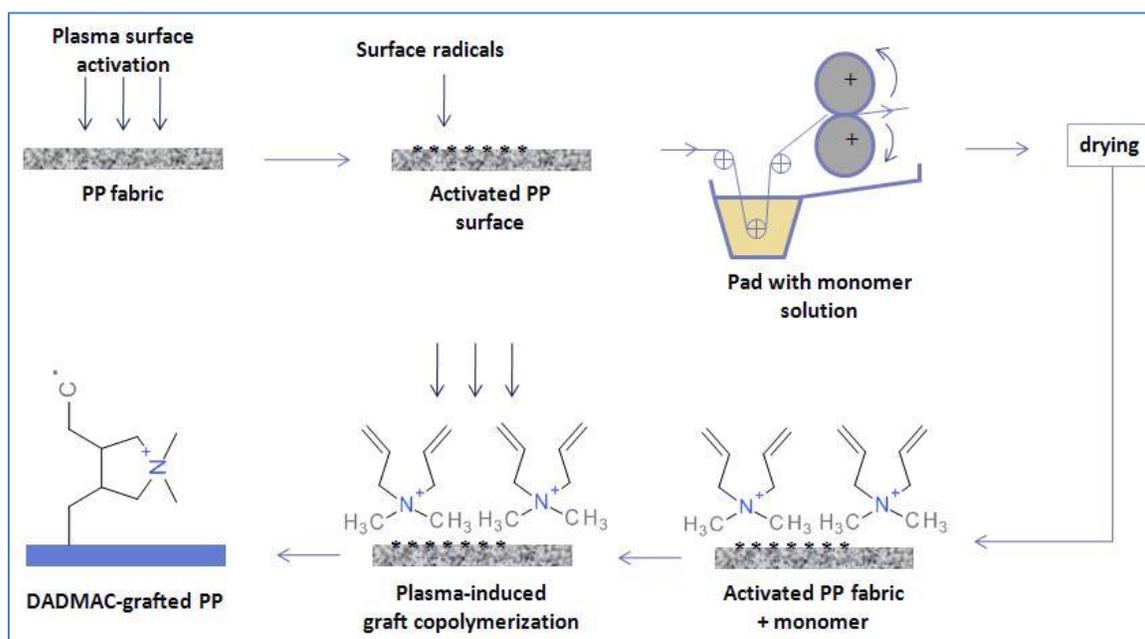


Figure 5-6 Plasma induced graft polymerization procedure illustration

Discussion: The goal behind this design of experiment was to determine whether plasma graft polymerization of DADMAC can be achieved and it is durable without heat and use of a cross-linker. The mass of the samples was recorded prior to grafting and after soxhlet extraction to determine the quantity of DADMAC compound grafted to the polypropylene substrate. All treated samples show very little or no increase in mass

indicating a low level of % grafting. Acid dye staining calculation of the charge density on the sample treated with DADMAC but were not Soxhlet extracted, and a quick statistical analysis with JMP software demonstrated that applying higher DADMAC % concentration did not contribute to higher surface charge density which means the surface of the substrate was saturated with the lower concentration of DADMAC, and any excess amount of unreacted DADMAC were washed away. Further analysis on the values of surface charge density and visual staining examination confirmed that the higher the time of pre- and post-plasma exposure, the stronger the staining by the acid dye, and hence, the higher values of surface charge density.

Higher pre-plasma exposure time using He/O₂ provided more free radicals on the surface which were used as an initiator to initiate and propagate the graft polymerization of the monomer after applying the DADMAC solution on the surface.

The plasma post-exposure step facilitates the free radical polymerization reaction on the very top layers of the monomer layer on the surface. Since the penetration depth of the plasma into the surface is limited to few nanometers, the free radicals and active species generated during the first plasma pre-exposure will not be enough to drive the reaction to completion. Hence, the second plasma exposure (post-plasma) should provide extra energy to drive the polymerization reaction thermodynamically to completion.

Both mass change results and surface charge density values confirmed that the grafting yield of DADMAC on the polypropylene was low. In effort to enhance the grafting yield of DADMAC, it was proposed to use a crosslinker, so that DADMAC can be tied to the substrate. The cross-linker applied was pentaerythritol tetracrylate, which contains four vinyl groups. This approach was proven to be successful in furnishing high grafting yield of polyDADMAC, which was durable. This technique was also used to graft antimicrobials like chitosan [16] and antimicrobial neem oil [17] form a covalent bond between epoxy adhesive and polymer [18] attach a fire retardant [19], improve hand and wrinkle resistance [20].

5.6.2.2 2nd DOE for DADMAC applied add-on % and significance of He/O₂ Plasma Treatment and the cross-linker effect on DADMAC grafting

Table 5-2, shows the second DOE of parameters and their values designed based on the fractional factorial design. The effect of only plasma approach was investigated in the first DOE, the purpose of this experiment was to determine whether adding a cross-linker to the reaction would produce a higher grafting yield and more durable finishing.

The treatment procedure was the same as in the previous part. Lower concentrations of DADMAC were applied because the first DOE demonstrated that higher % add-on of DADMAC does not contribute to the higher surface charge density values. Also longer pre- and post-plasma exposure times were applied in this design of experiment since the significant of exposure plasma exposure time was quite understood from the first DOE. The ratio of cross-linker to DADMAC was kept fixed at 1 to 10 moles. After extraction, samples were rinsed with running cold water, dried at room temperature, and then reweighed to determine the weight change for the grafting yield of DADMAC onto the polypropylene surface. Acid dye staining and surface charge density calculation were also carried out on all samples.

Discussion: Significant weight change was observed on samples before the treatment and after the soxhlet extraction which confirms the high grafting yield of DADMAC on the fabrics. Surface charge density values as the response data were analyzed using statistical software JMP 9. A model was fitted to the data with the four main factors, dropping the factor interaction terms (due to insignificance) from the model and predicted the best combination of factors where the response was maximized as shown in the prediction profiler in Figure 5-7. It was found that a combination of low plasma power, high DADMAC % add-on, high pre-exposure time and high plasma curing time (post-exposure) was working the best to achieve higher grafting yield and higher charge density values on the surface.

It was found that generating stable He/O₂ plasma was more viable in lower powers. The mixed plasma was more uniform in the volume of the plasma and no arcing was recorded which provided better condition for treatment of the polypropylene surface and was observed to be more effective rather than the higher power. Increasing the DADMAC concentration

raised the value of the charge density which confirmed that we are in the right experimental space for applying proper concentration of DADMAC in order not to saturate the surface. Likewise the previous DOE, both plasma pre-exposure and post-exposure had significant effect on obtaining higher charge density.

The optimized combination (low plasma power, high pre and post exposure time and high DADMAC %add-on) was validated by running 3 replicates and the new sample was created for determining the antimicrobial activity.

Table 5-2 2³ fractional factorial design with 3 center points for DADMAC applied add-on % and plasma exposure sequences

Run Order	Pattern	Parameters			
		Plasma Pre-exposure(Sec)	Plasma Power (W)	Plasma Post-exposure (Sec)	DADMAC add-on %
1	-++-	120	400	60	4
2	++--	0	800	60	4
3	+--+	120	800	60	2
4	++++	120	800	120	4
5	++++	0	800	120	2
6	0000	60	600	90	3
7	-+++	0	400	120	4
8	---+	120	400	120	2
9	0000	60	600	90	3
10	----	0	400	60	2
11	0000	60	600	90	3
12	-++-	120	400	60	4
13	++--	0	800	60	4
14	+--+	120	800	60	2
15	++++	120	800	120	4
16	++++	0	800	120	2
17	0000	60	600	90	3
18	-+++	0	400	120	4
19	---+	120	400	120	2
20	0000	60	600	90	3
21	----	0	400	60	2
22	0000	60	600	90	3

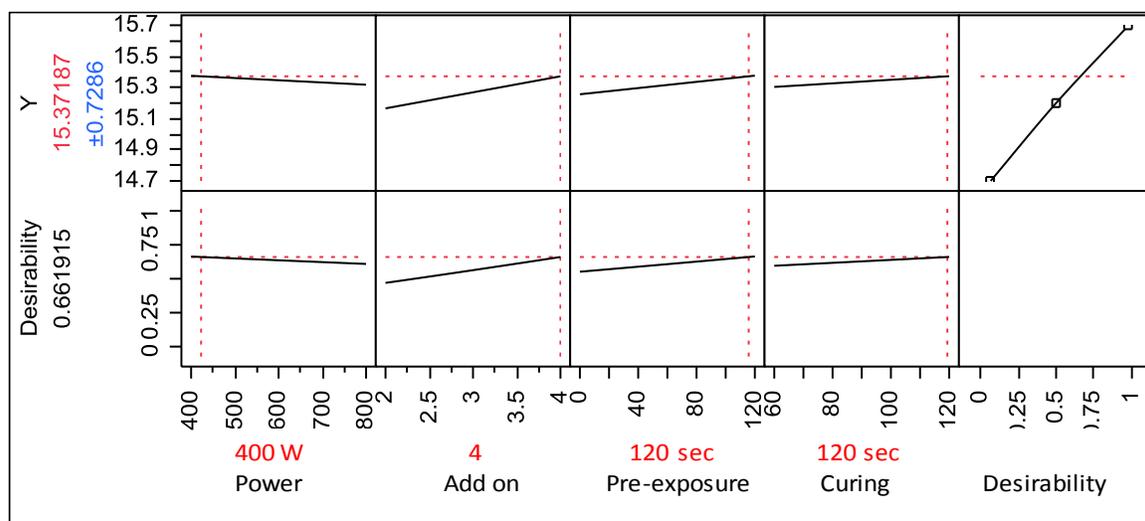


Figure 5-7 Prediction profiler for process parameters.

