ABSTRACT

SARMA, SUDHIR. Ionic-Modified Antistatic Finishes: A Combination of Nanotechnology and Atmospheric Plasma Treatment. (Under the direction of Drs. Xiangwu Zhang and A.M. Seyam)

The accumulation of static charge on textile material, and its subsequent discharge, presents major problems in the processing of textiles. It also becomes a marketing problem because consumers have to endure the unpleasant effects of static discharge like mild shocks, as well as the clinging and unwanted crumpling of fabrics. To combat the problem of static accumulation, antistatic finishes are added to the substrate. These finishes generally act by adding polar groups to the substrate, increasing the hydrophilicity and making it more amenable to dissipating away the excess charge.

This research investigated the effect of silica nanoparticles and ionic monomers on improving the antistatic properties of commercial grade polyester/cotton fabrics. 65%-35% polyester/cotton blended fabrics were treated with combinations of modified silica nanoparticles and ionic monomers like sodium vinylsulfonate and 2-acrylamido-2-methyl-1-propanesulfonic acid. The fabrics were exposed to atmospheric plasma to initiate the polymerization reaction on the fabric surface. The fabrics were then coated using a laboratory scale dip-pad process and were either air dried or oven dried depending on whether it was followed up by additional plasma treatment. The finished fabrics were evaluated using a surface resistance meter. The finished fabrics were also tested for durability to laundering.

The types of experiments that were carried out ascertained the effect of different processing parameters on the performance of the antistatic finish. The experiments

included: (1) application of different concentrations of silica nanoparticles to ascertain the effect of silica concentration on the finish properties; (2) the effect of plasma treatment time on the resulting finish; (3) the effect of plasma types, namely helium and helium-oxygen plasmas, on the resulting antistatic properties; and (4) the effect of plasma treatment procedure on the finish properties.

Results of the conducted experiments showed that the modification of the fabric surface using silica particles and ionic monomers yielded the desired results. The antistatic properties of the finished fabrics did show a significant increase after the application of the chemicals, indicated by lowered resistivity values. In addition, the antistatic properties of the finished fabrics improved when they were exposed to atmospheric plasma as part of the treatment process, as opposed to just treating the fabric with a combination of polymerization initiators and monomers in the presence of thermal energy.

Although the presence of silica particles did have an ameliorating effect on the static dissipating properties, with the best results being noticed at a silica concentration of 0.5 grams per liter (gpl) in the dispersion, the antistatic properties decreased first, and then increased sharply as the concentration of silica particles increased in the dispersion.

The usage of different gases for plasma also played a role in determining the properties of the finish. Of the two plasma types used: helium and helium-oxygen, helium-oxygen plasma yielded better properties when used in conjunction with silica particles and the ionic monomers, as the resistivity values of the helium-oxygen treated polyester-cotton

samples were up to ten times lesser than the values obtained by helium plasma treatment alone.

The rinsed samples showed a significant loss in antistatic properties, with the rinsed samples showing resistivity values that were higher by two orders of magnitude than the treated samples, indicating that the durability of the applied finish needs to be improved. The results obtained would fuel further interest in both the usage of nanosilica and the plasma treatment process to provide inexpensive and environmentally sustainable treatment.

Ionic-Modified Antistatic Finishes: A Combination of Nanotechnology and
Atmospheric Plasma Treatment

by
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A thesis submitted to the Graduate Faculty of
North Carolina State University
In partial fulfillment of the
Requirements for the degree of
Master of Science

Textiles

Raleigh, North Carolina

2009

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BIOGRAPHY

Sudhir Sarma was born in Manama, Bahrain. His family moved to Mumbai, India when he was five years old and has lived there since. He completed his undergraduate education from the University Institute of Chemical Technology, Mumbai and graduated with a B.Tech in the Chemical Technology of Fibres and Textiles in 2007. He was admitted to the College of Textiles at NC State University in the fall of 2007, as a fellow of the prestigious Institute of Textile Technology.

ACKNOWLEDGEMENTS

The writing of this thesis has been a journey that has allowed me to learn and experience tremendous growth as an individual. This would not be complete without the people who helped me at every step.

I would like to firstly thank my advisor and Chair, Dr. Xiangwu Zhang, whose knowledge, efforts, patience and encouraging attitude are beyond comparison. It was a great learning experience to have worked under Dr. Zhang. Deep gratitude is expressed for co-chairs Drs. A. Seyam and Peter Hauser, who have been involved with me in every step of my progress. I also express my appreciation and gratitude for committee members Dr. Henry Boyter and Dr. Ahmed El-Shafei, whose sound technical inputs helped lend depth to my work. Other people, whose technical support I have required in my research, need a mention: Lu Liu, Jeff Krauss and Khushboo Mittal.

The Institute of Textile Technology (ITT) has funded me and even otherwise, helped me all the way. Therefore I would like to acknowledge all the folks at ITT who have supported me all throughout. I have a big word of appreciation for Patrice Hill, whose dynamic presence has helped to knit us all into a cohesive team. I also thank Chris Moses, because his academic support and his brilliant Spector bass guitar have helped me 'play down' the times when they got rough!

My friends here at NC State have been truly responsible for keeping me in good spirits all along. A special "Thank You Very Much" to my friends at 2512: Khushboo Mittal, Priyadarshini Malshe, Dnyanada Satam and Neha Deshpande, who have kept me well

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CHAPTER 1: INTRODUCTION

The objective of this research was to develop an antistatic fabric finishing technology by introducing low-cost silica nanoparticles with ionic monomers onto the fabric surface through atmospheric plasma treatment. Static is a problem with textile materials and is caused due to tribo-electricity, first observed by Thales, a Greek philosopher sometime in 600 B.C. (Joachim, Wiggins, & Arthur, 1965) after rubbing amber with clothing made of hemp. He found a mysterious force on the amber attracting bird feathers to it. The word 'tribos' is Greek for 'rubbing' and the term 'electricity' originated from a Greek word referring to amber. In 'triboelectrification', a transfer of electrons occurs whenever two surfaces come into contact with one another (Henniker, 1962). Thus common substances can be classified under two types based on how the flow of electric current takes place through them: conductors and insulators.

Conducting materials do not allow for the accumulation of electrons and immediately transfer the electrons to the ground. Non-conducting materials however will accumulate charge. Metals like silver and non-metallic substances like ebonite are good examples of conducting and insulating materials, respectively. However, many textile materials fall somewhere in between perfectly conducting and perfectly non-conducting, in that they can transfer some electricity like conductors and also can hold electricity to an extent, like insulators. The rate at which the charge dissipates is contingent on environmental conditions like humidity and intrinsic properties like the molecular structure of the polymer and the impurities present in the polymer. Static discharges are created when the potential difference between the material and its immediate

surrounding reaches the discharge potential of air ($\sim 3 \times 10^6$ Vm^{-1}) (Wilson, 1985), the accumulated charge is released and equalized. Static accumulation can be controlled by the application of surface antistatic finishes that dissipate away the excess charge.

Most conventional antistatic finishes, like many other surface finishes applied to the substrate, are not durable to laundering. Conventional durable antistatic finishes are applied by the formation of a crosslinked polymer network containing hydrophilic groups. However, in these cases, it is often difficult to achieve a balance between the hydrophilicity of the groups and the durability of the finish because the greater the hydrophilic quality of the finish, the less durable it is. The demand for durable antistatic products increases as textile applications become more diverse.

The application of silica nanoparticles and nanotechnology in general, to the science of textile finishing has yielded good results in the past. The use of nanotechnology yields better results because nanoparticles have large surface energies and high surface area-to-volume ratios, which lead to better affinity of the finishing with the substrate being processed, as also increased durability.

In this research, we will use nanotechnology, i.e., the use of modified silica nanoparticles, in conjunction with ionic monomers, to create a new antistatic fabric finish. Ionic monomers are covalently grafted onto the surfaces of the fabric and the silica nanoparticles are used to form a network that can help dissipate static charge. The grafting of ionic monomers and the formation of the network are initiated by atmospheric plasma treatment.

Plasma treatment of textiles is an emerging field. Plasma technology has been used successfully to alter the surface chemistry of textiles, for a variety of end applications. Plasma technology is highly surface specific and is considered environmentally sustainable. The main use of plasma in this research is to initiate the graft polymerization reaction for attaching the silica nanoparticles and the ionic monomers to the fabric surface.

This research investigates the application of silica nanoparticulates on the fiber surface using atmospheric plasma, with the aim of imparting a durable antistatic finish to the substrate. The chemicals that will be used as part of this research are less moisture dependent than conventional antistatic finishes. This implies that these finishes are expected to work well even in conditions with less than fifty percent relative humidity, a point below which most conventional antistatic finishes become ineffective due to inadequate moisture content to provide ion mobility.

CHAPTER 2: LITERATURE REVIEW

2.1. Generation of static

The triboelectric series is an empirically compiled series where materials are arranged from top to bottom depending on their relative ability to lose or gain electrons, beginning with the most positively charged substance and ending with the substance carrying the most negative charge. A simple triboelectric series for fibers can be illustrated in **Table 2.1**.

Table 2.1. Triboelectric Series (Schindler & Hauser, 2004)

Positive end of the series	1. Glass
	2. Wool
	3. Nylon 6
	4. Nylon 6,6
	5. Rayon
	6. Cotton
	7. Acetate
	8. Hemp
	9. Silk
	10. Polyester
	11. Acrylic, Modacrylic
	12. Polyethylene, polypropylene
Negative end of the series	13. Polytetrafluoroethylene

For example if fibers of glass and polyester are rubbed together, glass acquires positive charges and polyester, a negative charge because polyester has better ability to gain electrons than glass (Henniker, 1962). On the contrary, the same polyester fibers will acquire positive charges when rubbed with polypropylene fibers because it has a greater tendency to lose electrons as compared to polypropylene.

2.2. Static in textile processing:

The processing of polymer fibers and fabrics may present problems in processing because of the accumulation of static charge on these fibers due to friction with machine surfaces (Kan, 2007). Charging may also occur due to exposure to ionized gases or

plasma or due to repeated deformation (Kan, 2007). When two dielectric polymer fibers or fabrics are rubbed against each other, one of them loses electrons and is positively charged while the other one accepts electrons and gets negatively charged. The propensity of a dielectric polymer to lose or gain electrons with respect to each other, makes them either positive or negatively charged, and this is listed in triboelectric series in **Table 2.1**. The electrostatic charges generated cause inconveniences like ballooning due to the repelling of fibers containing like charges. Charged fiber and fabrics attract dust and may need cleaning before further processing. The rate of charge dissipation from the charged fibers and fabrics depends on several factors such as the molecular structure of the polymer and environmental conditions such as humidity and impurities (Johnson, 1972; Li et al, 2004; Pionteck & Wypych, 2007).

Static also causes handling problems for fibers and fabrics. Static generated in fabrics interferes with the operation of computers and other sensitive electronic devices in or around which such textiles are used. Discharges of sufficient magnitude can cause fires as the spark caused can ignite flammable vapors and dust (causing dust explosions) (Seyam et al., 2009).

It is essential to incorporate certain chemical additives into textile substrates in order to overcome static charges for both processing and consumer use. There are different methods that are used to control static in textile processing. Most textile mills include conditions of high humidity in them in order to help dissipate any charge built up on the fibers. During processing, synthetic fibers are coated with spin finishes that are essentially lubricants and have antistatic agents added. Spin finishes enable the fibers to

be processed at higher speeds, with no static related problems. Antistatic agents can be either added to the bulk or to the surface of fibers (Berkey, Pratt, & Williams, 1988; Johnson, 1965; Pionteck & Wypych, 2007; Seyam, Oxenham, & Castle, 2005).

2.3. Antistatic textiles

Antistatic finishes are generally applied when the antistatic nature of the substrate is to be maintained for a longer time. Depending on how they are applied, antistatics include internal and external finishes. Internal antistatic agents are the ones which are added to the bulk of the polymer, forming a pathway for the charges to flow from the polymer surface to ground (Pionteck & Wypych, 2007).

External antistatic agents are applied externally from solutions to the textile surface through a variety of methods including padding baths, spraying, plasma grafting, vapor deposition etc. External antistatic agents have hydrophobic and hydrophilic functionalities in their molecular structure. The hydrophilic part orients itself towards the air and promotes the absorption of moisture, resulting in better ion mobility and dissipation. Conventional antistatic finishes include durable or non durable finishes depending on their ease of removal. The following sections discuss non durable finishes and durable finishes respectively.

2.3.1. Non-durable finishes (Pionteck & Wypych, 2007; Schindler & Hauser, 2004)

Non-durable antistatic agents are used to treat substrates that will not undergo repeated or any laundering in their lifetime. These include products like conveyor belts and driving cords.

i) Many common non-durable antistatic finishes are considered anionic and include compounds like esters of phosphoric acid, shown in **Figure 2.1**. Here the

phosphoric acid group ($-PO_3^{-2}$) containing finish is deposited onto the substrate and allows for charge dissipation. The durability of these phosphoric acid esters increases with the size of the molecule (Schindler & Hauser, 2004).

$$R-O-\overset{\displaystyle O}{\underset{\displaystyle O^-}{\overset{\|}{P}}}\!\!\!\diagdown O^- \quad 2A^+$$

$$R-O\!\!\left[CH_2-CH_2-O\right]_x\!\!-\overset{\displaystyle O}{\underset{\displaystyle O^-}{\overset{\|}{P}}}\!\!\!\diagdown O^- \quad 2A^+$$
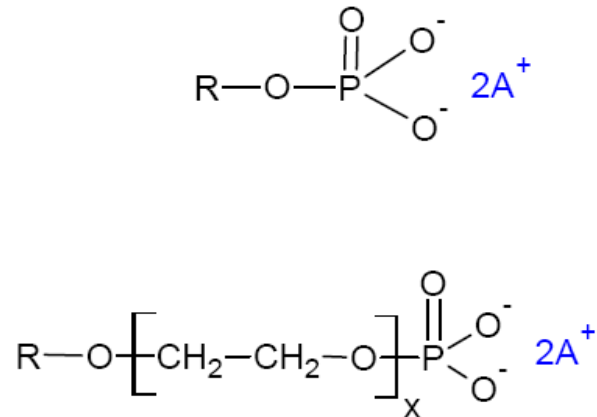
Figure 2.1 Phosphoric ester antistats (Schindler & Hauser, 2004)

Some other examples would include alkyl phosphates, ethoxylated secondary alcohols, glycerol mono- and distearate, sodium alkyl sulfonates, neutralized alcohol phosphate, sorbitan monolaurate and sorbitan monooleate. The chemical groups of these compounds include –OH, -ONa, -COOR, $-PO_4$ and $-SO_4$ functionalities. Esters migrate quickly onto textile surfaces, are relatively thermally stable and perform well even under low humidity conditions (Pionteck & Wypych, 2007; Schindler & Hauser, 2004).

ii) Another class of non-durable finishes contains quaternary ammonium compounds (Pionteck & Wypych, 2007; Schindler & Hauser, 2004). The most common compounds used are ditallowdimethylammonium chloride and dihydrogenated tallowdimethylammonium chloride. These fall under the category of cationic

antistatic finishes, due to the presence of a cationic group(N^+) that is quaternarily bonded. These compounds are applied by exhaustion processes as they have natural affinity for textile fibers (Schindler & Hauser, 2004), because of the presence of positive charges on their structure. These compounds improve pigment dispersibility and have fast and efficient migration properties. They generally exhibit good thermal stability due to the presence of saturated structures. Amines generally form aqueous solutions and have excellent dispersibility even in cold water (Pionteck & Wypych, 2007). Quaternary amines, shown in **Figure 2.2**, also impart softness to the fabric, which makes them extremely capable of value addition in the consumer sector, as antistatic finishes.

The important industrial processing methods of applying amine antistats include extrusion, calendaring, immersion, dipping, compounding, blow molding, sheet extrusion, spraying, surface printing etc. The important textile polymers which amines are applied on are PET, PP, PA and acrylic.

$$H_3C-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{N}}{}^+-CH_3Cl^-$$
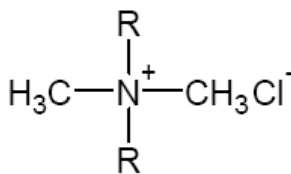
Figure 2.2 Quaternary ammonium antistats (Schindler & Hauser, 2004)

iii)   The third group of non-durable antistatic finishes includes non-ionic compounds. These are mostly ethoxylated fatty esters, alcohols and alkylamines (**Figure 2.3**). The ethoxy groups provide good hydrogen bonding, and as a consequence,

become moisture friendly or hygroscopic. The moisture in turn provides the required antistatic properties.
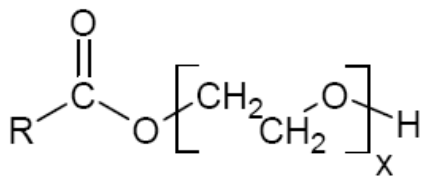
Figure 2.3 Non ionic antistats (Schindler & Hauser, 2004)

iv)   Mixtures of ionic and non-ionic antistatic finishes are also used to provide better antistatic properties. The ions provided by the ionic surfactant are mobilized by the moisture absorbed on account of the non ionic surfactant, providing better antistatic properties (Pionteck & Wypych, 2007; Schindler & Hauser, 2004).

2.3.2. Durable antistatic finishes (Schindler & Hauser, 2004)
Conventional durable antistatic finishes are obtained by forming a functional polymer network on the surface of the substrate. The polymer network has hydrophilic groups that assist in the dissipation of any charge. The polymers can be formed prior to application on fabrics or they can be formed on the surface of the substrate itself. Durable finishes are traditionally polyamines that are reacted with polyepoxides, shown in **Figure 2.4**. With these compounds, the level of hydrophilicity is inversely related to the fastness and durability of the finish. This happens because the hydrophilic polymer absorbs water, resulting in swelling and softening. In this state, the polymer becomes susceptible to removal by laundering and abrasion, thus reducing the effectiveness of its antistatic function. Due to the difficulty in finding the balance between hydrophilicity and durability, conventional durable antistatic finishes are still not widely used.
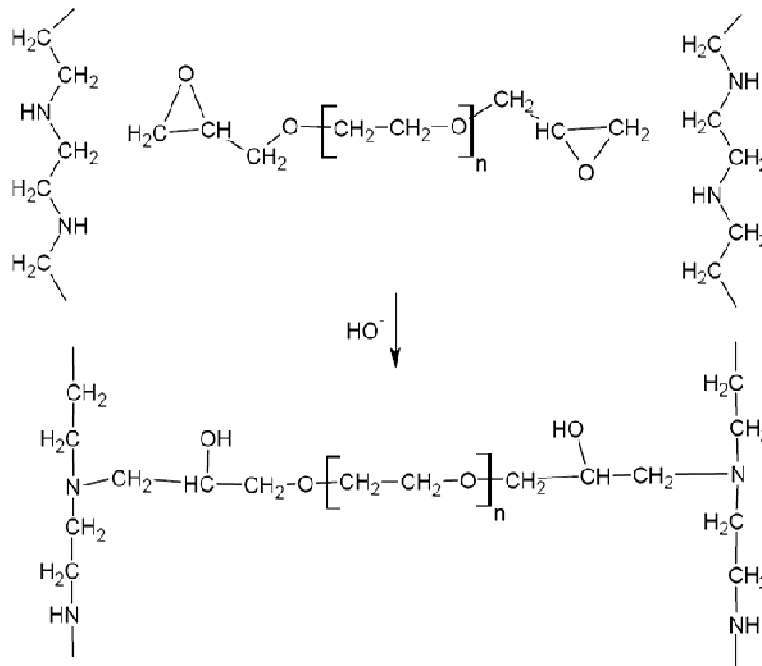
Figure 2.4 Crosslinking of polyamines to form durable antistats (Schindler & Hauser, 2004)

2.3.3. Conductive fibers (Pionteck & Wypych, 2007; Schindler & Hauser, 2004)

Conductive fibers are produced mainly for specialty applications like industrial fabrics, specialized apparel, and carpeting. Conductive fibers are often prepared by methods like dispersing metal or carbon particles in the polymer melt prior to extrusion, or by coatings of Ni or CuS on the fiber surfaces.

Metal fibers like steel are also often used and have the advantage of being durable, corrosion and chemical resistant. In addition, they have almost no effect on coloring and boast excellent washing characteristics. As a result, they are commonly used in processes such as injection molding, coating, and other textile extrusion methods. They are also used in heat resistant sewing yarns, shielding textiles, carpets and burner cloth.

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Furthermore, metal containing fibers can be incorporated with acrylic, polyester, polyamides and other thermoplastics (Schindler & Hauser, 2004).

In addition to metal and metal containing fibers, carbon and graphite containing fibers have high conductivities, and hence they can also be used with polymer fibers like polyethylene and polypropylene. Elemental carbon as graphite has good conducting properties.

In addition to carbon and metal materials, conventional metal oxides like those of tin (SnO_2), zinc (ZnO) and antimony (Sb_2O_3) are often dispersed into fibers and polymers in order to provide superior conductive properties. Their performance is independent of humidity, and they are sometimes used in paints, gas sensors, coatings and packaging foam (Guo et al, 2006). However, these oxides pose problems with the environment because they are often based on heavy metals.

The problem with extruded conductive fibers is the difficulty in achieving homogeneity (Schindler & Hauser, 2004). Alternatively, fibers can be constructed directly from stainless steel, aluminum and other metals. The problems with such metal fibers however, are their high costs and difficulties faced in installation and use (Schindler & Hauser, 2004).

2.4. Use of plasma in textile processing
2.4.1. Plasma chemistry
When a large voltage is applied across a space filled with a certain gas, the gas breaks down and starts conducting electricity. This is because individual molecules are split into negative and positive ions. The resulting ionized gas, called plasma, may contain

ions, excited molecules and energetic photons (Fridman, 2008; Shishoo, 2007; Yamaguchi, Nakao, & Kimura, 1996), meta-stable excited species or polymeric and molecular fragments (Fridman, 2008; Shishoo, 2007; Sinha, 2009). It is considered to be the fourth state of matter after solid, liquid and gas. The voltage at which plasma is formed and also the nature of the formed plasma, are collectively dependent on

a. The type of gas used

b. Variables like pressure and flow rate of the gas

c. The geometry and distance between the electrodes across which the voltage is applied, and

d. The nature of voltage that is supplied and the electrical circuitry. Examples would include direct current, alternating current, radiofrequency and microwave.

The interactive sequence is that as the temperature increases, the molecules gain energy and transform matter in the sequence: solid, liquid, gas and plasma (Shishoo, 2007). The free electrons in the plasma cause it to be strongly influenced by electromagnetic fields.

Plasma technology is considered to be beneficial and has gained widespread usage due to some of its major features:

1. Plasmas have unmatched physical, thermal and chemical range which can surpass the limits of application of conventional technologies. This allows for superior control over surface properties, with extraordinary precision (Fridman, 2008; Shishoo, 2007)

2. Plasma systems are thermodynamically unstable and are thus able to produce extremely high concentrations of chemically active species and still maintain very low bulk temperatures. This nature is advantageous from the point of view of textile processing, because textile materials are often damaged at high temperatures (Fridman, 2008; Shishoo, 2007).

3. Plasma technology is environmentally friendly (Shishoo, 2007). This factor becomes increasingly important as resources become scarce and the push towards sustainable technology becomes stronger.

2.4.2. Plasma modification on the surfaces of polymers and textiles

Plasma usage in the textiles industry is largely limited to the use of non-thermal atmospheric plasma (Fridman, 2008; Shishoo, 2007). Plasma technology has been widely investigated for its ability to impart a plethora of properties to the surfaces of various textile and polymer substrates. Atmospheric plasma treatment can bring about various changes in the surface properties, like wettability, surface electric resistance, dielectric permittivity, and permeability, among others. Plasma can influence the surface properties of the substrate by bringing about a chemical change due to the free electrons or physical changes. Surface activation often occurs due to reactive sites created on the surface by bond breaking. Other generic surface processes that occur are material volatilization and removal (etching), dissociation of surface contaminants leading to scouring, and deposition of coatings. In case of textile fibers, the depth of the surface that is affected by the plasma is typically less than 1000 Angstrom units (Å), so the bulk properties of the substrate remain unchanged (Shishoo, 2007).

The different components of atmospheric plasma stimulate chemical reactions on the polymer surface. Some of the products obtained from the reaction are free radicals, cross-links between polymer macromolecules and unsaturated organic compounds. The polymer surface also undergoes decomposition and the by-products of such reactions, along with gas phase products are also obtained (Fridman, 2008; Shishoo, 2007). Some common reactions that take place are outlined below (Fridman, 2008).

All plasma types initiate the growth of free radicals, formed on polymer surfaces by the scission of the R-H bonds and C-C bonds in the polymer macromolecules as shown in **Equations (2.1)** and (**2.2**)

$$RH \xrightarrow{e,\ hw} R(\bullet) + H(\bullet) \tag{2.1}$$

$$RH \xrightarrow{e,\ hw} R_1(\bullet) + R_2(\bullet) \tag{2.2}$$

Equation 2.3 shows the formation of unsaturated organic compounds

$$RH \xrightarrow{e,\ hw} R_1\text{-}CH=CH\text{-}R_2 \tag{2.3}$$

Equation (2.4) shows the secondary reactions that lead to the formation of molecular hydrogen by the recombination mechanism. **Equation (2.5)** shows the mechanism of hydrogen transfer with the polymer macromolecule

$$H(\bullet) + H(\bullet) \longrightarrow H_2 \tag{2.4}$$

$$H(\bullet) + RH \longrightarrow R(\bullet) + H_2 \tag{2.5}$$

The secondary reaction between atomic hydrogen and the organic radical R not only results in the formation of both molecular hydrogen (**Equation 2.5**), but also a non-saturated organic compound as shown in **Equation (2.6)**

$$H(\bullet) + R(\bullet) \longrightarrow R_1\text{-}CH=CH\text{-}R_2 \tag{2.6}$$
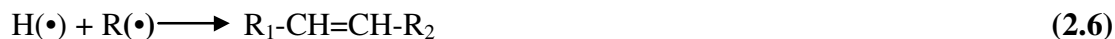
When oxygen plasma is used, the molecular oxygen in the gas phase is attached with the organic radical present on the substrate, and active peroxide radicals are formed as a result of the reaction, shown in **Equation (2.7)**

$$R(\bullet) + O_2 \longrightarrow R\text{-}O\text{-}O(\bullet) \qquad\qquad\qquad (2.7)$$

The radicals formed by plasma are able to act as initiators for a variety of surface chemical reactions on the substrate. The most common processes started by the RO_2 radicals are the formation of hydro-organic peroxide and other peroxides on the surface of the polymer substrate. This is indicated in **Equations (2.8) and (2.9)**

$$R\text{-}O\text{-}O(\bullet) + RH \longrightarrow R\text{-}O\text{-}O\text{-}H + R(\bullet) \qquad\qquad (2.8)$$

$$R\text{-}O\text{-}O(\bullet) + R_1H \longrightarrow R\text{-}O\text{-}O\text{-}R_1 + H(\bullet) \qquad\qquad (2.9)$$

Different types of plasma affect substrates differently and create different functional groups on the surface, leading to a great difference in the surface properties. For example, helium and argon plasmas create an abundance of free radicals on the surface, which go on to form O-C=O, C=O and O-CO-O functionalities (Fridman, 2008; Shishoo, 2007). With oxygen plasma, these functional groups are observed to increase significantly. The exposure to nitrogen plasma results in the formation of amine (R-NH_2), amide (R_1-NH-R_2), and imine ((R_1, R_2)C=N-H) groups on the polymer surfaces. Plasma based on other nitrogen or nitrogen compound containing gases also has the ability to introduce nitrogen compounds to the polymer surface, but the plasma nitrogenation depends on the type of gas used. For example, ammonia (NH_3) produces more amine groups whereas pure nitrogen produces more imine groups (Fridman, 2008; Shishoo, 2007).

Fluorine containing gases are also used to interact with and lower the surface energy of the substrate. Here, a different set of surface groups is formed, including C-F, CF_2 and C-CF. Common fluorine containing gases used for plasma treatment are CF_4, C_2F_6, C_3F_8 and CF_3Cl. The ratio C:F is important for the desired end use in that, higher ratios enhance polymerization whereas lower ratios are used for polymer etching and the introduction of polymer containing groups on the surface (Shishoo, 2007). Fluorine plasma treatment can impart a degree of hydrophobicity, which has been realized on most polymer surfaces. For example, Sarmadi (1993) demonstrated improved dyeability and water repellency on polyester surfaces. Nishikawa et al (1994) demonstrated that fluorine-containing plasma treatment on silk fibers can significantly improve hydrophobicity of the fibers.

2.4.3. Effect of plasma on cellulose and cellulosic fibers

Cellulose is used extensively in the form of wood, paper and fiber products for numerous end uses. The structure of cellulose comprises a basic repeating unit called cellobiose, consisting of two ringed glucose structures. The rings in the cellobiose unit are mutually inverted with respect to each other. Each ring is called an anhydroglucose unit (Shishoo, 2007). Each cellobiose unit contains six alcohol hydroxyl (-OH) groups which are capable of forming hydrogen bonds, both at intramolecular and intermolecular levels. The resulting structure of pure cellulose is therefore, highly crystalline and polar. Each cellulose chain typically has between 300 and 1700 repeating units for wood, and between 800 and 10000 for plant fibers like cotton (William, 1999). **Figure 2.5** Shows the structure of cellulose with a repeating unit
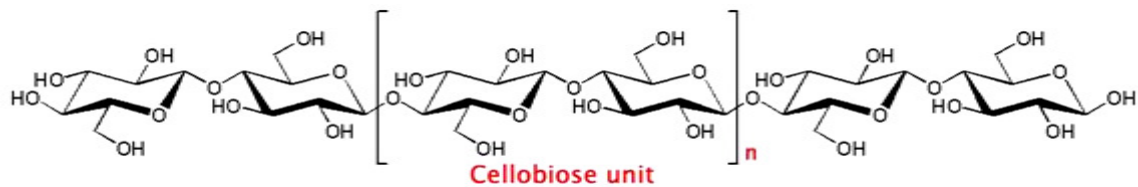
Figure 2.5 The structure of cellulose (William, 1999)

In most cellulosic fibers however, there are both amorphous and crystalline regions. The crystalline regions are characterized by ordered, tightly packed chains with a high degree of hydrogen bonding. The amorphous regions are characterized by a general disorder in the packing of the chains.

The effect of plasma on cellulosic substrates has generally been observed to alter wettability characteristics and increase surface energy (Pionteck & Wypych, 2007; Shishoo, 2007) of cellulosic fibers. Plasma treatment has also been proven to improve the surface resistivity properties of cotton (Berkey et al., 1988; Bhat & Benjamin, 1999; Pionteck & Wypych, 2007). Plasma treatment improves the dyeability of the cotton substrate after grafting with the right monomers, as demonstrated by Karahan et al (2008), where cotton substrates were dyed with acid dyes after plasma treatment.

Plasma treatment of cellulose creates free radicals on the surface of the substrate. It has been observed that the intensity of the free radicals created depends on factors such as the nature of the gas used, the type of plant fibers, the length of the cellulosic chains and plasma treatment time. Free radicals can be created at different sites on the anhydroglucose unit, as shown in **Figure 2.6.** It has been observed that most stable radicals are created at sites C_1, C_2 and C_5 [42]
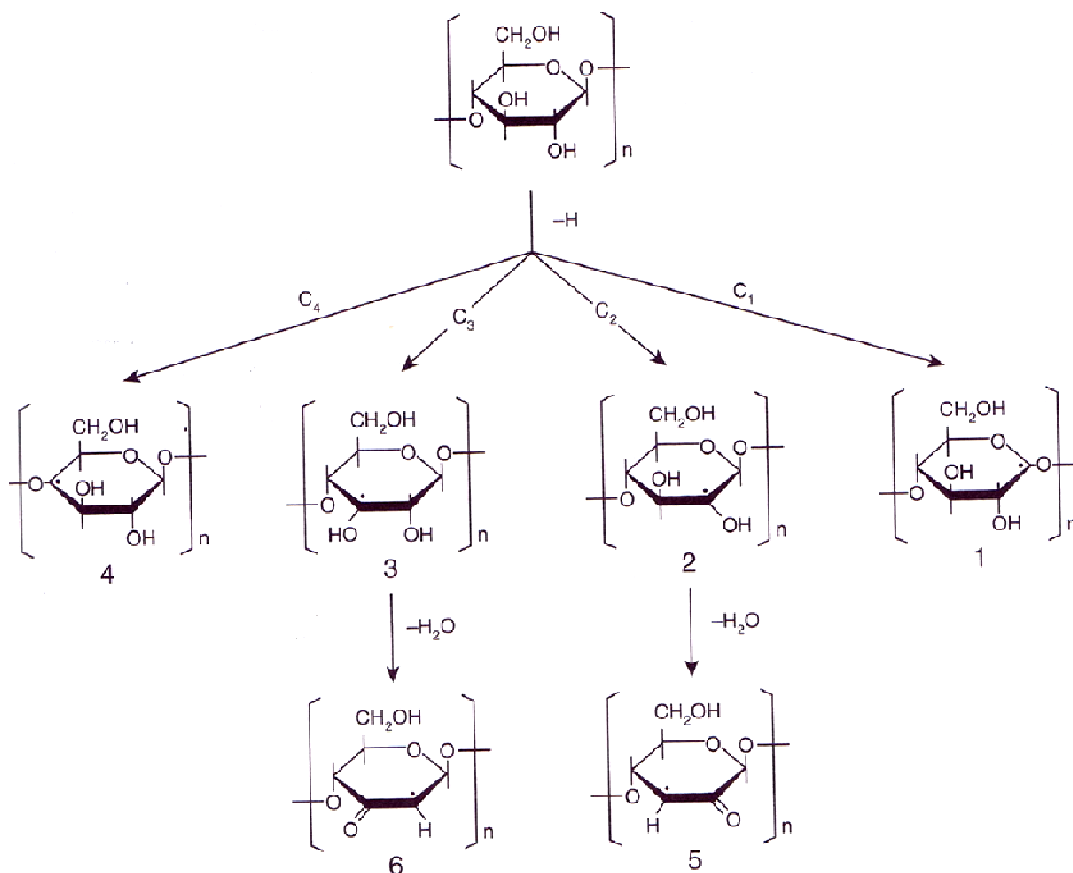
Figure 2.6 Free radicals on cellulose induced by plasma (Shishoo, 2007)

The free radicals formed by plasma help the grafting of monomers onto the surface of the substrate through plasma graft polymerization reaction. However, it has been observed that over time, the number of available functional groups decreases, as many functional groups migrate to the subsurface (Fridman, 2008; Nitschke, 2008; Shishoo, 2007).

2.4.4. Effect of plasma on synthetic polymers

Plasma treatment has a pronounced effect on synthetic polymers as regards hydrophilicity. Numerous research results have led to the establishment of a relation between plasma treatment and the resulting hydrophilicity of the synthetic polymer. A summary of results can be seen in **Table 2.2**.

Table 2.2 Surface energy and water contact angles before and after plasma treatment. (Sparavigna, 2008)

	Surface Energy Dynes/cm		Water contact Degrees	Angle
	Before	After	Before	After
Polypropyene PP	29	>73	87	22
Polyethylene PE	31	>73	87	42
ABS	35	>73	82	26
Polyamice PA	<36	>73	63	17
Polyester PET	41	>73	71	18
PTFE	37	>73	92	53

Different gas plasmas work to create different types of free radicals and polar groups on the surface of the substrate and therefore increase the hydrophilic properties, as well as adhesive properties (Fridman, 2008; Sharnina, Mel'nikov, & Blinicheva, 1996; Shenton, Lovell-Hoare, & Stevens, 2001; Shishoo, 2007; Sparavigna, 2008). Treatment of polyester, for example, with oxygen plasma leads to an increase in the number of oxygen containing polar groups such as –OH, -OOH and –COOH on the fiber surface (Fridman, 2008; Kan, 2007; Sharnina, Mel'nikov, & Blinicheva, 1996; Shishoo, 2007), which attract water molecules, and also help dissipate excess static charge (Kan, 2007). An increase in hydrophilicity also decreases the charge buildup and would thus improve the antistatic properties of the polymers. Plasma treatment has been shown to reduce the surface resistivity of polyester, with increasing plasma treatment time having a direct relation to decreasing resistivity and better antistatic properties (Bhat & Benjamin, 1999). This can also be, in part, attributed to the increase in wettability of polyester surfaces after treatment (Arkles & Larson, 2005; Wei et al., 2007).

Plasma treatment increases the surface roughness of the textile material due to the etching effect [Fridman, 2008; Inagaki, Tasaka, & Goto, 1997; Liu, Xiong, & Lu, 2005;

Shishoo, 2007), thus increasing the available surface area for carrying out grafting polymerization reactions. Thus plasma treatment has a significant effect on the behavior of textile substrates.