5.6.3 Customized Procedure: Plasma Assisted Grafting Polymerization Approach

5.6.3.1 1st DOE, screening for DADMAC applied add-on %, Significance of He/O₂ Plasma Treatment on DADMAC grafting and thermal Initiator

Table 5-3 shows the first DOE of parameters in the second approach of treatment and their values designed based on the fractional factorial design. Figure 5-8 illustrates the treatment procedure. The purpose of this experiment was to investigate further on how RF power, pre-exposure time and thermal initiator contribute to the formation of surface radicals and interact with each other and also the effect of thermal initiator and thermal treatment toward achieving higher grafting yield. The treatment procedure was the same as in the previous section excluding that the pre-exposure plasma power was fixed at 400 W, and the time of exposure was considered as the variable parameter. Adding ammonium persulphate as the kal, the plasma post-exposure step was replaced by a thermal curing after the padding process. Samples of fabric were plasma treated and padded with DADAMC and initiator solution at 100% wet pick up. The samples were dried at 70C for 2 minutes and thermally cured at 120 °C for 3 minutes. Soxhlet extraction was run on samples for +8 hours to remove all the un-reacted chemicals. After Soxhlet extractions, samples were rinsed with running cold water, dried at room temperature and reweighed to determine the weight change as the

first evidence of DADMAC grafting onto the surface. Acid dye staining and surface charge density measurement were carried out on all samples.

Table 5-3 2³ fractional factorial design with 3 center points for DADMAC applied add-on % and plasma exposure sequences

Run Order	Pattern	Parameters		
		Plasma Pre-exposure(Sec)	DADMAC add-on %	Thermal Initiator Weight %
1	000	45	3	0.6
2	+++	60	4	1
3	-++	30	4	1
4	+-	60	2	0.2
5	000	45	3	0.6
6	++-	60	4	0.2
7	--+	30	2	1
8	---	30	2	0.2
9	000	45	3	0.6
10	++	60	2	1
11	-+-	30	4	0.2

Discussion: All the samples showed very little or no change in mass after the extraction confirming low grafting yields. The surface charge density measurement and visual assessment of acid dye staining showed that the chemical was grafted onto the surface but not in large amount. Surface charge density data analysis also showed that high DADMAC %add-on has considerable contribution in increasing the charge density (2%>3%>4%) and higher mass change. Samples treated for longer time of plasma pre-exposure show slightly higher value of charge density compared to the samples treated for short plasma exposure time. The experiments were run in 3 different levels of thermal initiator to investigate the efficiency of the initiator in higher and lower concentration and also selecting the proper amount of it in respect to the different DADMAC percentage. The results indicated that the amount of thermal initiator should be optimized as well; higher value of initiator with both higher and lower DADAMC %add-on leaves burning defects on the polypropylene samples after the heating treatment signifying the very exothermic nature of the polymerization reaction between the DADMAC and the thermal initiator. Lower concentrations of initiator (0.2%) with either higher or lower DADMAC %add-on showed lower charge density values. Therefore, the mean value of the initiator at the center point was

selected as the optimum amount for the process. Attaining low grafting yield in this experimental, the same hypothesis as in section 5.6.2.1 was developed in this design-that adding a linker will improve the reaction efficiency and resulting in higher polymerization rate of the DAMDAC on the substrate.

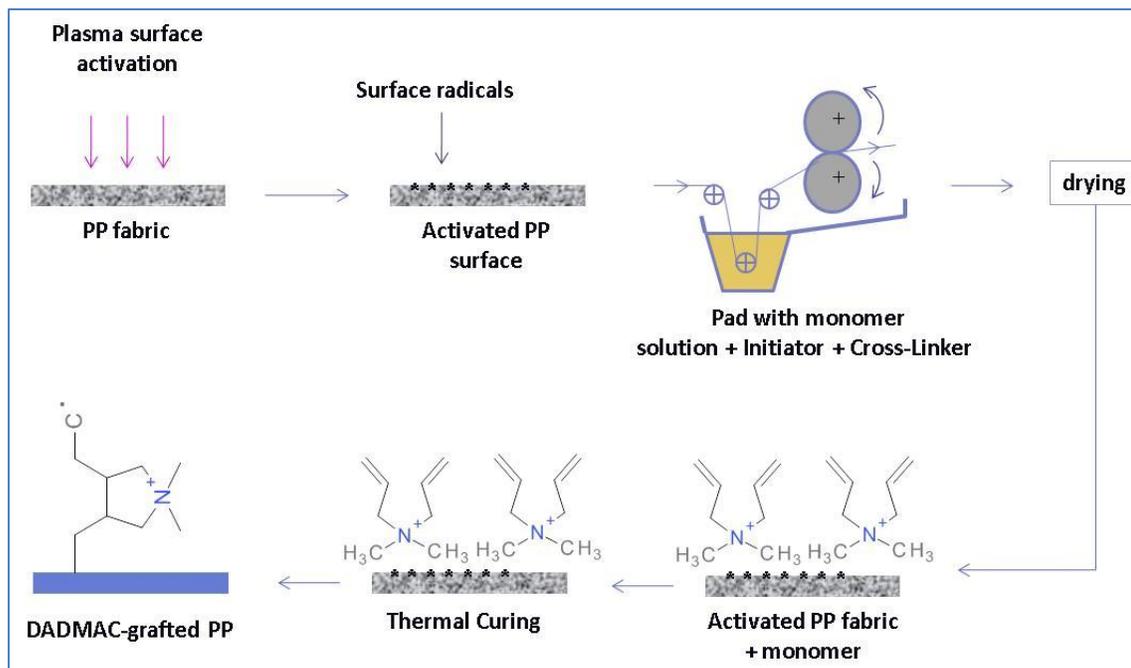


Figure 5-8 Plasma induced graft polymerization steps illustration

5.6.3.2 2nd DOE, Screening for DADMAMC applied add-on %, Significance of He/O₂ Plasma Treatment on DADMAMC grafting, thermal treatment and cross-linker

Table 5-4 shows the second DOE of parameters and their values designed based on the fractional factorial design. The purpose of this experiment was to investigate how adding a linker to the reaction will produce higher grafting yield and more durable finishing in the combined process of plasma and thermal treatments. The experiments were run in 3 different levels of DADMAMC % add-on and plasma pre-exposure time. The plasma power was fixed at 400 W. The amount of initiator was set at 0.5% of the DADMAMC weight and the ratio of cross-linker is constant and is selected (10: 1mol). Samples of fabric were plasma treated and padded with the solution containing a mixture of of DADMAMC, initiator, and s the cross-

linker at 100% wet pick up. The samples were dried at 70°C for 2 minutes and thermally cured at 120 °C for 3 minutes. After extraction, samples were rinsed with running water, dried at room temperature, then reweighed to determine the weight change. Acid dye staining and surface charge density calculations carried out on all samples.

Table 5-4 2³ fractional factorial design with 3 center points for DADMAC applied add-on % and plasma exposure sequences

Run Order	Pattern	Parameters	
		Plasma Pre-exposure(Sec)	DADMAC add-on %
1	++-	120	2
2	-+-	120	2
3	--+	0	4
4	+++	0	4
5	000	120	4
6	000	60	3
7	+--	0	2
8	000	60	3
9	-++	120	4
10	---	0	2
11	000	60	3
12	++-	120	2
13	-+-	120	2
14	--+	0	4
15	+++	0	4
16	000	120	4
17	000	60	3
18	+--	0	2
19	000	60	3
20	-++	120	4
21	---	0	2
22	000	60	3

Discussion: Significant weight change was observed on samples measured before the treatment and after the soxhlet extraction which confirms the high grafting yield on the fabrics. Surface charge density was calculated as the response and the data were analyzed using statistical software JMP 9. It was found that none of the factors contributed significantly towards the final response, and the mean response over the chosen experimental space did not vary significantly. Samples treated with low or high DADMAC % add-on show very close values of charge density, likewise, the same was observed for the samples treated

with high plasma exposure time or without plasma exposure. However, it was established that the measured response for all samples was better than the required threshold of 10^{15} charges/cm². A model was fitted to the data with the two main factors, dropping the factor interaction terms from the model and predicted the best combination of factors where the response was maximized as shown in the prediction profiler in Figure 5-9. While high % add-on and higher exposure times were expected to give more grafting on the surface, none of the factors were deemed statistically significant in the chosen experimental space. Therefore two combinations of factors were chosen to create new samples: 1. the combination maximizing the response (low power, high % add-on, high plasma exposure time) within the experimental space, and 2. the combination that was the cheapest in term of resource usage (low add-on, and low plasma exposure time) within the experimental space. The two optimized combinations were validated by running 3 replicates and the new samples were created for determining the antimicrobial activity.

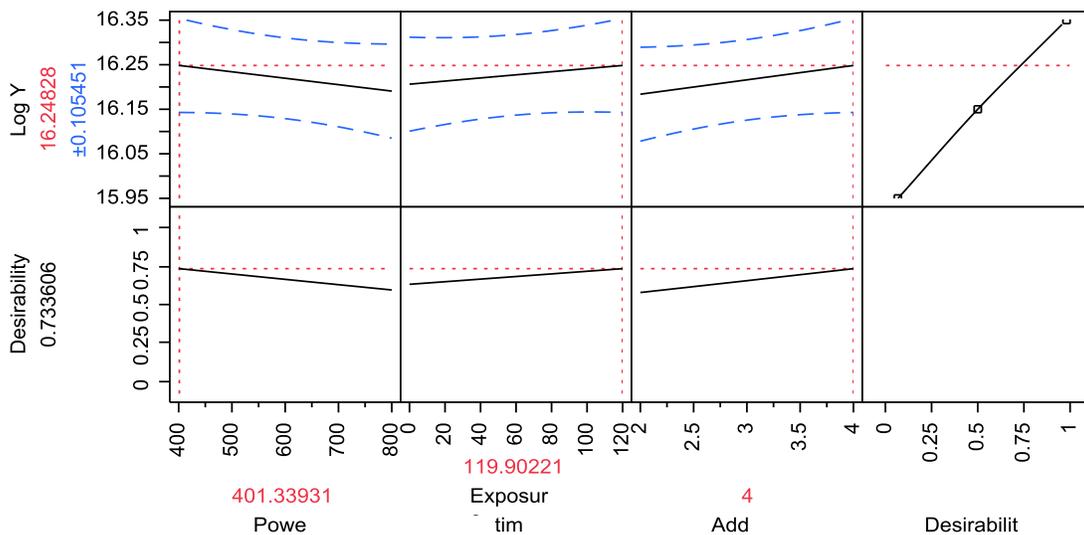


Figure 5-9 Prediction profiler for process parameters

5.6.4 Locating the experimental space for DADMAC % add-on

The purpose of this experiment was to investigate and correlate the effect of DADMAC applied add-on to the values of surface charge densities obtained on the polypropylene surface. A broad range of DADMAC percentage was selected and samples

treatment was carried out using both plasma-induced graft polymerization (PIGP) and plasma-assisted graft polymerization (PAGP) procedures at fixed plasma power (400 W), plasma pre-exposure time (120 sec.) and different DADMAC % add-on. The treated samples were all stained with acid dye, and the surface charge densities were calculated. Table 5-5 shows the experimental conditions and values of calculated surface charge density.

Table 5-5 Surface charge density values for different DADMAC % add-on

Run	DADMAC %-add-on	Surface Charge Density Treatment Method	
		PIGP	PAGP
1	0.5	15.91447	15.3298
2	1.0	15.8892	16.26359
3	1.5	14.7568	16.92558
4	2	15.70199	16.20706
5	3	15.86003	16.27441
6	4	15.28904	16.29086
7	8	N/A	16.23970
8	12	N/A	16.2328
9	20	N/A	16.2674

1st Discussion: Surface charge density calculations results showed that variation of DADMAC applied add-on in broad range of concentrations does not highly contribute to surface charge density values, i.e, samples treated at very low DADMAC percentages showed surface charge density values insignificantly smaller than the samples treated with higher DADMAC add-on. Visual assessment of acid dye staining demonstrated the add-on change better than the charge density values in which the pink color on the polypropylene fabrics treated at high add-on of DADMAC is slightly stronger than the fabrics treated at low add-on within each major procedure. The researcher believes that the acid staining method and the surface charge density calculations is not an accurate representation of the change in grafting yield on the fabrics. The reason behind this hypothesis was that the acid dye molecules were immediately absorbed on the most outer layers of the grafted chemical and saturated the surface of the substrate. The dye molecules were not capable to react with all

the quaternary sites of the DADMAC exist on the fabric and the values of charge densities calculated here were very rough estimates of the generated positive (quat) sites after treating polypropylene with DADMAC. The only characterization method that can help to fully understand the effect of different parameters in each procedure was the actual antimicrobial test method.

2nd Discussion: Both plasma induced graft polymerization and plasma assisted graft polymerization recognized as feasible routes for generating antimicrobial properties on polypropylene surface through grafting DADMAC. However, the efficiency of plasma assisted procedure combined with thermal treatment was better than the plasma induced process. Higher grafting yield (according to mass change measurement), stronger acid dye staining following with higher surface charge density values and higher antimicrobial activity were achieved on samples treated in the second procedure compared with the samples treated at the same conditions of plasma and DADMAC %add-on in the first procedure.

5.7 Results and Discussion

5.7.1 Reaction Chemistry

In conventional chain polymerization, an initiator (I) produces primary radicals that attack monomers and produce new and different free radicals. These free radicals attack and covalently bond to more monomers in a reiterated process, that leads for each activated monomer to grow fast and generating a long polymer chain. In plasma process, the generation of free radicals or peroxides on the surface of polypropylene substrate occurs via hemolytic scission of carbon-hydrogen and carbon-carbon bonds. Scission occurs when energetic electrons, atoms or molecules impact the surface of the substrate transferring sufficient energy to eject an atom or proton or split a carbon-carbon bond. Plasma-grafting between substrate and chemical has most often focused on a polymerizable chemical, generally with vinyl functionality. Vinyl group chemistry involves reaction between the monomer and a free radical produced on the backbone of the polymeric substrate. When an organic structure that is able to make a polymer is introduced into the surface and then exposed to the plasma, the polymer product is stratified onto the substrate surface. The monomer activation takes place because of the collision with high energy free radicals and

maybe electrons in the plasma volume. The mechanism that leads to polymerization are still the subject of many studies, but for some of them it was possible to identify main “reactive channels”, although quantification of reaction constants is still an objective [21]. Sometimes monomer fragmentation is also possible in case of collision with very high energetic free electrons which leads to formation of highly reactive radicals and ionic species. Yasuda used an external parameters, the so-called Yasuda factor which is defined as W/FM , where W is the power, F flow rate and M the molecular weight, a smaller Yasuda factor corresponds to less fragmentation. The power density of the plasma and the time of monomer residence in the plasma are the most influential parameters for the composition of the polymer layer with the surface. The monomer structure is preserved in low power but at high power the chemical composition on the surface can be different.

The activation of DADMAC takes place because of the collision with free ions and radicals in the plasma volume (in the post-exposure step) and also the species on the fabric substrate surviving from the pre-exposure step. Figure 5-10 briefly illustrates the attachment of DADMAC to the polypropylene. Published research conducted on polypropylene indicates that a free radical is most likely located on any carbon bound to two or more carbons [22]. DADMAC can be polymerized to poly-DADMAC by opening of the C=C double bond, attachment of a DADMAC monomer to the radical $R(\bullet)$:

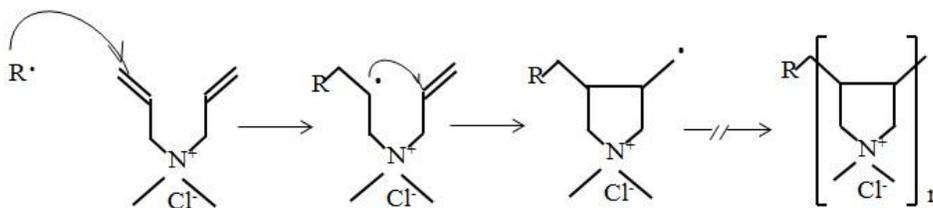


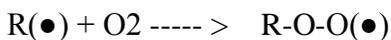
Figure 5-10 Schematic of DADMAC free radical polymerization

Plasma initiation of the chain polymerization is due to the formation of:

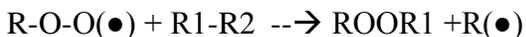
- Plasma free radicals
- Positive ion radicals
- Negative ion radicals

All these species are capable of initiating DADMAC polymerization and are formed from the absorbed monomers by electrons/ions.

Pre-exposure of the polypropylene surface to an O₂ containing plasma leads to the insertion of specific functional groups such as oxydrilic, carboxylic and peroxide groups, Friedman [23] explained the formation of the organic peroxide compounds occurs via a chain process, which starts with the insertion of molecular oxygen and the formation of initiator:



Further propagation of the plasma-initiated chain leads to the production of the organic radicals:



At this time, the polymer substrate activated in plasma is able to initiate the graft polymerization of the solution phase monomer. Oxygen free radicals are not stable and transform into carbonyls, hydroxyls, carboxyls, or carboxylic acids.

The role of adding pentaerythritol tetraacrylate as a cross-linker was discussed in section 5.6.2.1. Figure 5-11 illustrates the reaction of the cross-linker with monomer which subsequently continues reacting with the substrate and the other monomers.

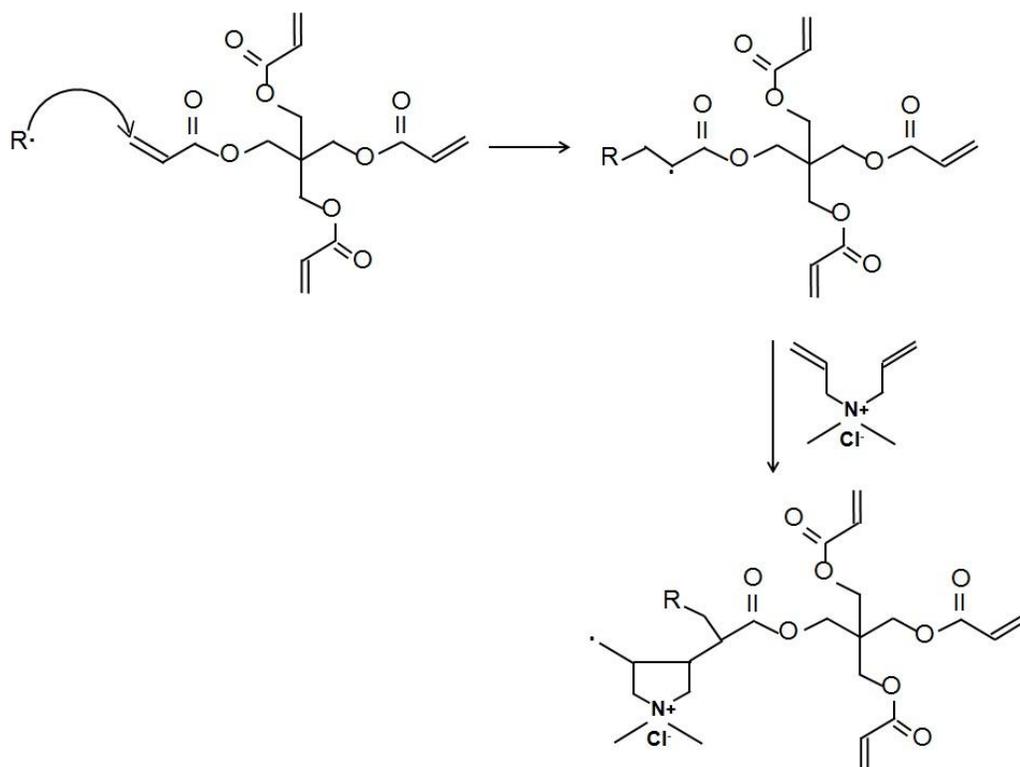


Figure 5-11 Crosslinker-monomer reaction scheme

5.7.2 FTIR

Grafting of DADAMC onto the polypropylene surface was verified by Fourier Transform Infrared Spectroscopy (FT-IR). Figure 5-12 shows the FTIR spectra for both control and DADMAC treated samples.