2.5 Graft polymerization on textiles

Graft polymerization involves treatment of the substrate with a free radical initiator to form free radicals on the substrate, following which monomers are grafted onto the surface by forming polymer chains. This results in a polymer film being deposited on the surface of the substrate. Graft polymerization has been carried out on a variety of substrates using a variety of free radical initiators. An example relevant to this research would be the graft polymerization of acrylamide onto maize starch using a potassium persulfate as a free radical initiator. In a research conducted by Khalil et al (1993), the effect of different concentrations of the persulfate as a free radical initiator was studied, along with other parameters such as monomer concentration, temperature, liquor ratio and time of polymerization. Potassium persulfate decomposes to form sulfate radicals [-$SO_4^-(.)$] and hydroxyl radicals [-$OH(.)$] owing to its reaction with water. Both types of radicals attack the starch macromolecules and produce starch macroradicals, which are active sites that are capable of initiating the grafting reaction of the polymers onto the surface. The maximum graft yields and efficiency values were achieved at persulfate concentrations of 30 mmol/L, as shown in **Table 2.3.**

Table 2.3. Effect of potassium persulfate concentration on graft yield and graft reaction efficiency of poly(acrylamide)-y-starch (Khalil et al., 1993)

$K_2S_2O_8$ conc. (mmol/l)	Nitrogen content (%)	Graft yield (%)	Graft reaction efficiency (%)
10	2.6	14.9	29.8
30	4.2	27.0	53.9
50	4.0	25.5	51.9
70	3.6	23.5	47.0
90	3.3	20.0	39.5
100	3.0	18.0	36.0

[a] Reaction conditions: maize starch 4 g, acrylamide 2 g, liquor ratio 5, time 1 h, temperature 60 °C.

2.5.1 Plasma-induced graft polymerization

Plasma-induced graft polymerization can lead to the attachment of solid polymeric materials with desired properties on textile substrates. Plasma grafting is an extremely functional tool in order to develop highly specific surface finishes. This is because different monomers can be used to carry out graft polymerization with plasma. Plasma finishing ensures that the polymer film formed is thin (in the order of a few nanometers), and thus provides great functionality while maintaining the bulk properties of the substrate intact. Also, crosslinking of polymers can be introduced during plasma treatment, with the advantage of being able to control the degree of crosslinking with plasma treatment to provide superior mechanical properties (Nitschke, 2008).

Many experiments in plasma-induced graft polymerization have been conducted. Turmanova et al (2007) investigated the grafting of vinyl monomers such as acrylic acid, 4-vinylpyridine or 1-vinylimidazole onto PTFE surfaces using plasma treatment. The mechanism by which the reaction takes place is shown in **Figure 2.7**.
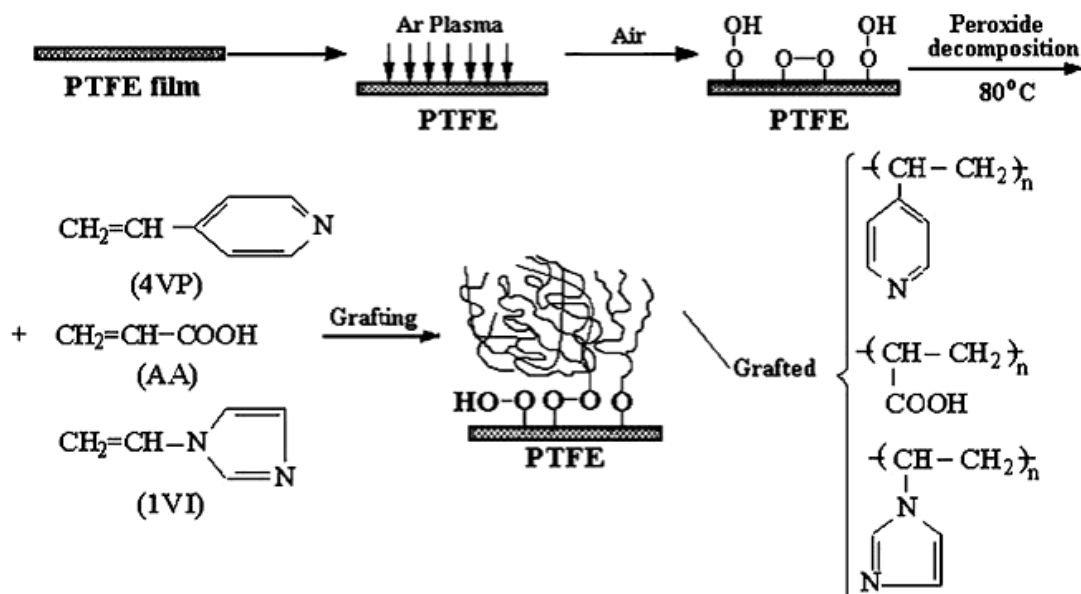
Figure 2.7 Schematic of graft polymerization using Ar plasma on PTFE surface (Turmanova et al., 2007)

Inagaki et al (1997) successfully grafted sodium vinylsulfonate, an ionic monomer, onto the surface of PTFE, by irradiating the PTFE surface with argon plasma and then dipping the treated fabrics in an aqueous vinylsulfonate solution. The mechanism here involves the formation of stable free radicals on the surface of PTFE that serve to initiate the polymerization reaction for sodium vinylsulfonate. The SEM image in **Figure 2.8** shows the polymerization process on the surface.
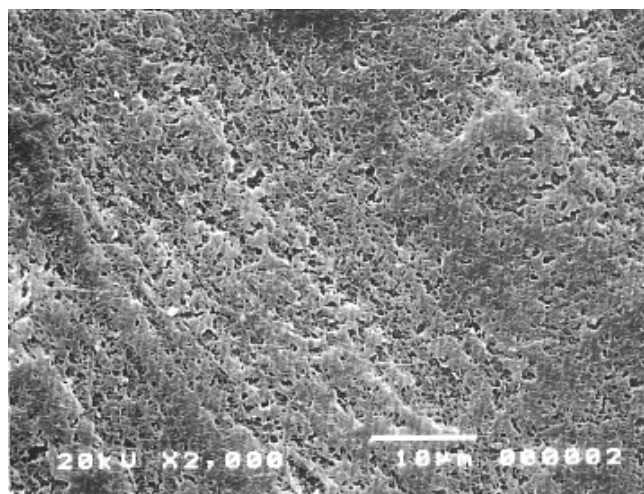
Figure 2.8: Polymerization of sodium vinylsulfonate on PTFE surface

In another research, Bech et al (2007) successfully graft polymerized carbohydrate monomers on the surface of PET by using the mechanism of double plasma treatment, wherein, plasma treatment was imparted to the raw fabric, followed by treatment with the monomer. This treatment was then followed up with another round of plasma treatment. This method would initially seek to form free radicals on the fabric surface by plasma treatment. The air drying method, after the initial plasma treatment would help in the formation of stable peroxides on the fabric surface (Bech et al., 2007; Fridman, 2008; Inagaki et al., 1997; Shishoo, 2007), which are now active sites for graft polymerization. The second plasma treatment serves to polymerize the monomers adsorbed on the fibers (Bech et al., 2007)

Plasma-induced graft polymerization is frequently employed to impart a varied set of functionalities to the polymer substrate in question. In case of a ubiquitous resource like cotton, which is hydrophilic, research has been carried out to make cotton hydrophobic, by employing graft polymerization techniques. In a research conducted by Tsafack and Levalois-Grützmacher (2007), cotton was rendered water repellent and flame retardant by low-pressure plasma induced graft polymerization of 1,1,2,2, tetrahydroperfluorodecylacrylate (a flame retardant monomer), with CF_4 plasma. Therefore, plasma induced graft polymerization is a clean and efficient way to achieve the desired functionalities on the substrate surface.

2.6 Use of nanotechnology for textile applications
Nanotechnology has slowly gained prominence in many fields of research. Some nanotechnologies alter properties at atomic and molecular levels. For example, nanoparticles have a high surface area to volume ratio and high surface energies that

make them more suited to coat textile surfaces (Wong et al., 2006). Therefore, nanotechnology has been used on textile surfaces to impart antibacterial properties, water repellence, wrinkle resistance and antistatic properties to the substrate.

Antistatic properties can be achieved by applying different nanoparticles on the surfaces of synthetic fibers. Some examples of nanoparticles used are ZnO, TiO_2 and antimony-doped tin oxide (ATO). These are semi conductive materials by nature and thus provide the requisite antistatic properties to the treated fabric (Wong et al., 2006).

2.6.1 Use of silica nanoparticles in textile applications

Adding silica nanoparticles is an inexpensive way of modifying the surface properties of a textile material. The most common supplication found for silica nanoparticles is the creation of water repellency (Maltig, Hauffe, & Böttcher, 2005). Silica nanoparticles can themselves form transparent layers that adhere well to the textile surface, with the common diameters of the nanoparticles being in the range of 10-50 nm. The application of silica nanoparticles is typically achieved by the sol-gel process, wherein nanoparticles are firstly formed from a chemical solution that reacted to form nanoparticles in colloidal form (sol) (Arkles & Larson, 2005; Helmut, 2006). The advantages of silica nanoparticles is that they are thermally stable to temperatures of up to 500°C, which implies that a wider range of application procedures and temperatures can be suited to them (Maltig, Hauffe, & Böttcher, 2005).

Fumed silica is prepared by the hydrolysis of silicon tetrachloride ($SiCl_4$) in a hydrogen-oxygen flame (Roe, 2008; Yerian, 2003). This substance undergoes decomposition and forms silica and hydrogen chloride. This process has been applied extensively by the

Evonik Degussa Corporation and is popularly called the "Aerosil®" process (Michael & Ferch, 1998; Roe, 2008; Zhang & Fedkiw, 2005):

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ (vapor) **(2.10)**

(Azom.com, 2008; Roe, 2008)

The formation of silica particles consists of several intermediate stages, initially forming protoparticles, and progressively coalescing while cooling, to form branched, chain like aggregates. The physical aggregates have a size of about 100nm, and they cannot be broken down again by dispersion. The fused silica nanoparticles can be characterized as having a low bulk density (0.02 to 0.05 g cm^{-3}), but high surface area values (100 to 400 m^2g^{-1}); the density of the aggregates are approximately 0.7 gcm^{-3}. By varying different parameters such as temperature of the flame, reactant concentrations and dwell time of the silica in the reaction chamber, it is possible to change the size of the particles, the size distribution and most importantly, the surface properties of the nanoparticles (Michael & Ferch, 2005; Roe, 2008). It is also possible to use another chemical process to after-treat the silica nanoparticles, in order to achieve special properties like hydrophilicity or hydrophobicity. This treatment can be done with halogen silanes, alkoxysilanes, silazanes or siloxanes. This can be explained better with a schematic diagram as shown in **Figure 2.9**. The fumed silica Aerosil® R711 used in this research is aftertreated with a methacrylsilane, as shown in **Figure 2.10**.
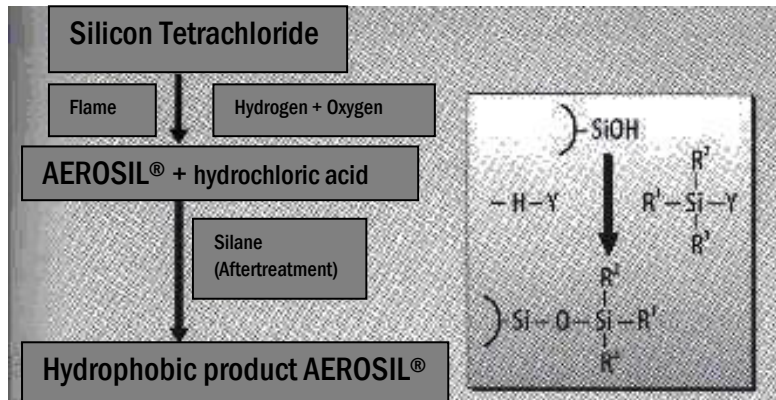
Figure 2.9 Chemical after-treatment of Si nanoparticles; a schematic diagram (Roe, 2008)
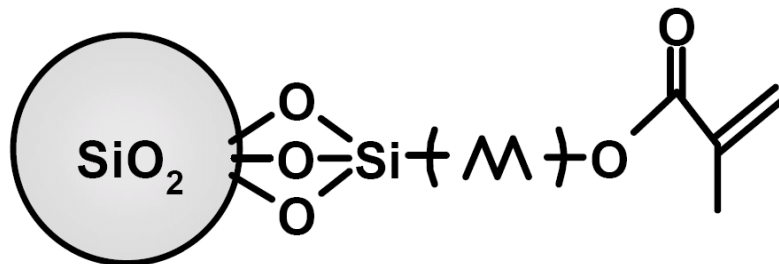
Figure 2.10 R711 particle structure

2.7 Relevant methods for testing fabric antistatic behavior

Many tests have been devised in order to test the electrostatic properties of textiles and

consequently establish a pattern for their antistatic behavior. Four major organizations

that publish electrostatic standards are the American Society of Testing and Materials

(ASTM), Electrostatic Discharge (ESD) Association, American Association of Textile

Chemists and Colorists (AATCC), and International Standard Organization (ISO).

These organizations have developed test methods to assess resistivity, static charge

generation and accumulation. There are three accepted categories of test methods which

measure the electrostatic propensity of textile materials. They are (1) direct

measurement, (2) indirect measurement, and (3) use of simulation (Holme, McIntyre, & Shen, 1998; Suh, 2008).

The direct measurement category typically consists of measuring electrical properties such as electrical field (E), potential (V), charge amount (Q), or the rate of electrostatic discharge, after developing charges on the material by standard treatments. Instruments like the electrostatic field meter and electrostatic voltmeter can be used for the measurement of electric field and potential on the surface of textile material, respectively. The obtained values can then be converted to charge density and charge per unit area, which represent the probability of an electrical discharge (Holme, McIntyre, & Shen, 1998; Suh, 2008).

The indirect method of treatment generally involves the use of other indicators like electrical resistance (R) or conductance of the textile materials. Resistance is the property of a substance indicating how it opposes the flow of an electric current through it. Conductance is the reciprocal of resistance, and it refers to the property of the material that allows current to flow through it when a potential difference is applied. They are still generally believed to represent electrostatic properties (Holme, McIntyre, & Shen, 1998; Suh, 2008)

The third category, simulation, consists of methods which study the behavior of textile materials in a situation simulating the end-use for which they are intended, instead of actual electrostatic properties (Holme, McIntyre, & Shen, 1998; Suh, 2008). Common tests in this category are the cling and walking tests. The cling tests observe and study the clinging behavior of textiles when charged with static electricity, as an indicator of

their static property. Walking tests simulate the action of walking on carpets, and observe static charges generated by walking, mainly on carpet materials.

2.7.1. Static dissipation methods for assessing electrostatic behavior
Static dissipation methods are generally reliable for testing antistatic properties of textile material. This is partly due to the fact that many thin polymeric films do not obey Ohm's law, and therefore, cannot be judged by their resistivity parameters alone. Also, the reading for resistivity has no information on the capacitance of the material, and charge is affected by adjacent earthed surfaces (Chubb, 2004; Suh, 2008). A generic method for the testing of static dissipation would involve the application of very high voltage to the fabric or polymer film, in order to charge it. After charging, the specimen is earthed to allow the pent up charge to dissipate. The time, from the time of grounding to the point of complete dissipation of charge, is regarded as the time of decay. Testing conditions are varied according to different testing methods that have been formulated, e.g. the Federal Test Standard uses 73 ± 3.5 °F and 15% R.H.

Several electrostatic devices have been developed for charging and assessing static on textiles materials. Examples of some of these include the National Aeronautics and Space Administration (NASA) Tribo-electric Tester, Shirley Method, John Chubb Instrumentation (JCI) Tribo-charging Tester (Chubb, 2004), Linear and Rubbing Tester (Seyam, Cai, & Oxenham, 2009). These devices employ different means of generating and dissipating charges on test specimens and measure electric properties under controlled parameters, which in turn influence the static characteristics of textiles (Suh, 2008).

One such developed testing system is the Rubbing tester, developed by Seyam et al. at
NC State (Seyam, Cai, & Oxenham, 2009). A schematic of the rubbing tester is shown
in **Figure 2.11**.
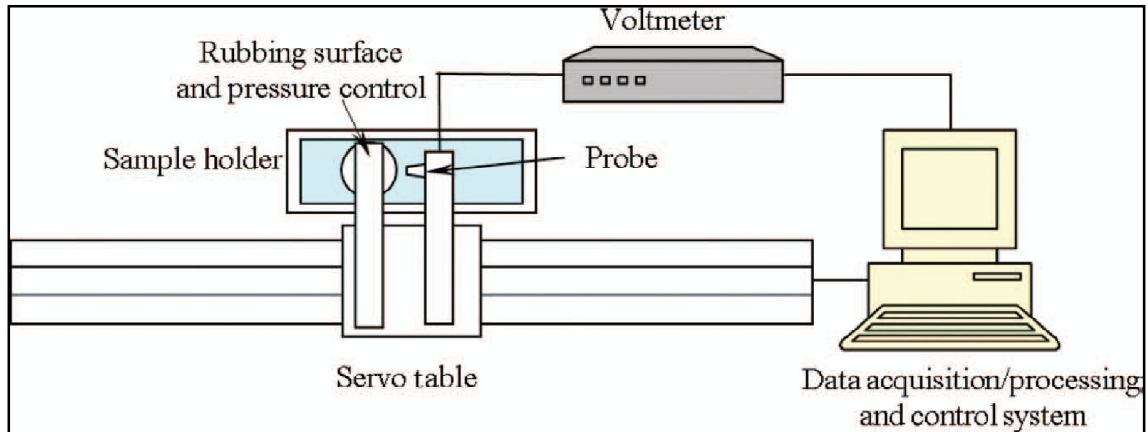
Figure 2.11 Schematic of the rubbing tester system (Seyam, Cai, & Oxenham, 2009)

This device is equipped with a sample holder to mount the test sample. Rubbing
material and a noncontact probe are attached to a servo table. The rubbing material
movement parameters (speed, stroke, number of cycles) are controlled by a computer
program and the rubbing pressure is measured by a pressure transducer. The sample is
rubbed with the rubbing material (usually Teflon), resulting in static charge being built
up on the fabric. The pressure between the rubbing surface and the test sample was
controlled by vertical motion of the rubbing surface. The static generation/dissipation
data are automatically collected by a standard data acquisition system that is connected
to a voltmeter which is connected to the probe (Seyam et al., 2009; Suh, 2008).

Another type of static dissipation test is performed with the Static Voltmeter
(Rothschild, Zurich, Switzerland). The fabric is fixed vertically and then rubbed with a
glass rod to charge it. The maximum charge generated is measured as also the half life

(time taken for the charge to drop to a half of the maximum measure). The fabric with the least half life has the best antistatic properties.

2.7.2. Resistance and resistivity measurement on textile materials

The electrical resistance and resistivity measurements are the most used indirect methods in electrostatic evaluation due their simplicity. The resistance of a fabric is measured by measuring the current passing through a fabric, under known voltage and electrode dimensions. The resistivity of the surface is defined as the resistance per unit fabric area and is calculated as follows:

$$R_s = \rho_s \times \frac{D}{W} \quad \text{(Suh, 2008)} \tag{2.11}$$

Where,

R_s = Surface Resistance (Ω)

ρ_s = Surface Resistivity (Ω/ sq.)