Firstly the presence of DADMAC on the polypropylene is appear upon the clear distinction between the treated sample and the substrate spectra observed from 1000-1800 cm^{-1} encompassing carbonyl, carboxylic, hydroxyl, C-N stretching and quaternary amine groups all characteristics of the DADMAC compound and the cross linker . The very strong C=O stretching peak between 1800 to 1625 cm^{-1} (peaks at 1635.3 and 1726.8 cm^{-1}) is attributed to the functionalities in the cross-linker. Strong C-O stretch occurs at 1260-1000 cm^{-1} which is apparent in the spectra at 1266.2 cm^{-1} . A variety of C-H₂ and CH₃ (saturated C-H) stretching and bending bands with sharp intensity appear between 2800 and 3000 which are assigned to the polypropylene as the substrate and decrease in magnitude as the percentage of DADMAC goes higher on the surface for 4% add-on sample.

The quaternary ammonium salt functionality ($R_4-N^+Cl^-$), has no N-H stretching vibrations however its presence is characterized by the appearance of peak at 1113-1161 cm^{-1} designated to the quaternary ammonium functionality. C-N stretching is also observed 1050-1150 cm^{-1} and specifically the peak at 1113.6 cm^{-1} .

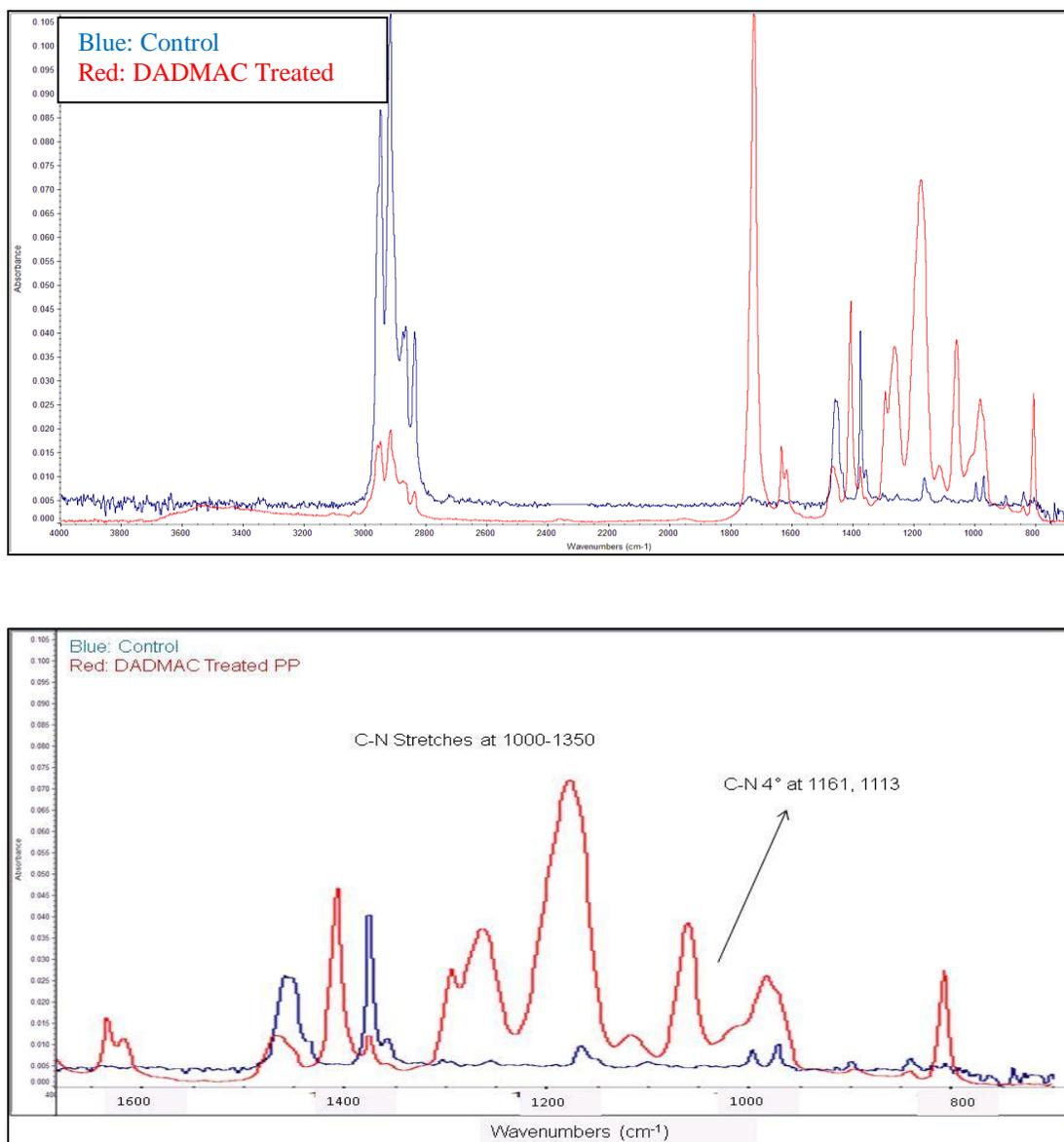


Figure 5-12 FTIR spectra of the control and DADMAC treated sample

5.7.3 SEM

A scanning electron microscope was used to examine the surface of the grafted polypropylene fabric. The control polypropylene nonwoven was thermally bonded and consists of fibrous regions intercepted with regions where fibers melted together under pressure. Both areas were examined at several magnifications. Figure 5-13 shows the images of control and DADMAC grafted polypropylene. Control polypropylene has a very smooth surface. After treatment significant difference was observed between the control and treated sample surfaces. The presence of grafted DADMAC was clearly visible as stretched, ubiquitous layers and clumps of chemical throughout the fibers surface. Images also showed that the polymerized layer of DADMAC had a relatively uniform distribution on the fibers which resulted in the uniform finishing on the fabric in macro dimension and provided uniform properties all over the sample.

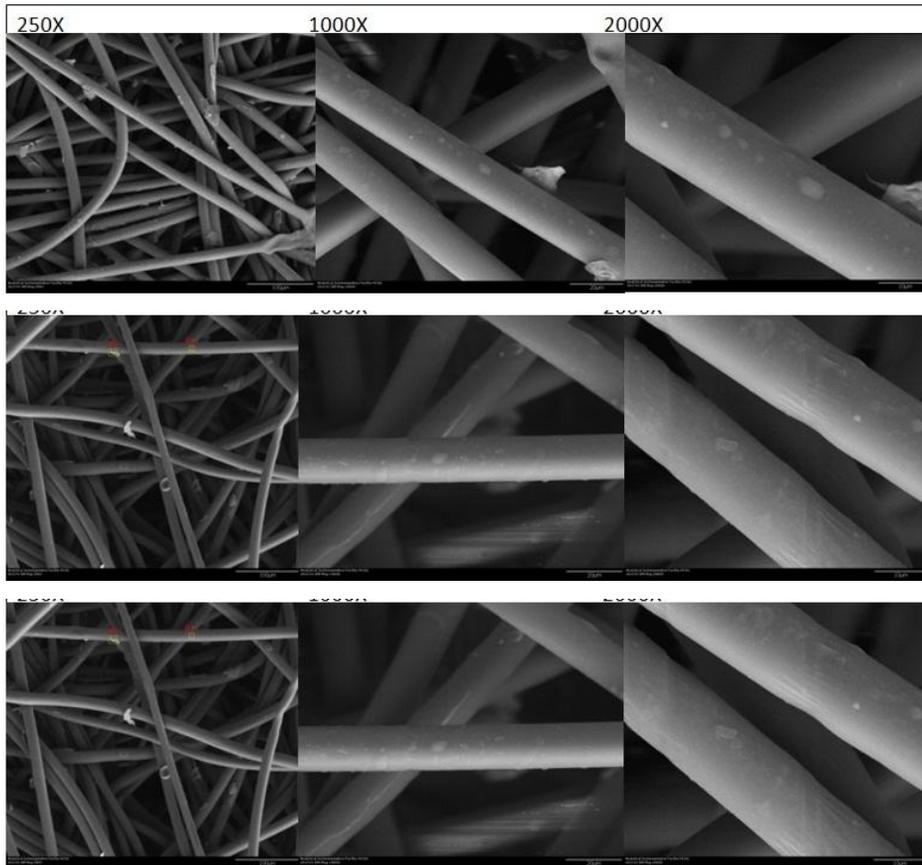


Figure 5-13 SEM micrograph of the control (first column) and the treated samples in two magnifications (2nd and 3rd column).

5.7.4 SEM-EDX (SEM- Energy Disperse X-ray Spectroscopy)

Table 5-6 shows the weight percentage of the elements identified on the control and treated samples and Figure 5-14 illustrates the EDX spectra of the control polypropylene and DADMAC treated samples before and after extraction. The control sample contained only carbon and a small quantity of oxygen. Following DADMAC treatment, the ratio of carbon decreased, and chlorine was observed on the surface of the polypropylene which confirmed the presence of DADMAC. The amount of chlorine on the un-extracted sample was much greater than the extracted sample which was expected (40.83 vs 14.7). No nitrogen was found on any of the treated samples before or after soxhlet extraction mainly because the amount of nitrogen was lower than the sensitivity range of SEM-EDX.

Table 5-6 Surface elemental composition on the control and DADMAC treated samples

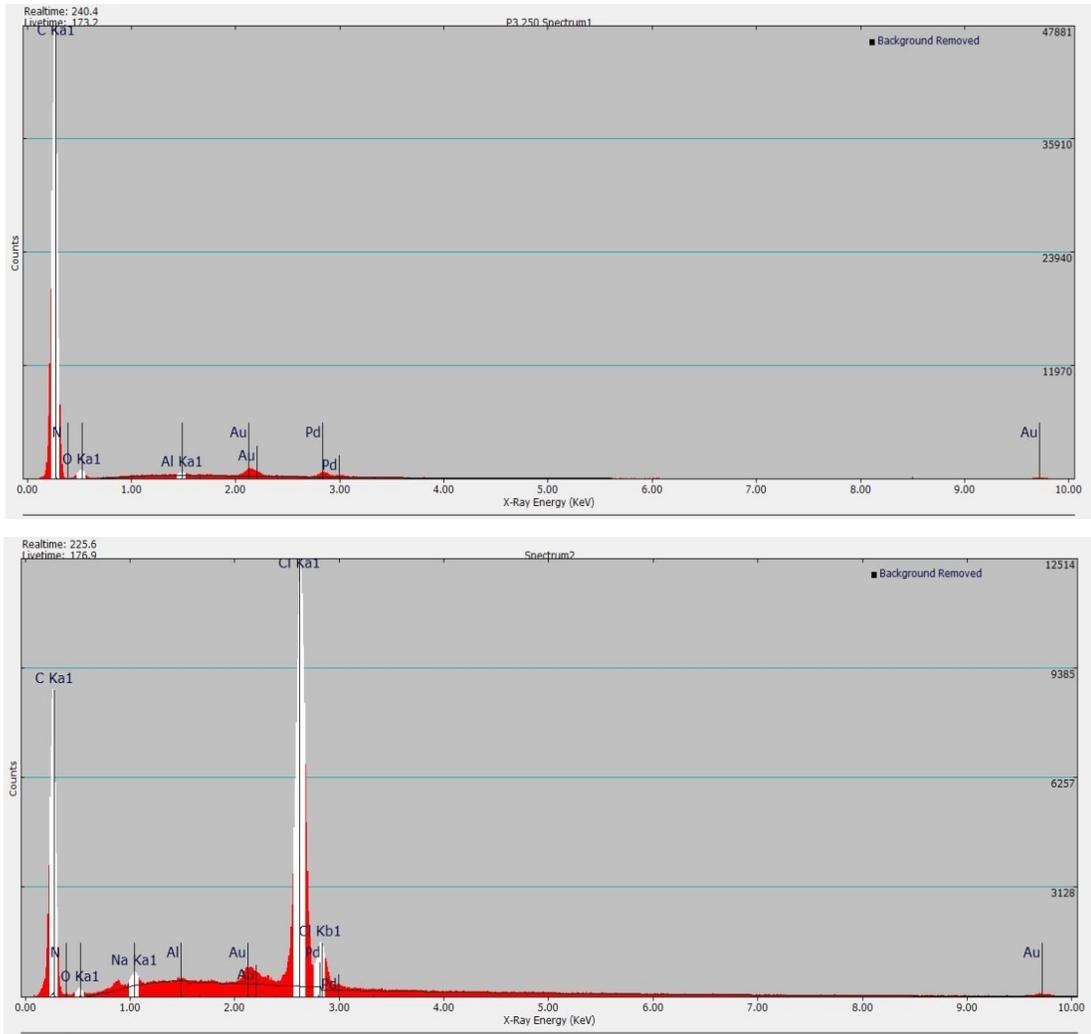
Treatment	C	O	N	Cl
Control	97.3	2.57	----	----
Treated PP (before extraction)	54.99	2.3	----	40.83
Treated PP (after extraction)	78.48	4.27	----	14.70

5.7.5 TOF-SIMS

Figure 5-15 illustrates the chemical mapping of a control PP fabric and DADMAC treated PP. The corresponding spectra are presented in Figure 5-16. The chemical images were acquired over a 200×200 μm and 120×120 μm area. The elements detected on the surface were distinguished by different colors and were shown in the color scale next to the image. The control PP fabric surface was fairly clean and was characterized by the PP (C₃H₆) ion fragment shown in Figure 5-15 along with some contaminants. The control surface was free of chlorine and nitrogen, as shown in the very dark image of Figure 5-15 (a).

Following DADMAC treatment, the polypropylene surface was covered by a thin layer of crosslinked DADMAC, which were characterized by Cl⁻, CN⁻, O⁻, C₂HO⁻, C₃H₃O₂⁻, C₃H₈N⁺, C₅H₁₀N⁺, C₈H₁₆N⁺ fragments, which were distinguished by bright green and red. However, the intensity of the nitrogen and chlorine fragments decreased significantly

following soxhlet extraction. It was hypothesized that most of Cl^- ions were ion exchanged by another counter ion from DI H_2O in the process of soxhlet extraction.



. **Figure 5-14** SEM-EDX spectra on the control and DADMAC treated samples

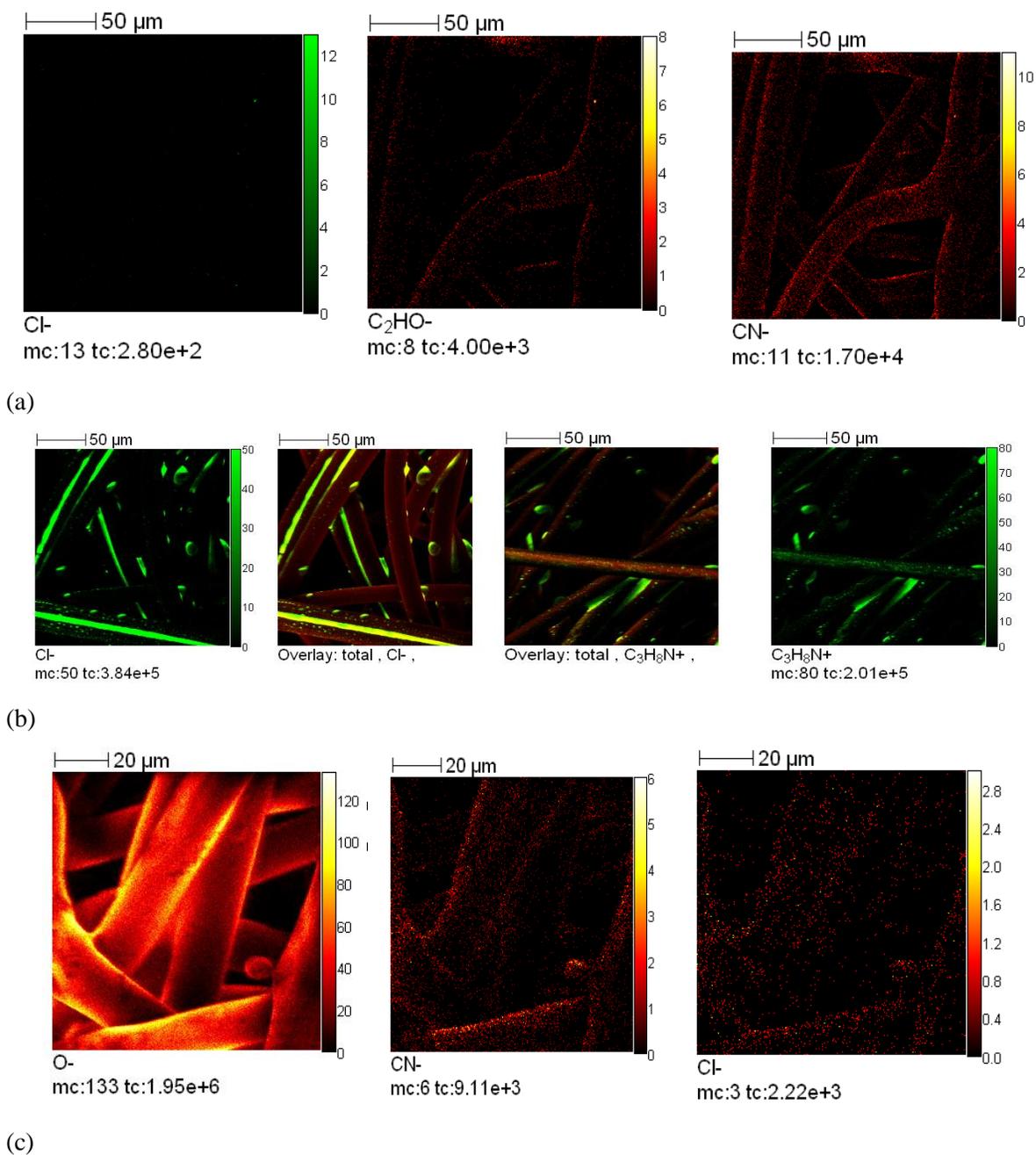


Figure 5-15 Chemical TOF-SIMS mapping of (a) control polypropylene fabric and (b) DADMAC treated sample before extraction and (c) DADMAC treated sample after extraction. Images are attributed to the indicate element or compound(s).