D = Distance between Electrodes (m)

W = Width of Specimen (m)

In case the electrostatic properties of fibers and yarns, however, a concept called volume resistivity is determined, where the results are calculated as indicated by **Equation 2.12**.

$$R_v = \rho_v \times \frac{D}{S} \quad \text{(Suh, 2008)} \tag{2.12}$$

 Where,

R_v = Volume Resistance (Ω)

ρ_v = Volume Resistivity ($\Omega \cdot$ m)

D = Distance between Electrodes (m)

S = Cross-sectional Area of Specimen (m^2)

2.7.2.1. Resistivity testing for planar textile surfaces

The ESD association suggested an apparatus to measure the surface resistance

(ANSI/ESD STM 11.11) (Electrostatic Discharge Association, 2001) and volume

resistance (ANSI/ESD STM 11.12), that could be used for the measurement of planar

polymer films and textile materials. In this case the apparatus consists of an electrode

assembly, a specimen support surface, and instruments for charge measurement and

fixtures for verification (Suh, 2008). The electrode assembly prescribed in this case is

the concentric ring electrode fixture.

The electrode assembly consists of two concentric rings to contact the test material

under test, schematically shown in **Figure 2.12**. The inner electrode is a solid disc,

having a diameter of 30.48 ± 0.64 mm. The outer electrode is a ring with an inner

diameter of 57.15 ± 0.64 mm and 3.18 ± 0.254 mm ring thickness (Suh, 2008;

Maryniak, Uehara, & Noras, 2003). This particular setup of the electrode is good for

measuring the surface resistance of the textile material. However an additional bottom

electrode (a flat conductive metal plate) is needed for volume resistance measurement

(Suh, 2008). For measuring volume resistance, the concentric rings are used as a top

electrode and the metal plate becomes the bottom electrode (Suh, 2008; Electrostatic

Discharge Association, 2001). The contact surface material of electrode assembly is a

conductive material with hardness between 50 and 70 on the Shore-A Durometer scale

and volume resistivity less than 10 ohm/sq. The total weight of electrode assembly is

approximately 2.27 kg ± 56.79 g. Instrumentation includes an ammeter and power supply (10 to 100 volts). Verification fixture attaches to the electrode assembly in order to check whether the system works as it should. With the verification fixture, the apparatus indicates about 5.0×10^5 ohms for low resistant fixtures and 1.0×10^{12} ohms for high resistant fixtures.
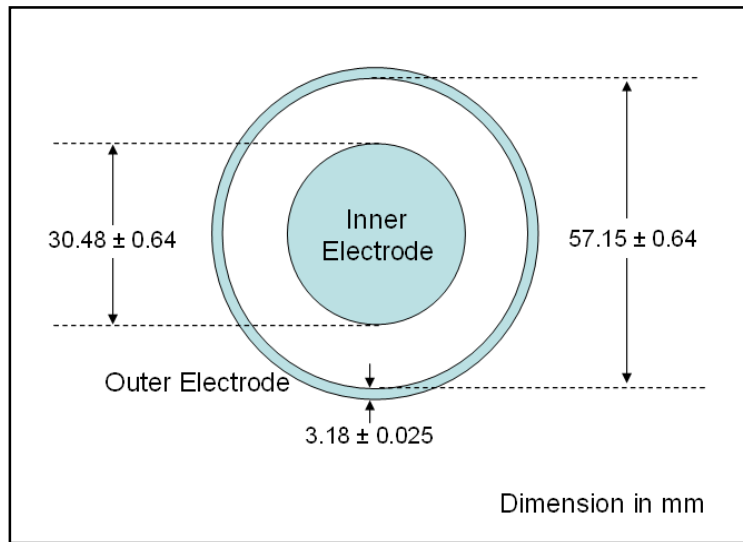
Figure 2.12 Concentric ring electrode (Electrostatic Discharge Association, 2001: ANSI/ESD STM 11.11 & 11.12)

In the method prescribed by the ESD association, the samples that are being tested should be greater than 76mm × 127mm and they require conditioning for a minimum of 48 hours in temperature and relative humidity conditions of between 23 ± 3°C and 12 ± 3% R.H. Resistance values of the samples can be obtained as a series of readings, with an average, minimum and maximum values of resistance from 6 samples needed to be reported as a result with the conditioning period, relative humidity and temperature. However, for the volume resistance, the thickness of the samples is also required.

AATCC test method 76: 'Electrical resistivity of fabrics' (American Association of Textile Chemists and Colorists, 2000): This method assesses the surface resistivity for fabric material, wherein either concentric ring electrodes or parallel plate electrodes can be used for measuring the electrical resistivity of fabrics. However, the use of a parallel plate electrode requires two sets of tests, in both length and width directions, with the electrodes located 25mm from each other. For concentric ring electrode, one set is enough because both length and width directions can be achieved simultaneously. The test specimen is placed in contact with the electrodes after conditioning in a chamber at a temperature range of 23 ± 3°C and humidity between 20 and 65% r.h., with lower humidity being preferred. Current passed through the specimen is measured after supplying between 80-100 volts of power to the electrode.

Resistivity of specimens is calculated from **Equation 2.13** for the parallel plate electrode and **Equation 2.14** (Suh, 2008; Maryniak, Uehara, & Noras, 2003) for the concentric ring electrode. The result should be reported in forms of the logarithm of the resistance (log R) with the number of specimens tested, environment conditions, and the direction of testing (in case of using parallel plate electrodes).

$$\rho = \frac{R \times W}{D} \qquad (\textbf{2.13})$$

$$\rho = \frac{2.73 \times R}{\log \frac{r_o}{r_i}} \qquad (\textbf{2.14})$$

Where,

ρ = surface resistivity (Ω)

R = measured resistance (Ω)

W = width of specimen (m)

D = distance between electrodes (m)

r_o = outer electrodes radius (mm)

r_i = inner electrodes radius (mm)

2.7.3. Resistivity values and their relevance to the textile industry

There is a certain range of electrical resistivity which makes the textile material safe for consumer and other industry applications. A value of 10^{11} ohm/square is considered to be indicative of a fabric with negligible static propensity (Schindler & Hauser, 2004). Also, some organizations like the Japanese Industrial Standard (JIS) and the Federal Test Standard (FTS) have chosen to define the problem along these terms:

- Insulative Material: Surface resistance $>1 \times 10^{11} \Omega$, or surface resistivity $> 1 \times 10^{12} \Omega/sq$

- Static Dissipative Material: Surface resistance between $1 \times 10^{4} \Omega$ and $1 \times 10^{11} \Omega$, or surface resistivity between $1 \times 10^{5} \Omega/sq$ and $1 \times 10^{12} \Omega/sq$.

Table 2.4 Surface resistivity of antistatic finished textiles relating to static propensity (Schindler & Hauser, 2004)

Surface resistivity range ($\Omega/sq.$) at 65% r.h.	Assessment
$1 \times 10^{6} - 1 \times 10^{8}$	Very good
$1 \times 10^{8} - 1 \times 10^{9}$	Good
$1 \times 10^{9} - 1 \times 10^{10}$	Satisfactory
$1 \times 10^{10} - 5 \times 10^{10}$	Limit of sufficiency
$> 5 \times 10^{10}$	Insufficient

CHAPTER 3: METHODOLOGY AND EXPERIMENTAL PROCEDURES

3.1. The approach of our research and its advantages

The approach of this research was to treat 65%-35% polyester-cotton blend fabrics with

a combination of functional silica nanoparticles and ionic monomers, in conjunction

with plasma technology.

The aim was to obtain an antistatic finish on the surface of the fabric with the purported

advantages of

1. Excellent antistatic properties,

2. Easy processing, and

3. Low cost

Plasma treatment modifies fabric surfaces both physically and chemically. Plasma

technology would help create active sites on the surface of the substrate. These active

sites or free radicals initiate the grafting polymerization reaction of the ionic monomers

on the fabric surface. Plasma treatment is a totally dry-processing technology, unlike

conventional wet-processing (Fridman, 2008; Shishoo, 2007).

Functionally modified silica nanoparticles are used in this research as they have very

small particle diameter (approximately 12 nm) and a large number of surface

methacrylate groups (~565 methacrylate groups/particle) (**Figure 2.10**). The silica

particles are themselves covalently bonded to the surface of the fabric. These help to

improve the roughness of the fabric surface and thus better the durability of the finish

on the fabric surface. The increased surface roughness leads to increased surface area

due to the undulations, and provides more sites for the monomers to attach and begin

polymerization. Ionic monomers that were used in this research were 2-acrylamido-2-

methyl-1-propanesulfonic acid (AMPS) and sodium vinylsulfonate (NaVS) (refer **Figure 3.1** and **Figure 3.2** for the chemical structures of AMPS and NaVS respectively) provide free ions which increase the surface conductivity of the fabric, thus imparting the desired antistatic properties.
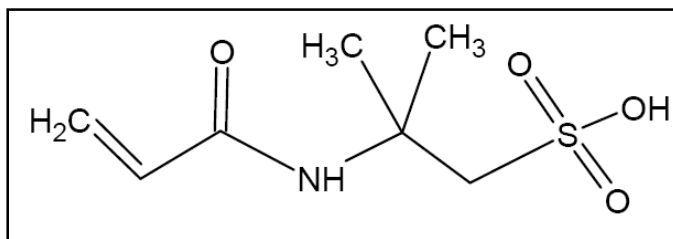
Figure 3.1 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS)
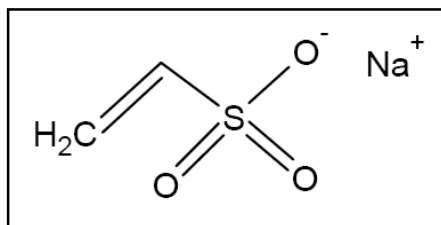
Figure 3.2 Sodium vinylsulfonate (NaVS)

Figure 3.3 gives a better idea of the attachment of the treatment to a cellulosic fabric. The crosslinkers work to form a three-dimensional network between the silica nanoparticle clusters and the ionic monomers. The attachment of the ionic monomers to the fabric surface through direct bonding and through the crosslinkers and on top of the silica nanoparticles help to give an uneven and rough surface which can help impart better antistatic properties.
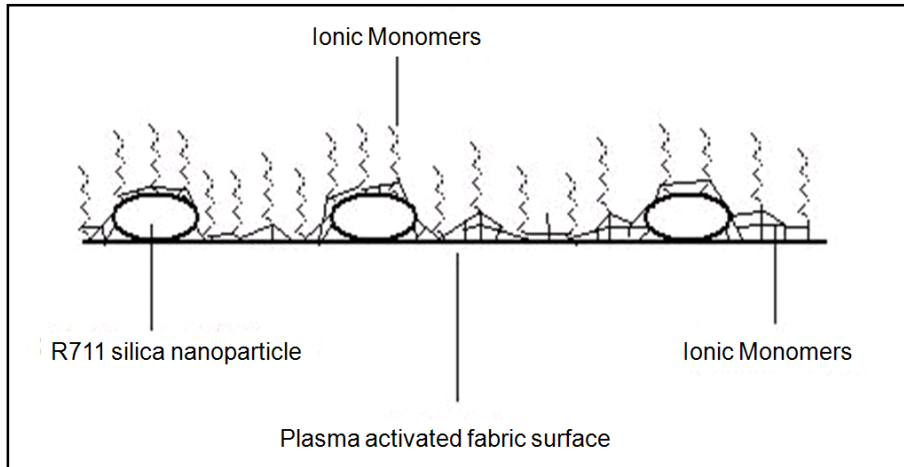
Figure 3.3 Mechanism of attachment of the chemical treatment to the fabric surface (Roe, 2008)

The plasma treated samples were also compared to samples that were prepared by thermally treating the substrate with a conventional free radical initiator, potassium persulfate ($K_2S_2O_8$).

3.2. Experimental design

This research investigated the effect of

1. plasma treatment times,

2. silica nanoparticle concentrations,

3. gases used for plasma treatment, and

4. treatment procedures

on the final antistatic properties of the finished fabric.

A design of experiment (DOE) was framed taking into account that there would be three treatment times with plasma, four different concentrations of silica nanoparticles, two gases for plasma treatment (helium and a helium-oxygen mixture) and three different procedures for treatment of the fabric.

Three treatment times were used only with helium plasma. However it was decided to use only two plasma treatment times when a mixture of helium and oxygen gases was being used. This was because a high treatment time did not prove to be beneficial to the antistatic properties when the tests were run with helium plasma initially.

The experiments were performed by changing different parameters within a defined procedure, and then repeating the same over three different procedures of treatment. The three treatment procedures varied in the use of plasma treatment. These procedures included plasma treatment after padding with the ionic monomers and silica nanoparticles, plasma treatment before padding, and plasma treatment both before and after the chemical treatment. The experimental design can be summarized in **Table 3.1** below.

Table 3.1 Experimental Design

Experimental Designs		Gas used for Treatment	Plasma treatment time	Silica nanoparticle concentrations used in the chemical dispersion.
I	Pad→Dry→ Plasma	Helium \	10 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
			20 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
			30 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
		Oxygen	10 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
			15 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
II	Plasma→Pad→Oven Dry.	Helium	10 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
			20 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
			30 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
		Oxygen	10 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
			15 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
III	Plasma→Pad→Oven Dry→Plasma.	Helium	10 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
			20 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
			30 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
		Oxygen	10 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl
			15 seconds	0 gpl, 0.5 gpl, 1 gpl, 2 gpl

The above experiments were carried out with two ionic monomers, NaVS (sodium vinylsulfonate) and AMPS (2-acrylamido-2-methyl-1-propanesulfonic acid), used separately with different concentrations of silica nanoparticles. The concentration of ionic monomers was maintained constant throughout the conducted experiments at 1% (w/vol), which would translate as 10 grams per liter of aqueous solution. The experimental procedures are explained in the next section. Three fabric samples were used for each combination of parameters.

3.2.1. Control samples
'Control samples' were always made for every section of treatments. These samples were treated like the other samples, but without any chemicals on their surface.

3.2.2. Treatment with a conventional free radical initiator
In order to compare the effects of plasma treatment with the conventional treatment methods in achieving graft polymerization, a set of samples was treated using potassium persulfate as a free radical initiator, instead of plasma. These samples were not plasma treated and the concentrations of silica nanoparticles used in this case were 0.5 gpl and 0.1 gpl.

3.3. Experimental procedure and testing methods
3.3.1. Dispersion preparation:
Silica nanoparticles were added to an aqueous solution of ionic monomers and dispersed vigorously for at least 30 minutes. The monomer concentration was fixed at 1% (w/vol), or 10 gpl. After this treatment, ultrasound was used to break down the size of the aggregates, and stirring was commenced again using a magnetic stirrer for up to 18 hours. No dispersing agent was added.

3.3.2. Fabric preparation:

The fabric used throughout the research was a scoured 2×1 twill, 65%-35% polyester-cotton blend, which was obtained from the College of Textiles Pilot Plant. The experiments were carried out on pieces of fabric that measured 15cm×15cm. Since the fabric is a 2×1 twill weave, there is an unequal distribution of the warp thread on either side of the fabric. Therefore, the 'face' (the side which has a greater proportion of exposed warp thread) of the fabric was chosen and marked as the side which would be treated with atmospheric plasma. Frayed edges on the cloth were removed.

3.3.3. Chemicals and equipment used in this research
3.3.3.1. Aerosil® R711 silica nanoparticles

Aerosil® R 711 silica nanoparticles were used in this research and have been described as fumed silica aftertreated with a methacrylsilane. These nanoparticles have an average particle size of 12 nm and up to 565 methacrylate groups/particle (**Figure 2.10**).

A single silica nanoparticle would look like the diagram shown in **Figure 3.4**. This is not to scale and is drawn for representative purposes only. The fuzzy hair-like structures on the diagram are the functional groups that are attached to the silica nanoparticle surface. The functional groups can be involved in the grafting polymerization.
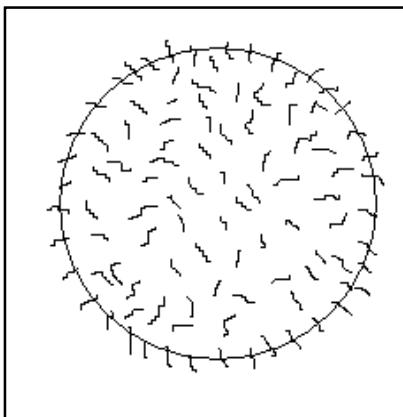
Figure 3.4 Representation of a single silica nanoparticle

3.3.3.2. Ionic monomers

The ionic monomers used in this research were sodium vinylsulfonate (NaVS) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) to provide high surface conductivity.

3.3.3.3. Potassium persulfate (free radical initiator)

A 99% pure potassium persulfate powder was obtained from Sigma- Aldrich®, for its use in experimentation as a free radical initiator.

3.3.3.4. Atmospheric plasma treatment machine

The machine used to conduct the experiments on the substrates was the APJeT APPR (Atmospheric Pressure Plasma Reactor). This machine is scaled to a capacity that can suit research and development, and the APPR Model 300-13 is housed in room 3231 in the College of Textiles. **Figure 3.5** is an image of the APPR model 300-13.
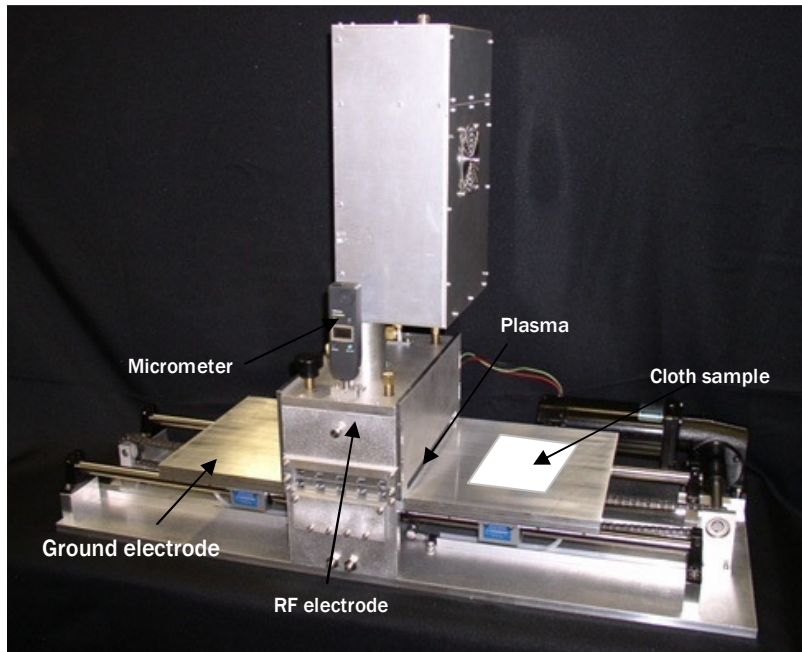
Figure 3.5 APPR 300-13 atmospheric plasma treatment machine (www.apjet.com, 2009)

In the APPR 300-13, the substrate is placed on a metal plate electrode and conveyed by motor drive through the plasma inside the rectangular center assembly. The machine can be operated and adjusted for both batch and continuous operations by attaching rolls on both the 'in' and 'out' ends to dispatch and collect the cloth. Thus it can be used economically for test runs.