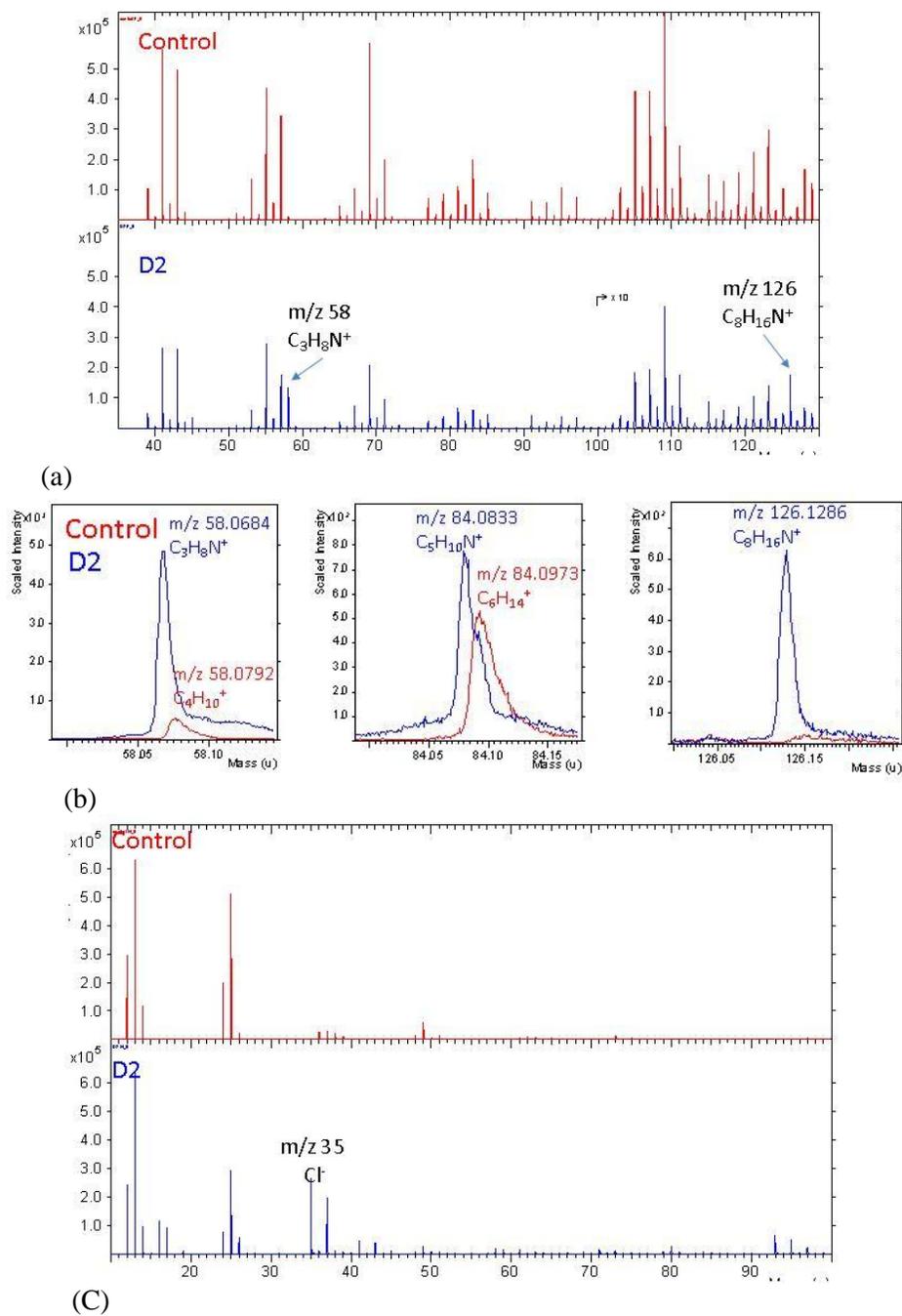


Figure 5-16 (a) Partitioned spectra of reference PP fabric characterized by the fragment ion of PP (C_3H_5) and positive ion fragments, (b) Depth profile of DADMAC treated sample characterized by positive ion fragments, (c) Partitioned spectra of reference PP fabric and DADMAC treated sample characterized by negative ion fragment

5.7.6 XPS

XPS was performed on both control and plasma grafted samples to determine the exact surface chemical composition. Figure 5-17 shows the XPS spectra for control PP, and DADMAC treated PP after extraction. Table 5-7 illustrates the relative intensities of the elements observed on three samples. The control sample contained only carbon and a small quantity of oxygen. Treating PP with DADMAC will increase the oxygen content by about 75% which is mainly due to the cross-linker presence. Surprisingly enough no level of nitrogen or chlorine functionalities were detected within the XPS depth resolution (3-5 nm) on any of the samples either extracted or non-extracted. However, the TOF-SIMS technique with higher depth resolution (0.3-0.5 nm) confirmed the DADMAC grafting onto the surface.

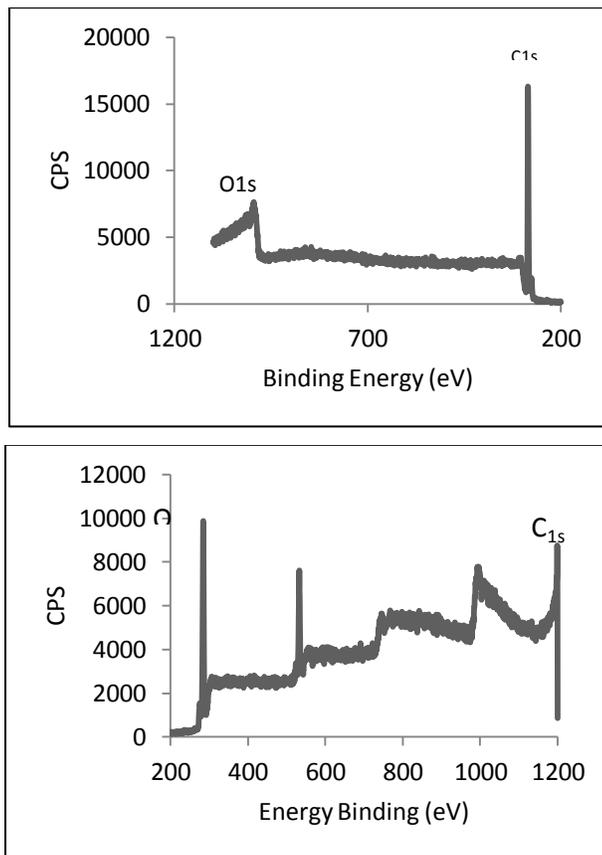


Figure 5-17 XPS spectra of the (a) control polypropylene and (b) DADMAC treated polypropylene.

Table 5-7 Relative intensities of chemical composition of Polypropylene control fabric and DADMAC treated.

Treatment	C	O	N	Cl
Control	98.45	1.55	----	----
Treated PP (after extraction)	84.95	15.05	----	----

5.7.8 Focused Ion BIM (FIB)

FIB images of the control and DADMAC treated sample are shown in Figure 5-18. Both secondary electron beams and topographical contrast resulting from differential sputtering of the cross section surface can be employed to distinguish between the two layers of polymers (DADMAC and PP). When the sufficient contrast is not achievable to clearly distinguish the two components (substrate and the treatment), it is hard to characterize the treatment layer on the top of the substrate. Chemicals with very similar elements like two organic compounds including mostly carbon and hydrogen do not provide much contrast since their secondary electron imaging provides similar topographical contrast, which is difficult to differentiate them.

The thin bright layer observed in images with 95 and 55 nm thickness is attributed to the DADMAC layer on top of polypropylene core surface. Further investigation with TEM instrument or different sputtering levels is also helpful to have more clear images.

5.7.9 Acid Dye Testing-Visual Assessment

The DADMAC chemical contains nitrogen groups and quaternary amines that should bind to the acid dye, unlike the polypropylene substrate. As expected, polypropylene control sample did not exhibit any staining with the acid dye as shown in Figure 5-19. However, samples treated with DADMAC using both approaches were stained at different levels depending on the treatment conditions. Generally, samples treated using the plasma-assisted approach were stained stronger than the samples treated using the plasma-induced approach using the same concentration of DADMAC because the grafting yield of the the latter approach was greater. Samples treated at higher concentrations of DADMAC and cross-linker showed some nonuniformity in dyeing which was mostly attributed to the non-

homogenous solution of DADAMC and cross-linker since the pentaerithrotetraacrylate was not soluble in water. Hence, better staining/dyeing uniformity could have been achieved if the crosslinker was water soluble.

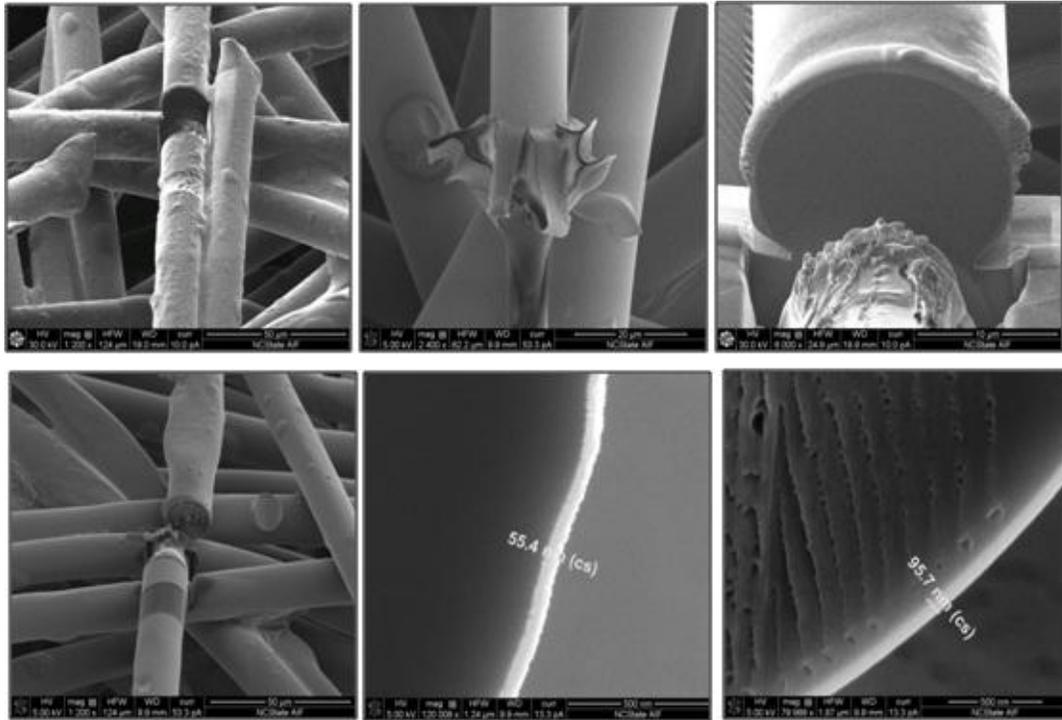


Figure 5-18 Micrograph of (a) cross-section of control and (b) DADMAC treated fibers.