3.3.3.4.1. Using the plasma machine

Two gases were used in this research: helium and a helium-oxygen mixture. The flow rate of the gas mixture was adjusted to 40 standard liters per minute (slpm). The helium-oxygen mixture was adjusted so that oxygen constituted 1% of the volume of gas mixture, and helium, 99%.

3.3.3. Procedures
3.3.3.1. Pad→ Air Dry→Plasma

The Fabric was dip-coated with the mixtures, padded at 80% expression, dried under atmospheric conditions and fed into an atmospheric plasma system, APPR Model 300-13, to carry out the surface treatment. The drying was carried out under atmospheric temperature and pressure, to prevent any polymerization reaction from occurring due to heat activation. The sample was then conditioned at 21°C and 43% relative humidity for 48 hours.

3.3.3.2. Plasma→ Pad→ Oven Dry

In this treatment procedure, the raw fabric samples were plasma-treated and immediately dip-coated with the prepared dispersion and padded at 80% expression. The treated sample was then oven dried at temperatures between 100°C and 115°C for one hour. The sample was then conditioned at 21°C and 43% relative humidity for 48 hours.

3.3.3.3. Plasma➔Pad➔Oven Dry➔Plasma.

This procedure incorporated plasma treatment as the beginning and ending steps to the procedure. The raw fabric samples were first plasma treated, followed immediately by the padding and drying process. The drying was carried out in an oven at temperatures between 110°C- 115°C for one hour. The dried sample was subjected to another round of plasma treatment, and later subjected to conditioning in the environmental room at 21°C and 43% relative humidity for 48 hours.

3.3.3.4. Treatment procedure with potassium persulfate initiator

In this procedure, firstly, a solution of potassium persulfate was made to the required concentration of 30mmol/L. The fabric samples were first padded through the monomer and silica nanoparticle dispersion. After this, the samples were padded through the potassium persulfate solution. The samples were then cured in the oven at 110°C for 1 hour.

3.3.3.5. Rinsing of the samples to evaluate fastness of the finish

The treated samples were conditioned between 24 hours to 48 hours in the environmental room at 21^oC and 43% relative humidity. A comparison test was carried out by subjecting the samples to a rinse test. In this procedure, the sample was taken and held under a stream of running tap water. The fabric was lightly wrung and contorted to enable the flow of water through the substrate. The procedure was carried out for a minute under running cold water at $17-20^oC$. The fabric was then squeezed to remove any excess water, oven dried for 45 minutes to 1 hour at 110^oC and then conditioned at 21^oC and 43% relative humidity.

3.3.4. Testing

Evaluation of the antistatic properties of the treated fabrics was carried out by determining the surface resistivity properties of the fabric before and after treatment. In order to check for the durability of the finish on the fabric surface, it was also important that the surface resistivity of the fabric be measured after rinsing. In order to verify some of the results of the testing, a certain number of samples was also subject to testing that assessed their ability to dissipate charge. This was done with a contact charge dissipation device that was designed at NC State. The testing was carried out under controlled environmental conditions, with the entire apparatus being housed in the Environmental Room in Lab 1311 of the College of Textiles.

The Environmental Room is a walk-in chamber equipped with an air controller (by Generation and Control, Inc.) and insulated panels (by Kysor Panel Systems) for efficient temperature and humidity control. The dimensions of the room are 3.25 m (width) × 2.64 m (length) × 2.64 m (height). The temperature and relative humidity of this room can be controlled between 7°C-60°C and 10%-95% relative humidity (Suh, 2008). In this research, a temperature of 21°C and relative humidity of 43% were used.

3.3.4.1. Surface resistance measurement

Testing was carried out using a surface resistance meter, manufactured by Trek. Inc. This meter is an electrode assembly consisting of two electrodes arranged in a concentric fashion to contact the material being tested. The inner electrode is a solid disc having a diameter of 30.48 ± 0.64 mm. The outer electrode is a ring having 57.15 ± 0.64 mm inner diameter and a ring thickness of 3.18 ± 0.3 mm. The device conforms to the ANSI/EOS/ESD S.11.11 standard for testing materials, and is also compatible with

the AATCC Test Method 76, for measuring the electrical resistivity of fabrics. The total weight of the electrode assembly is 2.27 kilograms. The resistance range that can be tested at a voltage of 10V ranges from 10^3 to 10^{13} ohms. The results however, required surface resistivity, which is the surface resistance over a unit area.

Figure 3.6 Concentric ring electrode and electrode setup

The prepared samples measuring 15 cm × 15 cm were conditioned for 24 to 48 hours at 21°C and 43% humidity. The samples were then tested for resistivity using the resistance meter, in conformance with the AATCC test method 76, testing the electrical resistivity of fabrics. The fabric sample was placed on a non conducting surface and three readings for resistance were taken by placing the concentric ring electrode on different locations of the fabric surface and noting the values for resistance. The resistivity of the sample was then calculated according to **Equation (3.1)**

$$\rho_s = \frac{2\pi R_s}{\ln \frac{D_2}{D_1}} \qquad \textbf{(3.1)}$$
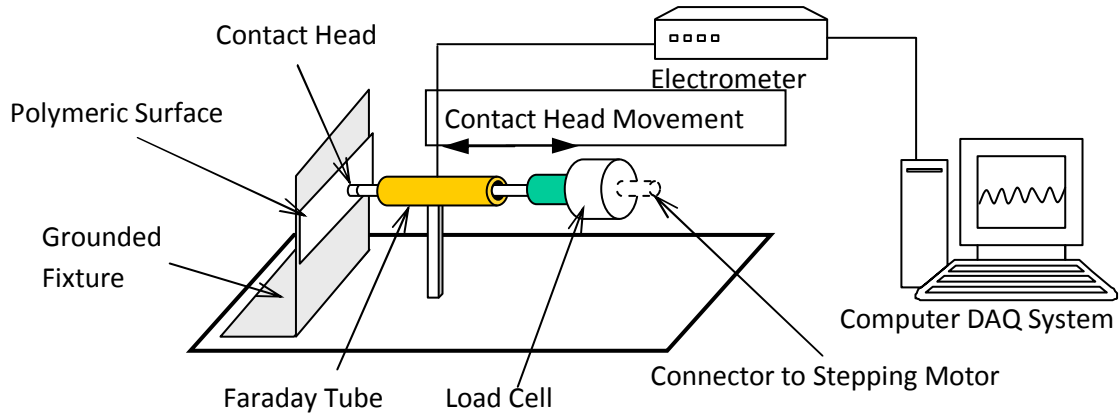
Where

ρ_s = surface resistivity (Ω/cm^2)

R_s = measured surface resistance (Ω)

D_1, D_2, = electrode diameter (cm)

3.3.4.2. Contact charge generation and dissipation

Figure 3.7 Contact charge generation/dissipation measurement device (Seyam et al., 2008)

Surface resistance measurement is an indirect method. In order to further understand the antistatic properties of treated fabrics, contact charge generation and dissipation were carried out. **Figure 3.7** shows the device that was used to measure the amount of electrostatic charge generated on the fabric sample (6 mm diameter) placed on a contact head, which was contacting a polymeric surface (such as Teflon used in this work) (Seyam et al., 2008). The Teflon piece was connected to a grounded metallic fixture, which was used to impart charge to the fabric sample. A Faraday tube was used for probing the charge amount on the sample affixed to the contact head. For each contact, the step motor drives the contact head with controlled speed and pressure to establish contact between the Teflon piece and the surface of the tested fabric, and then the contact head was withdrawn into the Faraday tube. Thus static charge amount was collected after each contact and separation (cycle). The procedure was repeated in order

to measure the change of static accumulation after certain number of contact cycles that enabled the evaluation of saturation charge (maximum charge that the surface can accumulate). The charge amount was measured by a Keithley 6514 electrometer. The contact force was monitored by a pressure load cell. The desired test parameters (contact pressure, number of contacts, rate of data collection, and contacts/minute) were automatically controlled through a user interface. The static generation/dissipation data were automatically recorded using computer data acquisition (DAQ) system. The entire device was housed inside a walk-in environmental room where temperature and humidity conditions were controlled at 21°C and 43% relative humidity (Seyam et al., 2008).

3.3.4.3. Scanning Electron Microscope Analysis

Microscopic images of the treated fabric samples were taken to help observe the finish on the fabric, before and after rinsing. The images were obtained on a field-emission scanning electron microscope (FESEM), JEOL model JSM-6400F. Elemental analysis was performed on another SEM, the Hitachi s-3200N in the Analytical Instrumentation Facility at North Carolina State University (NCSU).

CHAPTER 4: RESULTS AND DISCUSSIONS

## 4.1.SEM imaging of plasma treated fabrics

Some selected samples that were plasma treated were observed under SEM to observe

the appearance of the chemical finish on the surface of the treated fabrics. SEM imaging

was performed only on samples that had a combination of ionic monomers and 0.5gpl

of silica nanoparticles. SEM images were also performed after the samples were rinsed

in order to assess if the antistatic finish applied to the fabrics was present or washed off.

In addition, elemental analysis was also performed on selected samples to confirm the

presence of the finish on the fabric.

4.1.1. SEM results of AMPS treated fabrics before and after rinsing

Figure 4.1 shows the dispersion of silica nanoparticles and polymer grafts on the

surface of the individual fibers. As shown in **Figure 4.1a**, individual fibers have small

white clusters on them. **Figure 4.1b** is the magnification of one such spot on the surface

of the fiber. These clusters are in fact networks of silica and the formed polymer. They

differ in size and shape throughout the fabric surface and the distance between each

cluster varies. The results show that silica nanoparticles do not spread evenly on the

surface; they tend to form clusters on the fiber/fabric surface. Silica particles help form

rough surfaces, thereby increasing the surface area and providing more sites for the

monomers to attach and begin graft polymerization.
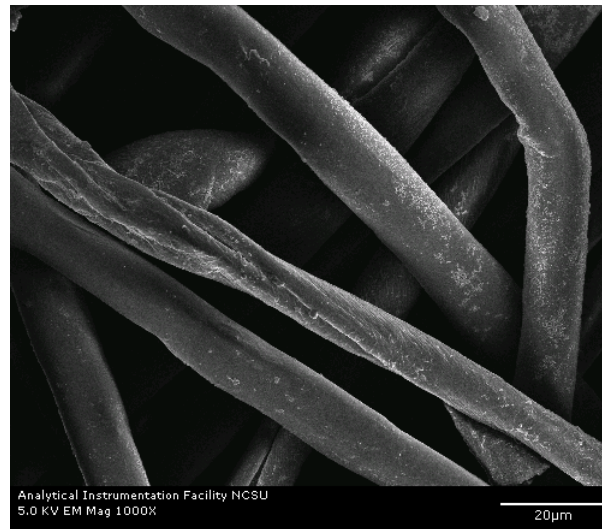
a)
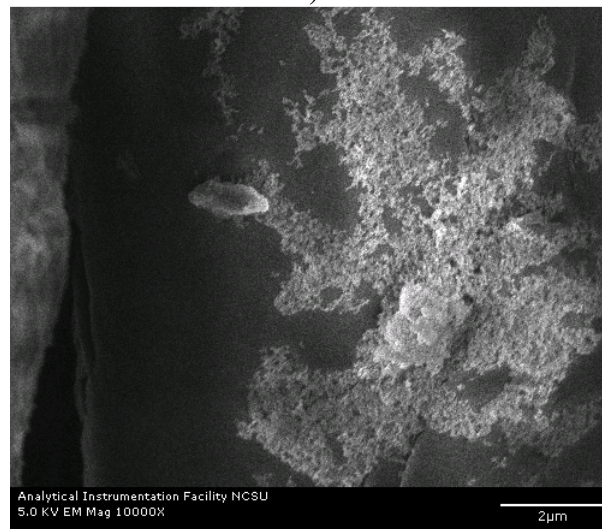
b)

Figure 4.1 Scanning electron micrographs of samples treated with a combination of AMPS/0.5gpl silica/helium plasma at a) 1000X magnification and b) 10000X magnification

Figure 4.2 shows the presence of silica nanoparticle clusters before and after rinsing the

fabric.
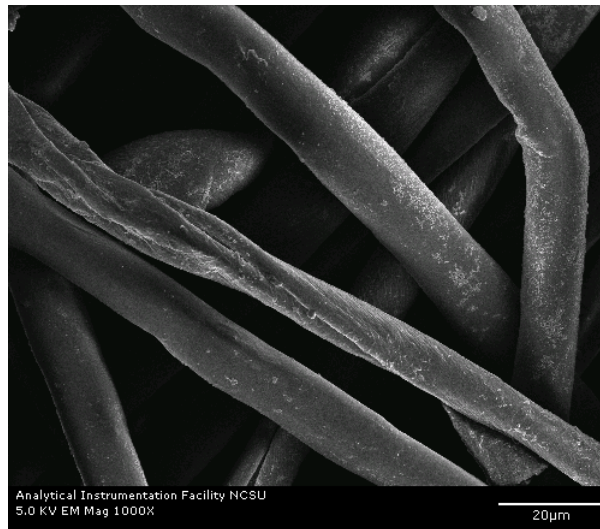
a)
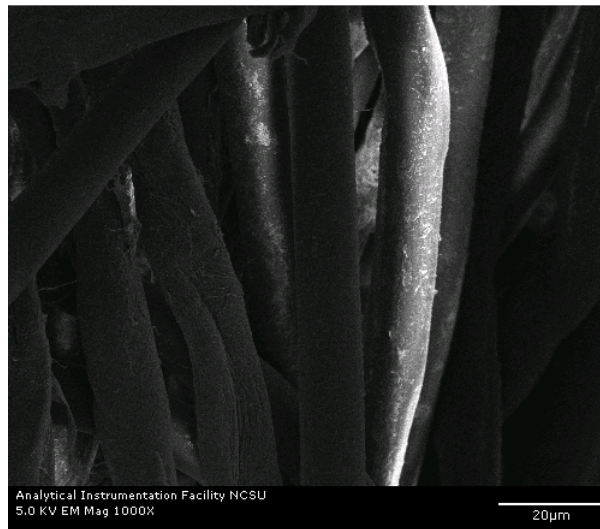
b)

Figure 4.2 Scanning electron micrograph images of helium plasma treated AMPS/silica samples a) before rinsing b) after rinsing

It is evident from **Figure 4.2b**, that there are definitely some clusters of nanoparticles and polymers that are left even after rinsing. The delicacy of the rinse test in this research, however, is a matter of consideration. One would surmise that these nanoparticles would get washed away if subjected to a full wash fastness test.

4.1.2. SEM results of NaVS treated fabrics before and after rinsing

SEM images were also taken for samples that were treated with NaVS and silica nanoparticles (0.5 gpl concentration). Figure 4.3 shows the affixed polymer-nanoparticle networks on the fiber surface. The size and shape of these clusters does not apparently change upon the addition of a new monomer (i.e., NaVS) for graft polymerization.
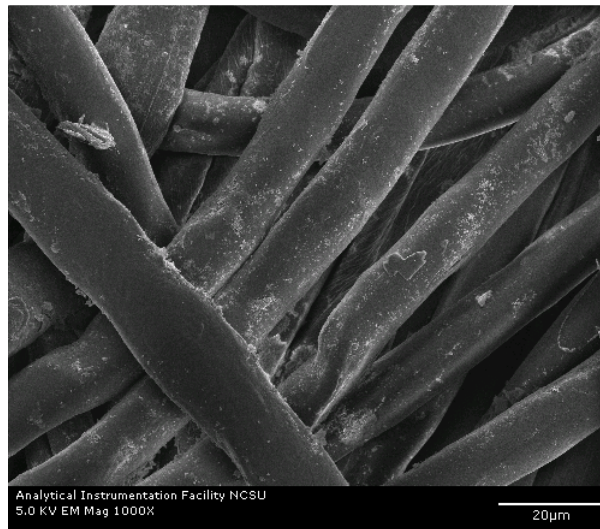
a)
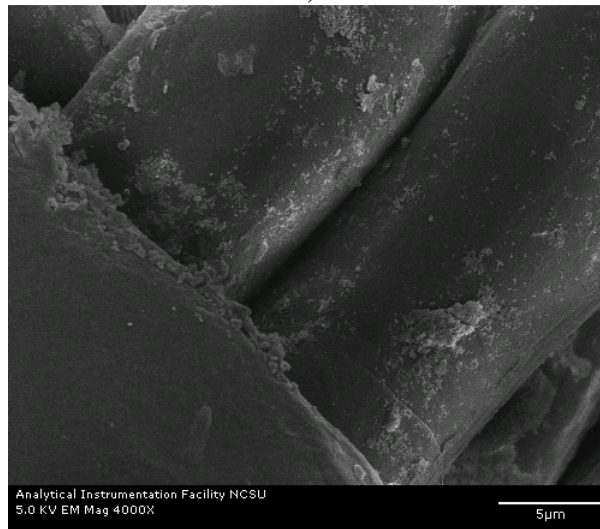

b)

Figure 4.3 Scanning Electron Micrographs of samples treated with NaVS/0.5gpl silica/helium plasma at a) 1000X magnification and b) 4000X magnification

Figure 4.4 compares SEM images of samples .before and after rinsing.
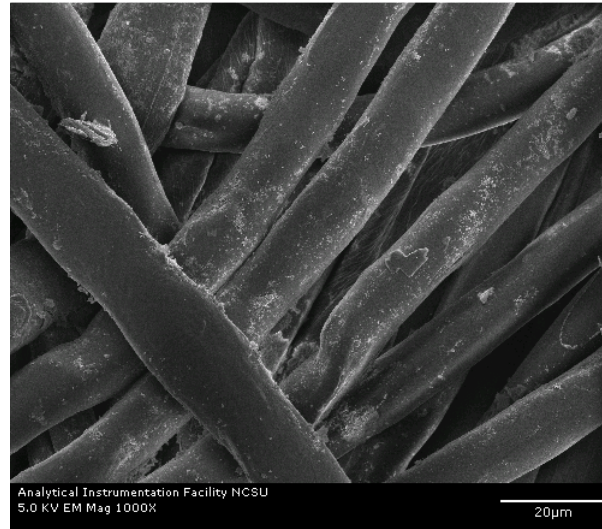
a)
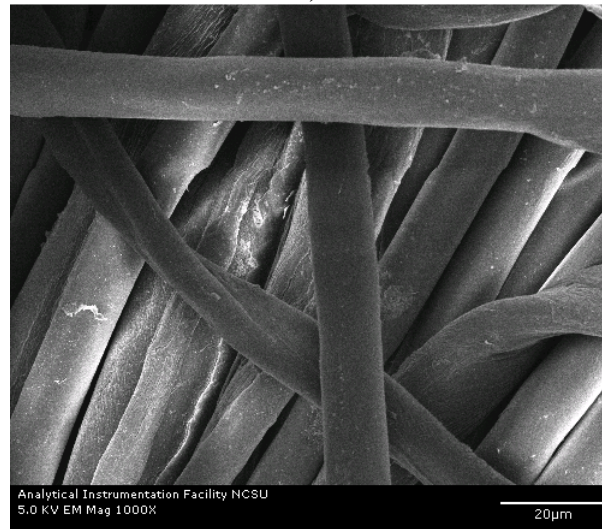
b)

Figure 4.4 Scanning Electron Micrograph images of a sample treated with NaVS/0.5gpl silica/helium plasma a) before rinsing and b) after rinsing

It can be observed in **Figure 4.4a** that there seem to be much more white 'crusts', than in **Figure 4.4b**, which represents a rinsed sample. It is quite possible that many of these nanoparticle-polymer clusters were washed away from the region, resulting in a far smoother and cleaner looking appearance of the individual fibers.