Figure 5-19 Acid dye staining on the control and DADMAC treated samples.

5.7.10 AATCC 100 Antimicrobial Testing

The antimicrobial used in this research was diallyl dimethylammonium chloride (DADMAC), a monomer bearing quaternary ammonium group and is able to polymerize and forms an antimicrobial polymer. DADMAC has been widely used in textile processing and textile production as antistatic agent, color fastness improver, and antimicrobial agent [15]. Plasma-aided graft copolymerization of DADMAC on polyethylene film to render it antimicrobial was reported [15].

The presence of the grafted chemical on the surface was confirmed by some surface characterization methods discussed so far. However, the performance of the treatment was established by evaluating the treated samples by AATCC TM-100.

5.7.10.1 Antimicrobial Activity on Samples Treated via Plasma-induced Graft Polymerization

Table 5-8 shows the summarized results of AATCC 100 test for *Klebsiella pneumonia* (gram negative bacterium), which were carried out on 3 samples treated at three different concentrations of DADMAC using the plasma-induced graft polymerization approach. Samples treated with the lowest concentration of DADMAC (0.5%) showed the highest antimicrobial activity (4 log reduction) while sample treated at 2% add-on showed no antimicrobial activity. This confirms that effective graft polymerization happens only if the thickness of the monomer layer on the substrate is thin enough for the plasma to penetrate through and complete the grafting and polymerization reactions. Elevating the DADMAC % add-on using this approach will increase the thickness of the monomer on the substrate which limits the plasma-induced polymerization to the very top layers leading only to homopolymerization and no grafting. Hence, all the un-reacted and non-grafted monomer and homopolymer were washed away during the extraction step leaving only the grafted polyDADMAC on PP. Figure 5-20 shows the illustration of the colony formation reduction on the control and treated samples. The test was not performed for *S. aureus* bacterium. However, the researcher expects higher antimicrobial activity for gram positive micro-organism compared to *K. pneumonia* because of the results obtained in section 5.7.10.2.

Table 5-8 Average CFU values per sample and %reduction for control and treated samples

Microorganism	Test Substrate	Contact time	Average CFU/Swatch	% Reduction vs Control
K. Pneumoniae ATCC 4352	PP-DADMAC 0.5% add-on	Time Zero	2.36E+05	>99.99 %
		24 Hrs	< 5	
	PP-DADMAC 1.0% add-on	Time Zero	2.36E+05	90.99 %
		24 Hrs	1.53E+06	
	PP-DADMAC 2.0% add-on	Time Zero	2.36E+05	None
		24 Hrs	5.37E+ 07	
Control		Time Zero	1.95E+05	N/A
		24 Hrs	3.86+07	

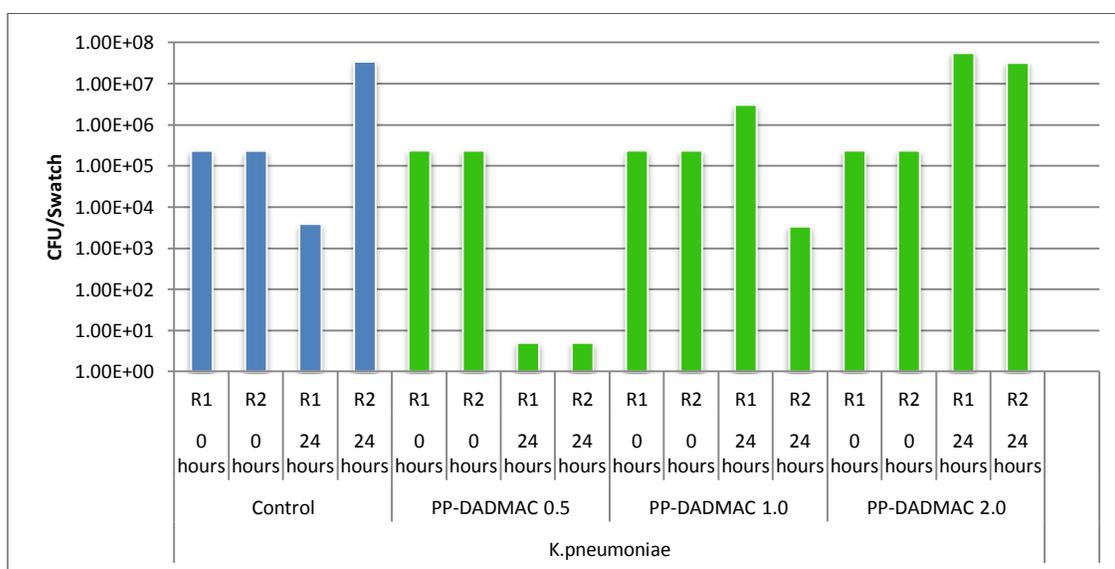


Figure 5-20 Antimicrobial activity results on the control and treated samples against *K. pneumoniae*.

Figure 5-21 shows the antimicrobial activity on a sample treated with of 4% solution of DADMAC with no cross-linker (the treatment procedure discussed in section 5.6.2.1). The grafting procedure was carried out by plasma exposure at 400 W for 120 seconds. The results showed 4 log reductions in bacterial colony growth after 24 hours against *K. pneumoniae*, without any cross-linker, which was significant.

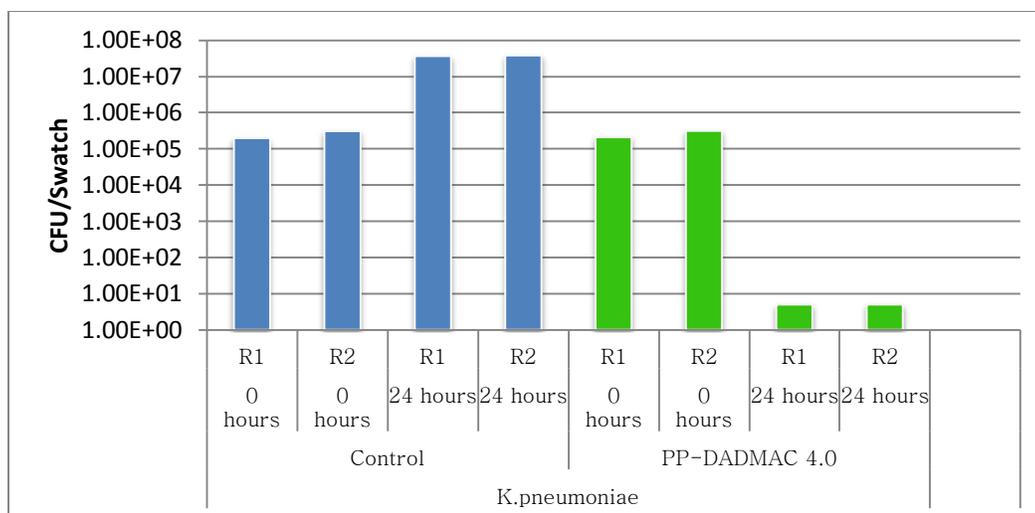


Figure 5-21 Antimicrobial activity results on the control and treated sample against *K. pneumoniae*.

5.7.10.3 Antimicrobial activity on samples treated via plasma assisted graft polymerization

The antimicrobial results are summarized in table 5-9. Polypropylene samples treated with DADAMAC in two concentrations (2% and 4%) both show very high antimicrobial activity against two types of bacteria: a gram positive bacteria, *Staphylococcus aureus*, which is the bacteria which causes staph infections, and a gram negative bacteria, *Klebsiella pneumoniae*, the bacteria responsible for pneumonia. In terms of % reduction, both samples reached up to 99.9999% for the *S. aureus* bacterium and 99.999 % for *K. pneumoniae* bacterium. Defining the antimicrobial activity in term of the reduction of colony forming units (CFU) shows 6-log reduction.

Higher DADMAC concentrations do not contribute to higher antimicrobial activity since sample with lower DADMAC add-on (2%) showed higher antibacterial activity compared to the 4% add-on sample. Bound antimicrobial chemistry functions through ionic interactions between a microbe's anionic cell wall and the quaternary nitrogen of the DADMAC compound. Disruption of the charge balance ruptures the cell wall, which eventually kills the bacteria. Thus, the orientation of the DADAMC molecule and its concentration on the surface of the fabric contribute significantly to the antimicrobial properties of the fabric and must be controlled. Both samples were more resistant against the

gram positive bacterium, *S. aureus*, rather than the gram negative bacterium. The effectiveness of the DADAMC treatment is clearly illustrated in Figures 5-22 and 5-23 for the two microorganisms.