4.1.3. Elemental analysis of fabrics under SEM

It could be debated that the little clusters found on the surface of the fibers, observed under SEM, are not polymer-nanoparticle networks. Thus, elemental analysis of the samples was carried out in order to confirm the presence of the polymer network on the substrate. The monomers used in this research were sodium vinylsulfonate (NaVS) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). These were bound to the substrate surface with fumed silica nanoparticles. If one were to break all these chemical structures down to their elemental constituents, the main elements that would indicate the presence of these materials would be silicon (Si), sulfur (S) and oxygen (O). Carbon (C) is present everywhere, including the fabric (polyester-cotton) and therefore the change in carbon content brought about by the growth of polymer chains on the substrate would be negligible. A change in oxygen content after surface treatment would be easier to notice than carbon, although oxygen is already present in both cotton and polyester molecular structures. An increase in the sulfur content would indicate that there are a good number of sulfonic acid ions due to the polymerization of both the ionic monomers. An increase in silicon (Si) would obviously indicate the presence of silica nanoparticles in that particular region.

It would be wise in this case to draw a comparison between the elemental compositions of a raw fabric and a fabric that has been treated with the antistatic finish. Elemental analysis of fabrics was performed on the Hitachi S-3200N SEM machine, by means of energy dispersive X-ray spectroscopy (EDS). **Figure 4.5** and **Figure 4.6** show the elemental analyses carried out on untreated and finished fabrics respectively.

Figure 4.5 Energy Dispersive Spectroscope analysis of untreated fabric
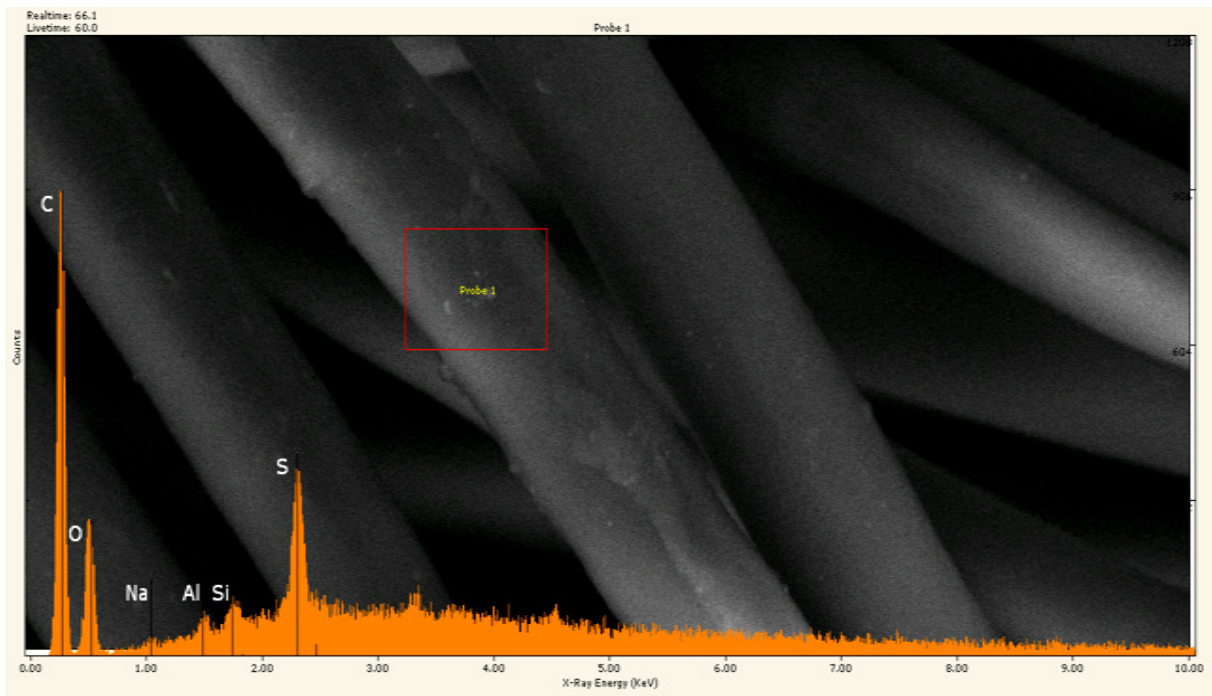
Figure 4.6 Energy Dispersive Spectroscope analysis of plasma treated fabric containing NaVS/0.5gpl silica

The results, obtained from **Figure 4.5** and **Figure 4.6** clearly reflect certain trends. It must firstly be noted here that the presence of aluminum (Al) in both charts is indicative of foreign impurities (such as clay) in the fabric. From comparison, it can be noted that the raw fabric had lower levels of sulfur and silica and comparatively lower levels of oxygen. The higher levels of sulfur and oxygen in **Figure 4.6** suggests that the sodium vinylsulfonate underwent polymerization on the surface of the fiber, forming poly(vinylsulfonic acid). This results in a large number of localized sulfonic acid groups that are capable of dissipating charge, and thus function to increase the antistatic capability of the fabric. In case of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), polymerization occurs and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) or PAMPS is formed, which would show up on the EDS analysis as pronounced sulfur and oxygen peaks.

The antistatic capabilities of the finished fabric are discussed in the next section.

4.2. Resistivities of fabrics treated by: I. pad → air dry → plasma treatment

The treatment procedure in this experimental design consisted of padding the polyester-cotton samples through the chemical dispersion and allowing them to dry under atmospheric conditions, followed by plasma treatment. The treatment time and concentration of silica nanoparticles were varied.

4.2.1. Helium plasma treatment
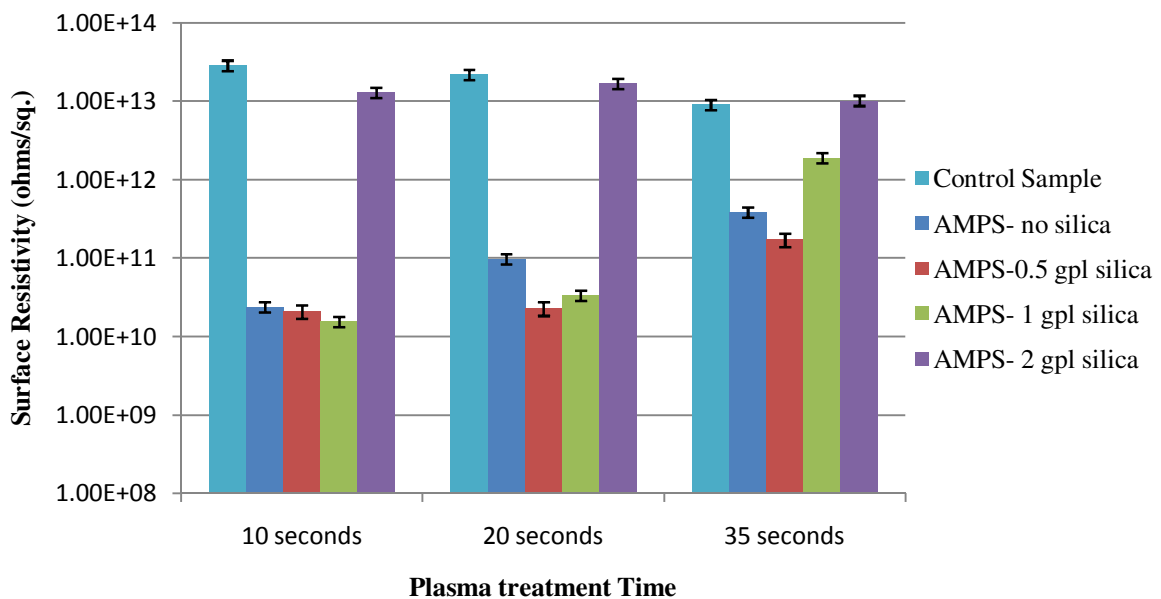
Figure 4.7 Surface resistivity of AMPS/silica/ helium plasma treated samples by the pad→air dry→ plasma treatment method

Helium plasma was used to treat the polyester cotton samples used in the experiment. Different parameters, such as silica concentration, monomer type, and plasma treatment time, were changed which led to different trends that are discussed in the following paragraphs.

Within a particular frame of plasma treatment time, a general trend is observed, in that the control samples have the highest resistivity of all the fabrics treated. The resistivity decreases as silica concentrations in the dispersion increase. However, it is seen that the trend bottoms out and the resistivity of the samples increase as the concentration of silica nanoparticles increases beyond 0.5 gpl for treatment times of 20 and 35 seconds; and 1 gpl for a plasma treatment time of 10 seconds. In this case, it is observed that the resistivity of the samples treated with AMPS and silica is lesser than the resistivity of the samples with only ionic monomers on them. The silica nanoparticles help crosslink and attach a large number of monomers to the substrate surface. A greater number of monomers polymerizing would imply that there are more charges that would help dissipate the built up static charge and thus lower the surface resistivity. At higher concentrations of silica nanoparticles, however, the suspicion is that the silica nanoparticles form too many aggregates on the surface of the substrate and do not serve their purpose of crosslinking the monomers effectively. Silica in itself is a charge insulator and cannot dissipate static effectively.

The effect of plasma treatment time can also be studied from **Figure 4.7**. Across times of plasma treatment, it is noticed that as the treatment times increase, the resistivity of treated samples increases. The control samples however show decreasing resistivity as the time of plasma treatment increases. It has been shown in earlier works (Bhat & Benjamin, 1999) that the static dissipating properties of raw polyester and raw cotton increase with increase in plasma treatment times. However, in case of the treated samples, an increase in the plasma treatment time can possibly cause depolymerization

of the formed polymers, and weakening of the substrate due to excessive etching (Shishoo, 2007). Overexposure to plasma could also result in the formation of stable non-reactive species as a possible result of excessive radicalization due to the longer treatment times (Shishoo, 2007), therefore reducing the number of free ions to dissipate away static charge.
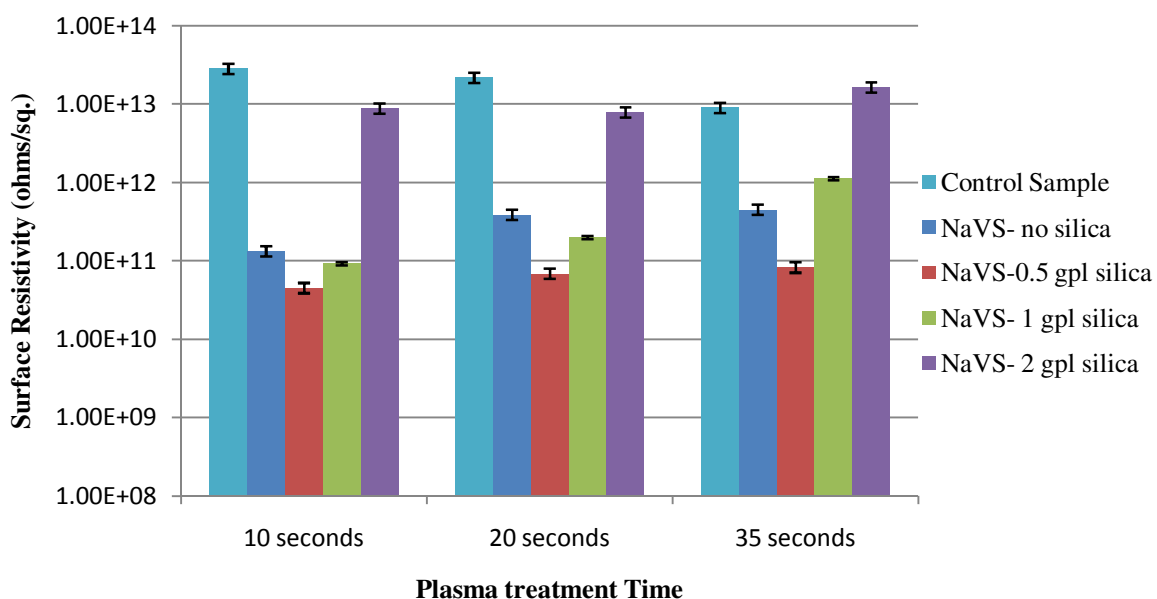
Figure 4.8 Surface resistivity of NaVS/silica/helium plasma treated samples by the pad→air dry→plasma treatment method

In the case of **Figure 4.8**, the results for the same treatment with NaVS are plotted as a series of columns. It is seen that the trend followed here is consistent with the trends observed in **Figure 4.7,** indicating that the general trends of resistivity remain irrespective of the type of ionic monomer used for treatment.

4.2.2. Helium-oxygen plasma treatment

In this section, polyester-cotton fabric samples were treated with two different ionic monomers, and later exposed to plasma treatment with a combination of Helium-oxygen plasma. The results of these experiments can be summarized in **Figure 4.8** and **Figure 4.9** for AMPS and NaVS treatment, respectively.
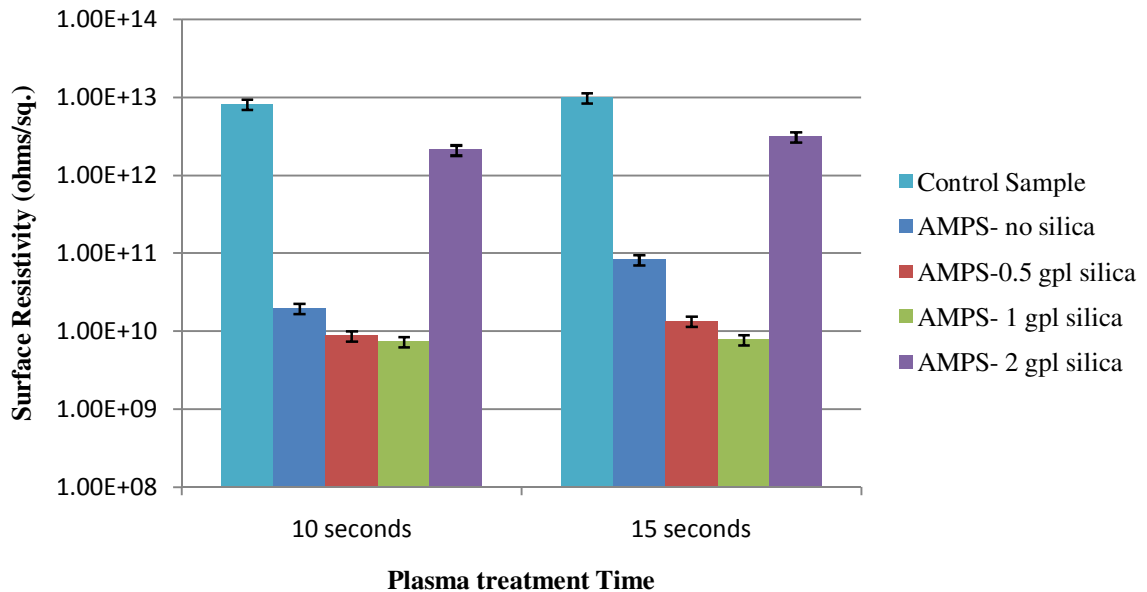

Figure 4.9 Surface resistivity of AMPS/silica/helium-oxygen plasma treated samples by the pad→air dry→ plasma treatment method

The treatment times with He-O plasma were limited to 10 and 15 seconds. The results obtained in this case showed clear trends as explained below. In this case, with AMPS, all the plasma treated samples have lower resistivity values than the control samples. The control samples thus, have the highest propensity to retain static charge on them. There is a remarkably big difference (up to 3 orders of magnitude) between surface resistivity of the control samples and the lowest resistivity values obtained with samples that were treated with a combination of ionic monomers and silica nanoparticles.

The effect of concentration of silica nanoparticles follows a certain trend in this case. It is observed that for the same plasma treatment time, the resistivity of the samples decreased as silica nanoparticles were added to the dispersion with which they were treated. The lowest resistivity was observed at nanoparticle concentrations of 0.5gpl. However, the values here tended to bottom out and as the silica concentrations in the dispersion increased, we noticed that the corresponding resistivity values increased.