Table 5-9 CFU values and %reduction for control and treated samples

Microorganism	Test Substrate	Contact time	CFU/Swatch	% Reduction vs Control
K. Pneumonioc ATCC 4352	PP-DADMAC 4% add-on	Time Zero	6.02E+04	99.99987%
		24 Hrs	1.25E+06	
	PP-DADMAC 2% add-on	Time Zero	7.00E+04	99.99996%
		24 Hrs	1.50E+01	
	Control	Time Zero	1.95E+05	N/A
		24 Hrs	3.86+07	
S. Aureus ATCC 6538	PP-DADMAC 4% add-on	Time Zero	1.95E+05	>99.999986%
		24 Hrs	<5	
	PP-DADMAC 2% add-on	Time Zero	1.95E+05	>99.99991%
		24 Hrs	<5	
	Control	Time Zero	1.95E+05	N/A
		24 Hrs	3.86+07	

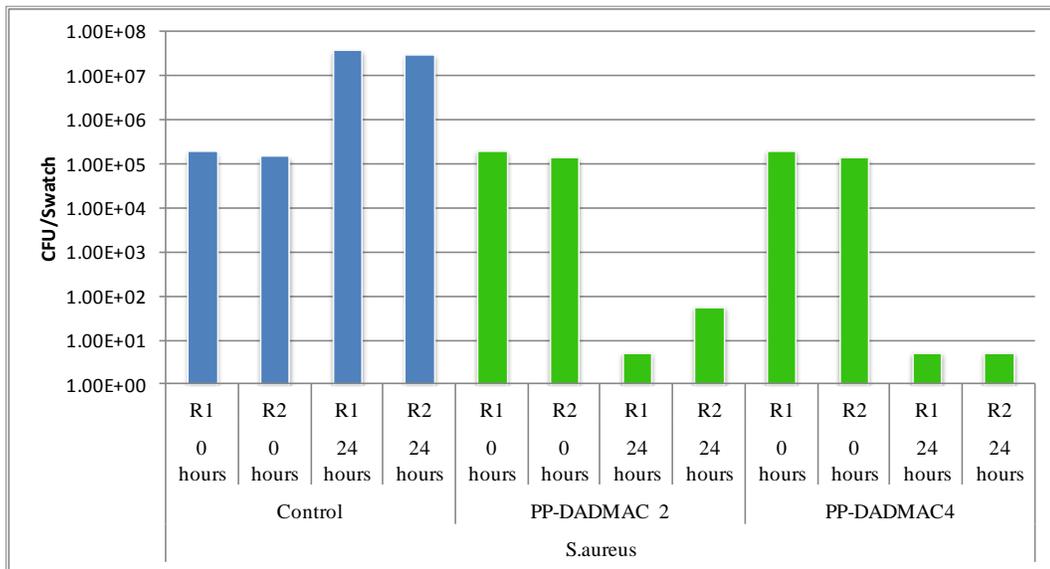


Figure 5-22 Antimicrobial activity results on the control and treated samples against *S. aureus*.

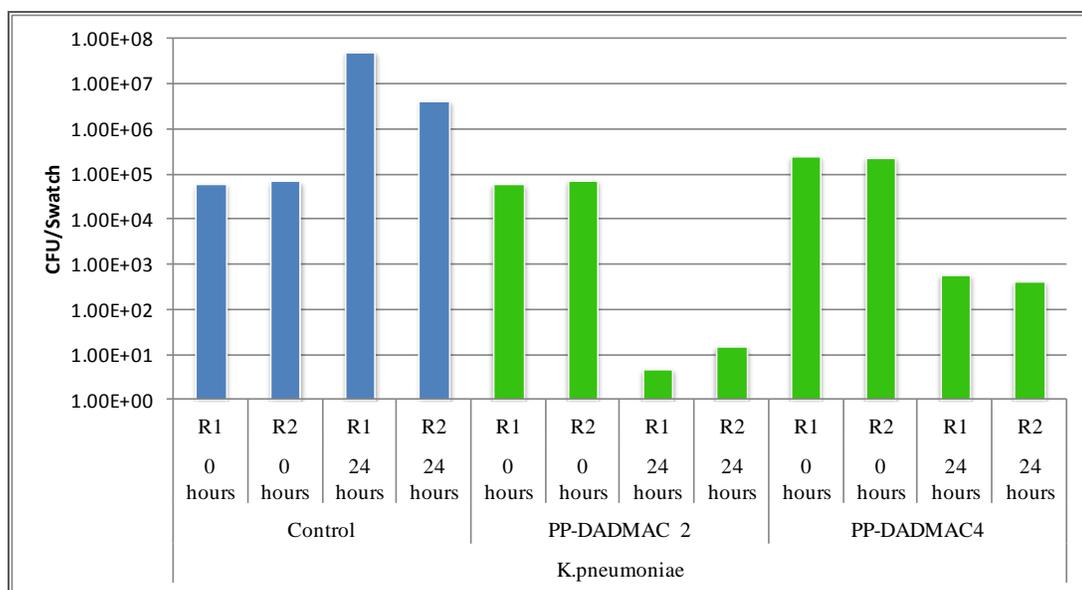


Figure 5-23 Antimicrobial activity results on the control and treated samples against *K. pneumoniae*

5.8 Conclusions

This work was focused on developing a process of successfully graft polymerizing DADMAC on polypropylene nonwoven fabric to achieve high antimicrobial activity. Plasma pre-exposure was established to have a significant effect to polymerize and graft the polymer onto polypropylene by generating free-radicals on the surface of the substrate. Thermal curing in presence of a thermal initiator and a cross-linker was found to be successful for graft polymerizing DADMAC on polypropylene. An assessment of charge density on the fabric surface through acid dye uptake confirmed the presence of quaternary ammonium cation on the surface. The presence of polyDADMAC on the nonwoven fabric surface was further confirmed by FT-IR and TOF-SIMS. Furthermore, the surface was analyzed using SEM which showed the presence of polyDADMAC on the surface. Results of AATCC Test Method 100 confirmed high antimicrobial potential of polyDADMAC grafted on polypropylene nonwoven fabric with 6 log reduction in the bacterial colonies for *K. pneumoniae* and *S. aureus* for both the samples prepared using the cheapest and best combinations of factors confirming that the response was constant over the chosen experimental space. Both plasma induced-graft polymerization and plasma-assisted graft

polymerization were found to be successful approaches for generating antimicrobial properties on polypropylene surface through grafting DADMAC. However, the efficiency of the plasma-assisted approach combined with thermal treatment was higher than the plasma-induced approach.

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Appendix

Appendix A

Calculation of Monomer Percent Add-on

Parameter (units)	Symbol used
Speed (in terms of exposure time, Seconds)	s
Flow rate of monomer (mL/min)=	f
Sample length (inch)	l
Sample width (inch)	w
Sample weight (g)	wt
Monomer density (g/mL)	ρ

The length of the plasma chamber is 8", so to calculate the speed in inches per minute:

$$\frac{8''}{s \text{ sec}} * \frac{60 \text{ sec}}{\text{min}} = \frac{480}{s} "/\text{min}$$

To calculate how many minutes the sample is exposed to the applicator, invert the formula and multiply by length of the sample:

$$\frac{s \text{ min}}{480 \text{ ''}} * l'' = \frac{ls}{480} \text{ min}$$

To determine the volume of monomer applied in milliliters, multiply by the flow rate and the percentage width (width of stage is 12") that the sample takes up:

$$\frac{ls}{480} * f \text{ mL/min} * \frac{w''}{12''} = \frac{lsfw}{5760} \text{ mL}$$

To determine the weight of the monomer applied, multiply by the density:

$$\frac{lsfw}{5760} \text{ mL} * \rho \frac{\text{g}}{\text{mL}} = \frac{lsfw\rho}{5760} \text{ g}$$

Percent add on is determined by dividing the percent of monomer by the weight:

$$\% \text{ Add - On} = \frac{lsfw\rho}{5760 * wt} * 100$$

Appendix B

Procedure and Calculation for the quantitative determination of Surface Charge Density by Dyeing with Acid Dye Sirius Red FB3

1. A dilute solution of acid dye Sirius red FB3 was prepared and its absorbance was measured to determine the λ_{\max} at 531nm. A series of dilute solutions of the dye were prepared as standard solutions for generating a calibration curve for dye concentration determination from absorption measurement (Figure X).

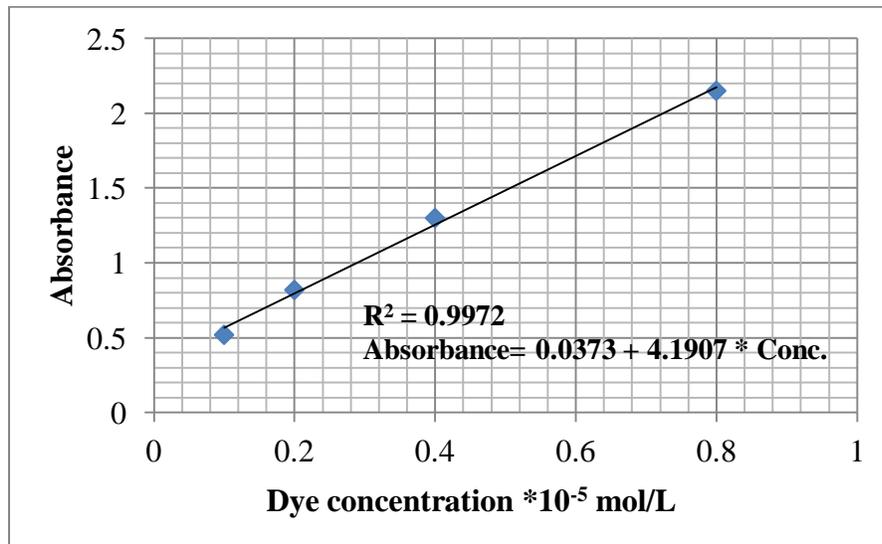


Figure X. Calibration curve for standard dye solutions.

2. 0.102 g of Acid Red 1 (MW = 509.42) was exactly weighed and dissolved in cold distilled water to make 100 ml, 2×10^{-3} M dye solution. For charge density measurements, 5 ml solution was diluted to 500 ml to make a 2×10^{-5} M stock solution.

3. Approximately 0.1 g fabric swatch was immersed in 20 mL dye stock solution (LR= 1:200) and stained in a water shaker bath at 30°C for 24 hours. After staining, the sample was washed with 10 mL distilled water at 30°C for 60 minutes to remove any unbound dye from the fabric surface. The stain effluent and wash effluent were mixed and the volume was made

up to 30 mL with distilled water for standardization. This procedure was carried out for an untreated fabric swatch (control) and DADMAC treated samples.

5. Absorbance measurement for each sample was carried out at $\lambda_{\text{max}} = 531 \text{ nm}$ with Cary 300 UV-Vis Spectrophotometer and the associated software Cary Win UV v.3.00(182) (Varian).

6. Dye concentration left in the effluent was determined using the linear regression model and the information was translated to the amount of dye picked up by the fabric.