Across plasma treatment times, a tendency toward an increase in resistivity was observed in the samples that were not treated with silica nanoparticles. The increase in resistivity is very slight in the case of increasing silica nanoparticle concentrations, and at 0.5gpl concentrations, the increase in resistivity over plasma treatment times can be considered negligible.
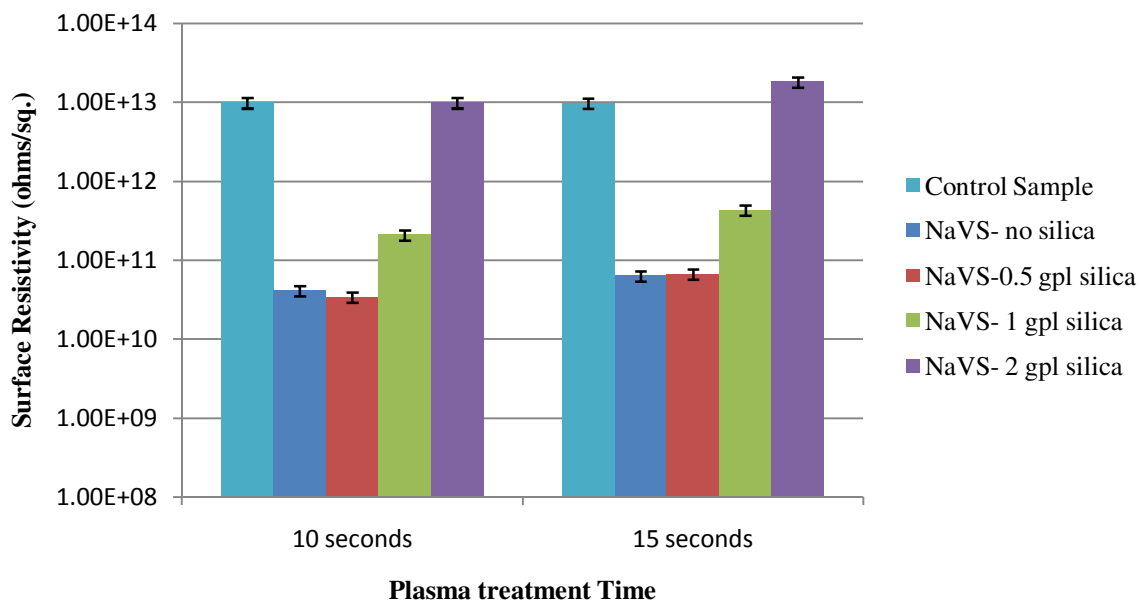

Figure 4.10 Surface resistivity of NaVS/silica/helium-oxygen plasma treated samples by the pad→air dry→plasma treatment method

Figure 4.10 shows the surface resistivity when helium-oxygen plasma treatment was imparted to samples that were padded and treated with a combination of NaVS and silica nanoparticles. In this case again, the control samples had resistivity values that were higher than the most of the chemically treated samples (barring the samples that were treated with 2gpl of silica). The surface resistivity values of the samples decreased as silica nanoparticles were added to the dispersion with which the samples were padded. The lowest values for resistivity were obtained when the concentration of silica nanoparticles in the dispersion was 0.5gpl, although it can be noted that the treated samples that had only ionic monomers in them were fairly low and had almost the same surface resistivity.

4.3.Resistivities of fabrics treated by: II. plasma treatment → pad → oven drying

In this procedure, the raw fabric samples were treated with atmospheric plasma. The plasma treated raw samples were then padded with the dispersion, followed by drying in an oven.
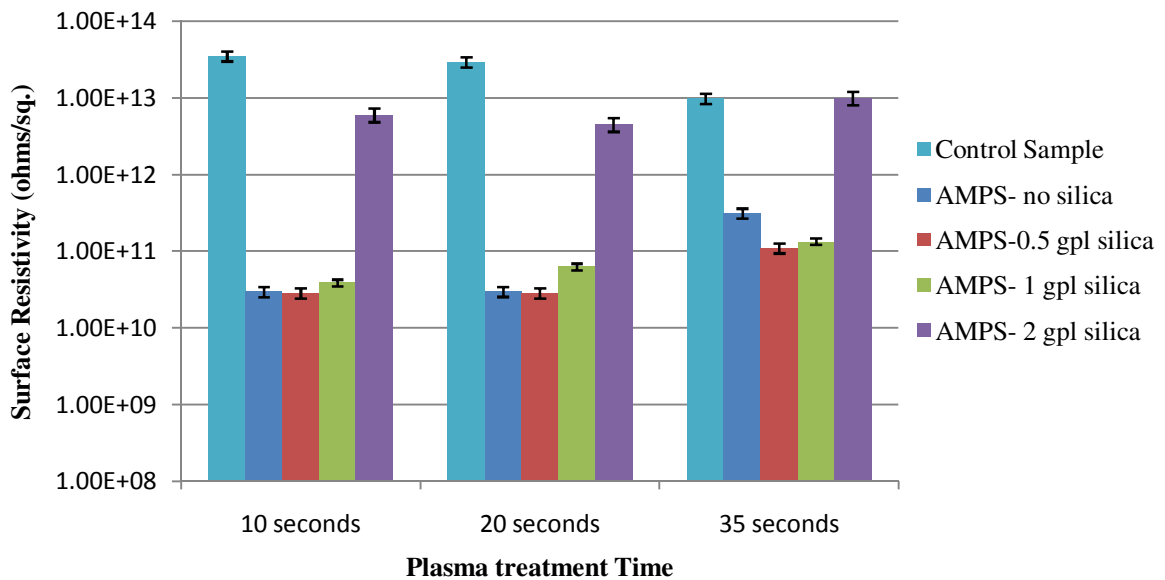
4.3.1. Helium plasma treatment

Figure 4.11 Surface resistivity of AMPS/silica/helium plasma treated samples by the plasma treatment→ pad→ oven dry method

Figure 4.11 shows the trends of surface resistivity of samples treated with AMPS and silica nanoparticles. The results for this procedure bear a resemblance to the results discussed for experimental design I in **Section 4.2**. It is noticed that the control samples have the highest resistivity among all the measured samples, in most cases.

The effect of different concentrations of silica nanoparticles gives rise to a certain trend in this case too. For the same plasma treatment time, the resistivity of the samples decreased as the concentration of silica nanoparticles increased in the dispersion bath.

The general trend was that a dip was observed over a particular range of silica concentrations between 0 and 1gpl. However, it must be noted that at concentrations above 1gpl, the resistivity showed a sharp increase, indicating that too much silica in the dispersion was detrimental to the antistatic properties of the fabric.

Across plasma treatment times, a tendency toward a slight increase in resistivity was observed in the samples that were treated with chemicals. The resistivity was the highest for the plasma treatment time of 35 seconds. However, as also noted in **Section 4.2.1**, the resistivity of the control samples decreased with increasing plasma treatment time.
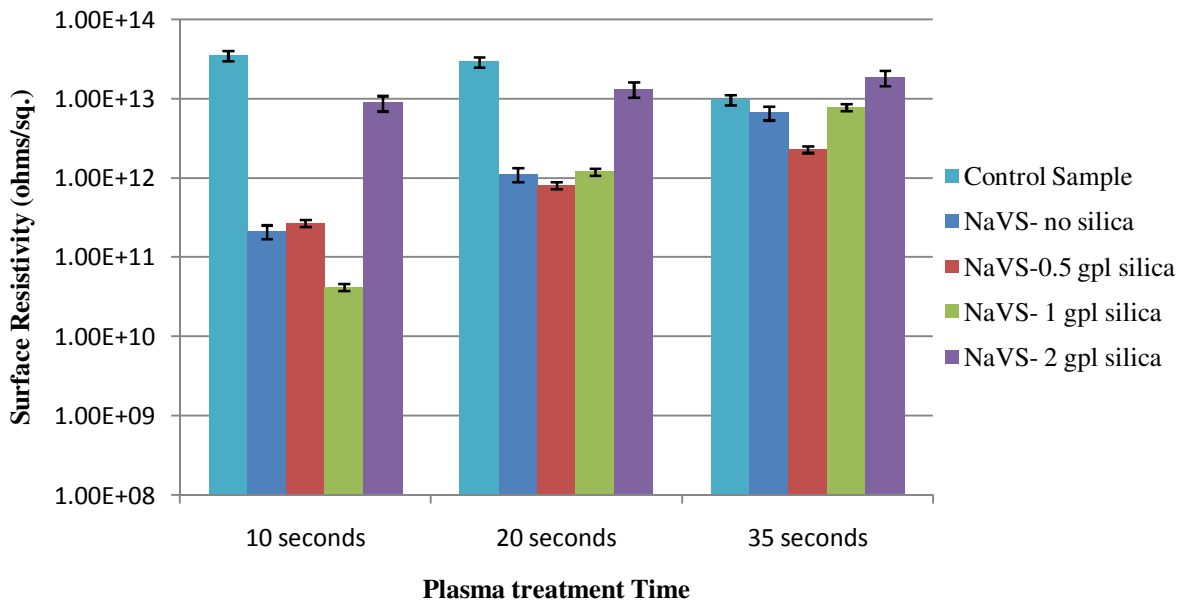

Figure 4.12 Surface resistivity of NaVS/silica/helium plasma treated samples by the plasma treatment→ pad→ oven dry method

In **Figure 4.12**, the only change in the procedure is the use of ionic monomer NaVS instead of AMPS. We notice that for samples that had been treated for 10 seconds, the minimum surface resistivity was observed when a combination of NaVS and 1gpl silica was used. However, with longer plasma treatment times, the minimum resistivity was observed at 0.5gpl of silica nanoparticles. The same trend is observed as far as silica concentrations in the dispersion are concerned, i.e., silica nanoparticles reduce resistivity values of the treated fabric up to an optimal concentration.

With increasing plasma treatment time, the resistivity of all but the control samples increased. Since the control samples are just raw fabrics that were plasma treated, they tended to respond positively to increasing plasma treatment times, i.e., their resistivity values were lowered (Bhat & Benjamin, 1999).

The next section discusses trends in the surface resistivity upon application of the same method with a different type of plasma.
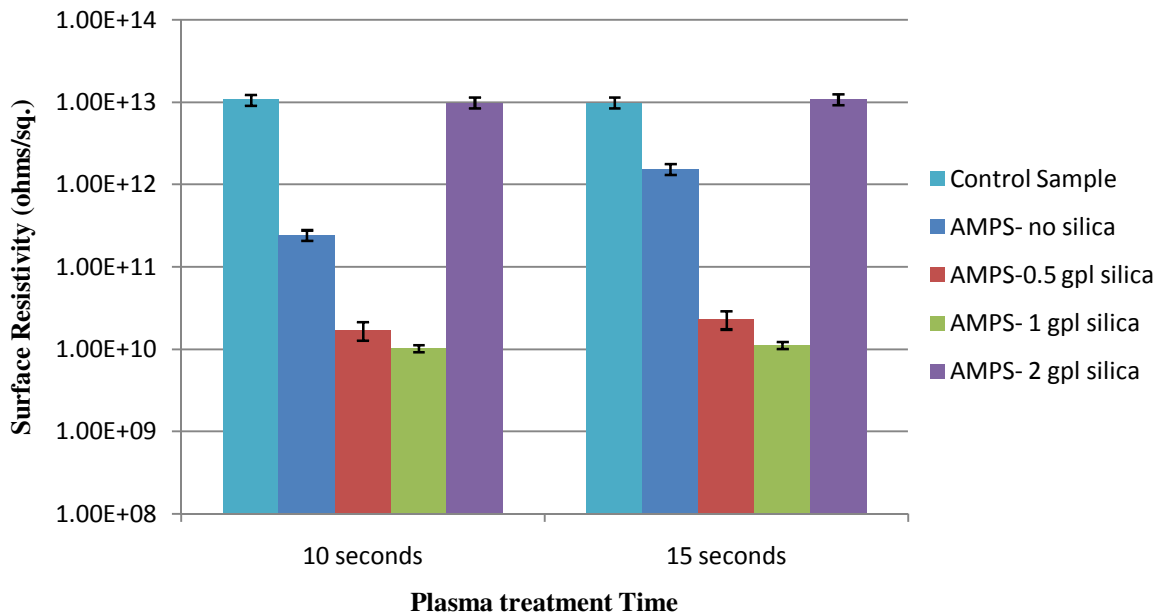
4.3.2. Helium-oxygen plasma treatment

Figure 4.13 Surface resistivity of AMPS/silica/helium-oxygen plasma treated samples by the plasma treatment→ pad→ oven dry method

Figure 4.13 summarizes the test results for samples treated with AMPS, silica nanoparticles and helium-oxygen plasma. It is observed that the control samples have the highest resistivity among all the treated when the silica concentration is lower than 2 gpl. The addition of nanoparticles seems to improve the antistatic properties of the fabric samples.

For the same plasma treatment time, the resistivity of the samples decreased as silica nanoparticles were added to the dispersion. The lowest resistivity was observed at a nanoparticle concentration of 1gpl concentrations at treatment times of 10 seconds. As the concentration of silica nanoparticles was increased beyond 1gpl in the dispersion, the surface resistivity values increased. As discussed in **Section 4.2**, it can be seen that

excess concentrations of silica nanoparticles are detrimental to the antistatic properties of the finished fabric.

Across plasma treatment times, a tendency toward a slight increase in resistivity was observed in all the samples, the effects in this case being pronounced in case of the samples that had no silica nanoparticles on them.

Figure 4.14 Surface resistivity of NaVS/silica/helium-oxygen plasma treated samples by the plasma treatment→ pad→ oven dry method
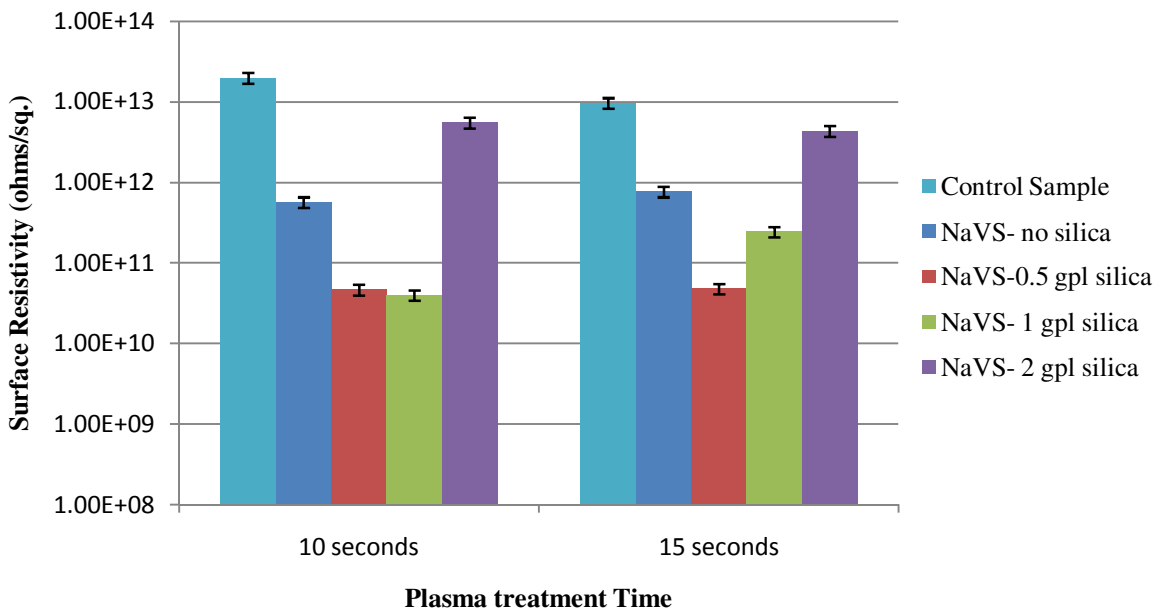
Figure 4.14 shows the resistivity results of fabrics treated with NaVS, silica nanoparticles, and helium-oxygen plasma. The trends observed are similar to the trends discussed for **Figure 4.13**. It can be said that the effect of plasma treatment time and concentration of silica nanoparticles seem to follow trends that are almost independent of the type of ionic monomers used in this research.

4.4.Resistivities of fabrics treated by: III. plasma → pad → oven dry → plasma

This method of treatment involves the usage of plasma twice. The first plasma treatment

is imparted to the raw fabric in order to prepare it for the chemical padding process. The

second treatment with plasma is carried out after drying the chemically treated fabric in

an oven. The control samples are subjected to plain plasma treatment twice.

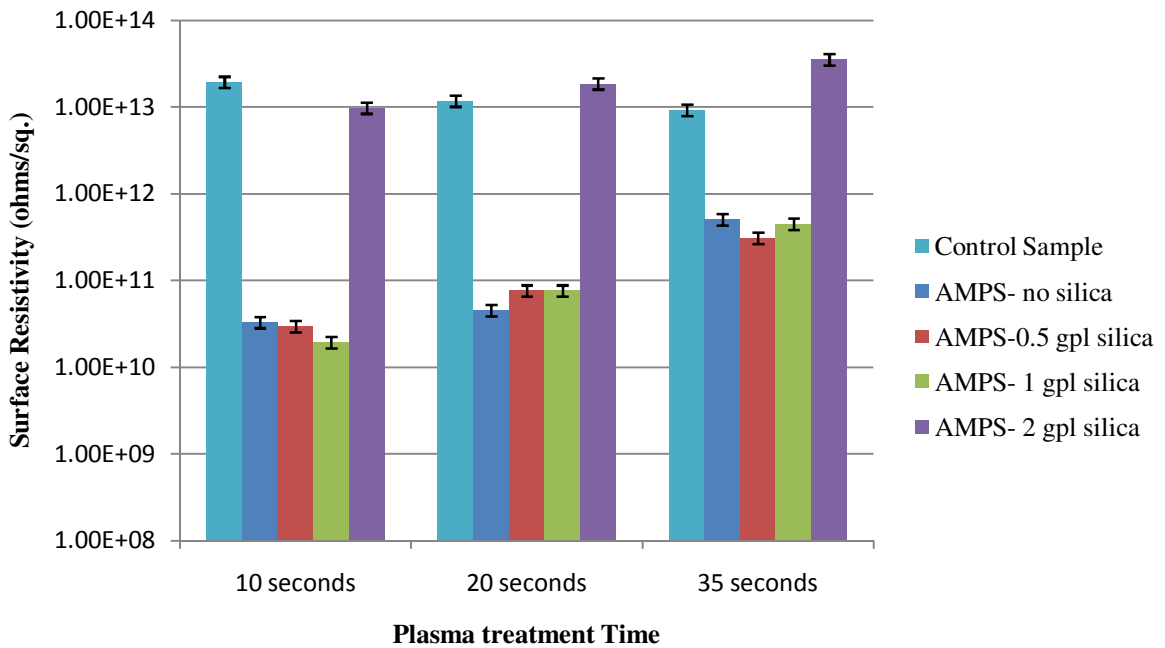**4.4.1. Helium plasma treatment**

**Figure 4.15 Surface resistivity of AMPS/silica/helium plasma treated samples by
the plasma treatment→ pad→ oven dry→ plasma treatment method**

Figure 4.15 shows the effects of treatment time and concentration of silica

nanoparticles on the surface resistivity behavior of the treated polyester-cotton samples.

A slightly different scenario can be seen in terms of trends observed as an effect of

silica nanoparticle concentration. In this case we can observe that the control samples in

this case have lower resistivities than the corresponding samples treated with AMPS

and 2gpl of silica nanoparticles after plasma treated for 20 seconds and 35 seconds

respectively. This can be attributed to the fact that these samples was plasma treated twice, and therefore the control samples have been exposed to up to 70 seconds of plasma treatment. This improves the antistatic properties of the control sample. The trends here as regards silica nanoparticle concentration are fairly clear in that, excess concentrations of silica (greater than 1gpl) are a clear deterrent to effective antistatic function, as deduced from the increased surface resistivity of the samples. It was also seen here that increasing plasma treatment times led to progressively increasing surface resistivity values in all but the control samples.
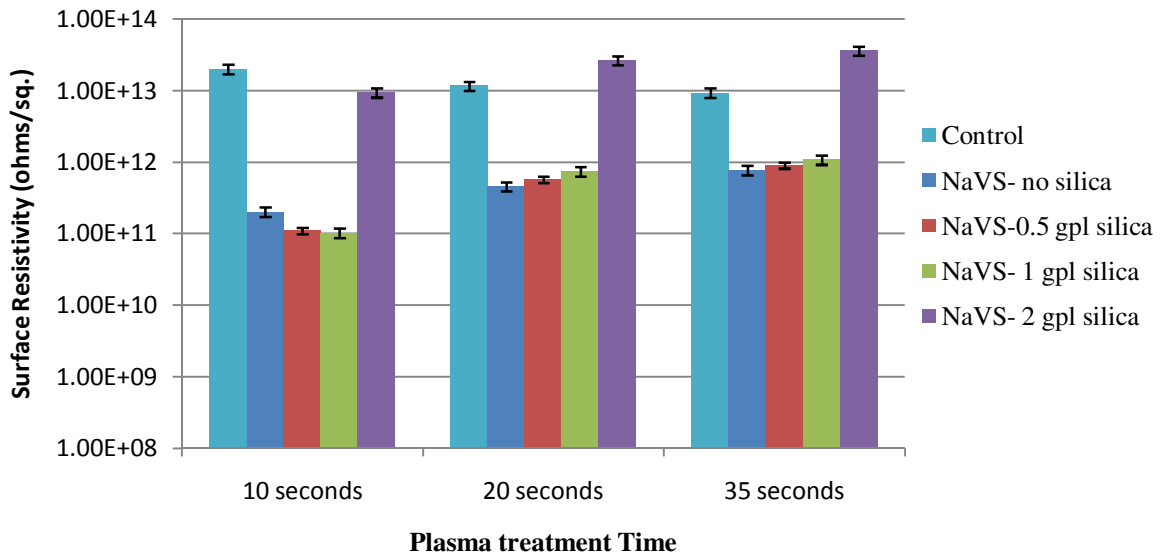
Figure 4.16 Surface resistivity of NaVS/silica/helium plasma treated samples by the plasma treatment→ pad→ oven dry→ plasma treatment method

In **Figure 4.16**, which shows the results obtained after changing the ionic monomer to NaVS, it is seen that the control samples have the highest resistivity among all the measured samples when the plasma treatment times is 10 seconds. However, because of the "double plasma treatment" (Bech et al, 2007) imparted to the fabrics, the resistivity

of control samples drops considerably as the plasma treatment time increases. Again, the results make it clear that there is an optimum concentration of silica nanoparticles which imparts the best resistivity values to the fabric being treated. The right ratio of silica nanoparticles to ionic monomers on the substrate is essential for proper crosslinking of the polymers with the substrate and each other; these help in the improvement of the antistatic properties of the fabric being treated.

4.4.2. Helium-oxygen plasma treatment

Figure 4.17 Graph showing surface resistivity of AMPS/silica/helium-oxygen plasma treated samples by the plasma treatment→ pad→ oven dry→ plasma treatment method
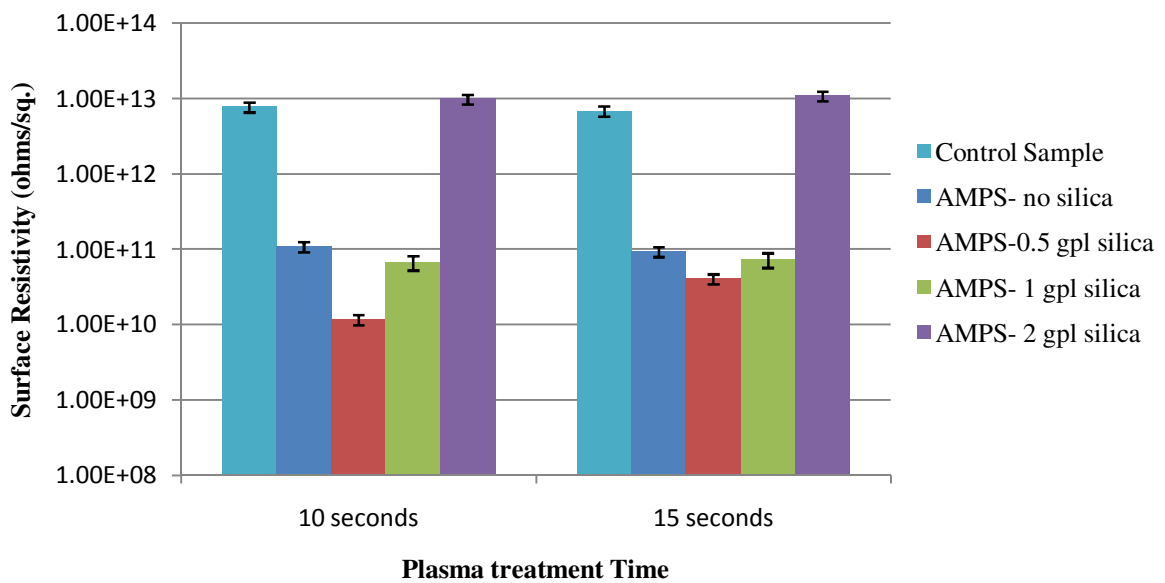
Figure 4.18 Surface resistivity of NaVS/silica/helium-oxygen plasma treated samples by the plasma treatment→ pad→ oven dry→ plasma treatment method
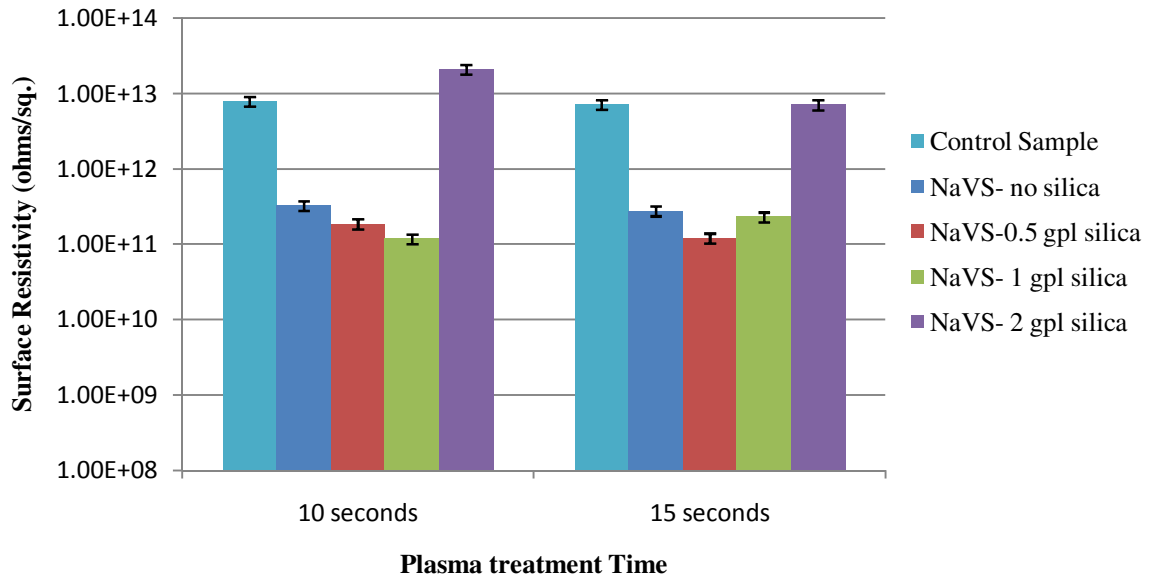
Figure 4.17 and **Figure 4.18** present a summary of the surface resistivity results for helium-oxygen plasma treatment using AMPS and NaVS respectively, where plasma treatment is carried out twice. Of the samples tested in this procedure, the control samples had higher resistivity values over most samples that were chemically treated. Like in all other treatment procedures that we have discussed, the relatively high silica concentrations of 2 gpl worsen the antistatic properties of the fabric. The general trend was that a dip was observed over a particular range of silica concentrations between 0 and 1 gpl. A concentration of silica nanoparticles from 0.5 to 1 gpl yields the best results for this experimental procedure, and the lower plasma treatment time of 10 seconds yields better values for the chemically treated fabric samples.

4.5. Comparing plasma treatment methods with conventional graft polymerization

This work was carried out in order to test the merit of subjecting the fabric to plasma treatment to initiate the graft polymerization reaction, as against conventionally inducing the graft polymerization by the use of a free radical initiator. Potassium persulfate was used in this method to circumvent the plasma treatment approach in that, the samples were only treated with the nanoparticle and monomer dispersion, followed by treatment with the free radical initiator. This treatment was carried out with lower concentrations of silica, as these were the most effective at imparting antistatic properties as discussed in **Sections 4.2**, **4.3** and **4.4.** The experiments were conducted for the purpose of comparison.
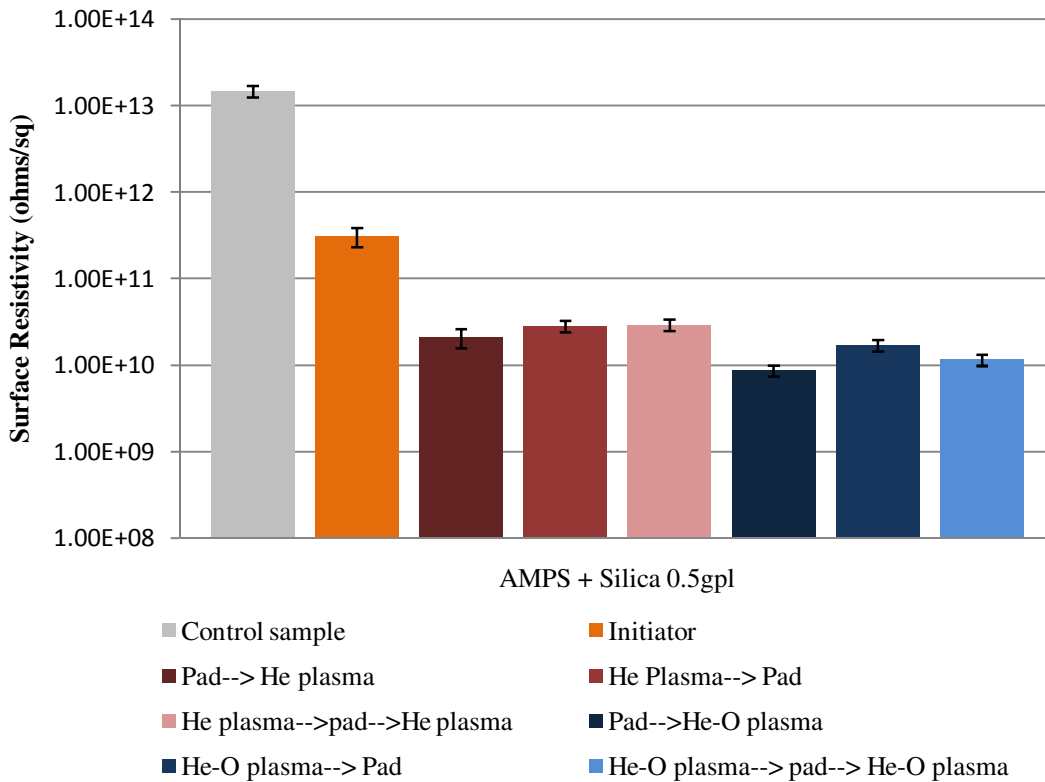
Figure 4.19 Surface resistivity of AMPS/0.5gpl silica samples obtained by different treatment methods
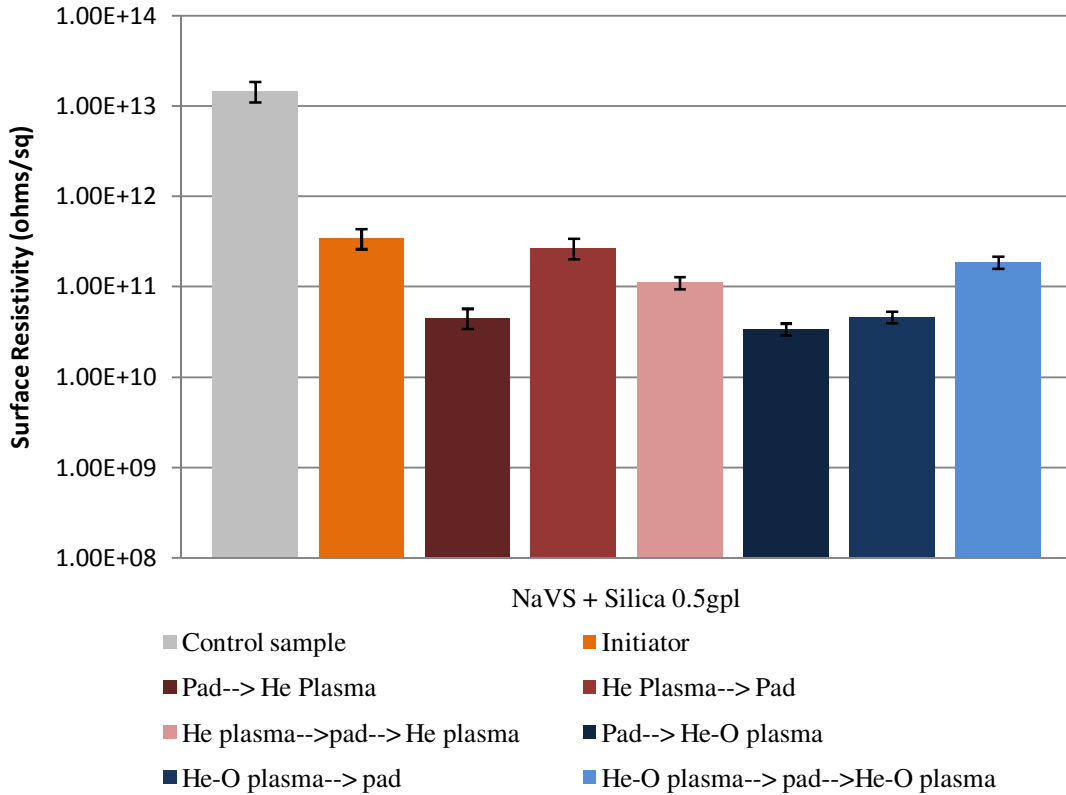
Figure 4.20 Surface resistivity of NaVS/0.5gpl silica samples obtained by different treatment methods

Figure 4.19 is a comparison between different methods of treatment used to obtain samples with antistatic properties. The monomer used was AMPS. It can be seen that the samples treated with potassium persulfate initiator have higher resistivity values than all other treatment methods where plasma was used. It should however be noted that the resistivity values of all samples are considerably well below the control samples (greater than two orders of magnitude). **Figure 4.19** shows a clear distinction between the samples that were plasma treated and samples treated with the free radical initiator. **Figure 4.20**, in which NaVS was used, we see that the difference between the plasma treated samples and the initiator treated samples exists, but is not as pronounced as seen in case of the AMPS treated samples.

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4.6. Effect of treatment procedures

Each of the treatment procedures used in this research served to activate the fabric differently. In the first procedure, or experimental design I, plasma tends to create ions on the surface of the monomers and the chains of the functionally modified silica particles, in addition to the fabric surface, when applied to a fabric that has been treated with chemicals. In experimental design II, the raw fabric was treated with plasma and then dipped in the chemical bath. Exposure of the raw fabric to air results in the creation of relatively stable peroxide compounds on its surface (Bech et al., 2007; Inagaki et al, 1997; Fridman, 2008; Shishoo, 2007). These compounds are semi-stable, and they react with the chemistry applied to the fabric surface, forming bonds and providing active sites for the graft polymerization reaction to take place. This was studied in experimental design II as the procedure involved treating the raw fabrics with plasma first, followed by padding with the chemical dispersion. When a system of "double plasma" (Bech et al., 2007) is used, all the aforesaid reactions take place, which in turn influence the properties of the finish in a different way.

In this research, different plasma treatment times were used for different concentrations of silica. To make a simple comparison, results obtained with a concentration of 0.5 gpl of silica and 10 seconds of plasma treatment time were taken.

Figures 4.21 and **4.22** illustrate a comparison of different treatment procedures, where helium plasma was used with AMPS and NaVS, respectively.
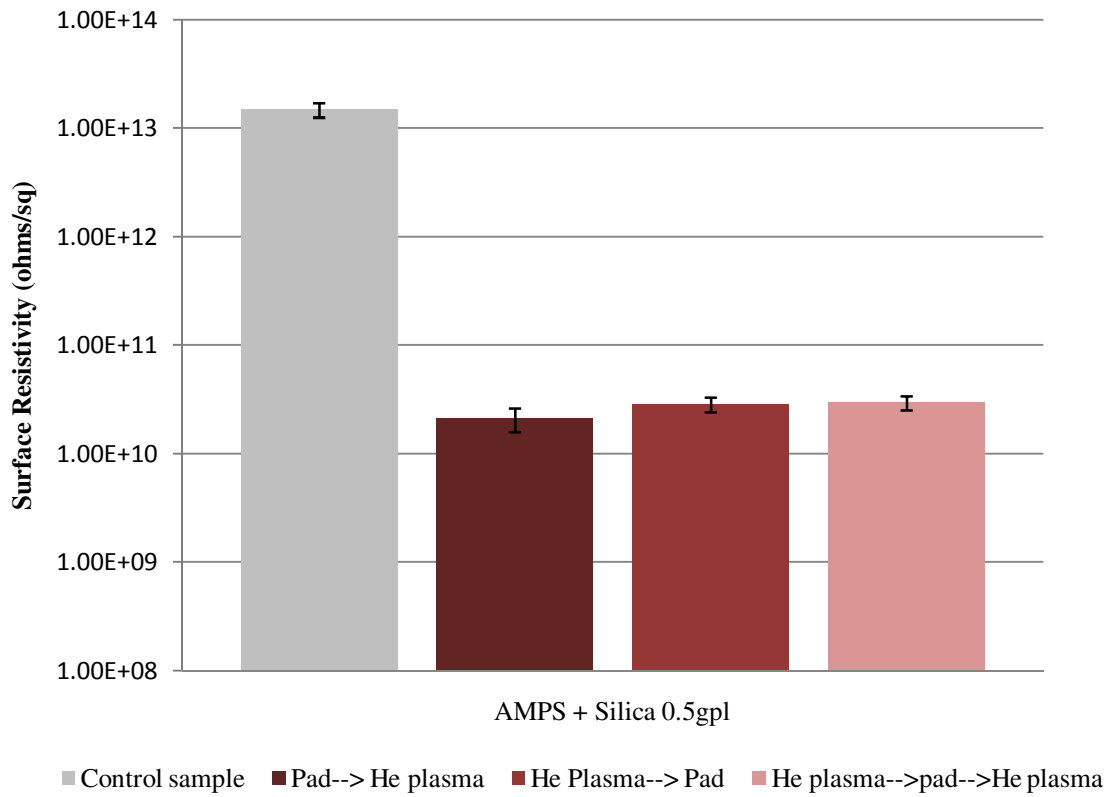
Figure 4.21 Comparison of treatment procedures with AMPS and helium plasma
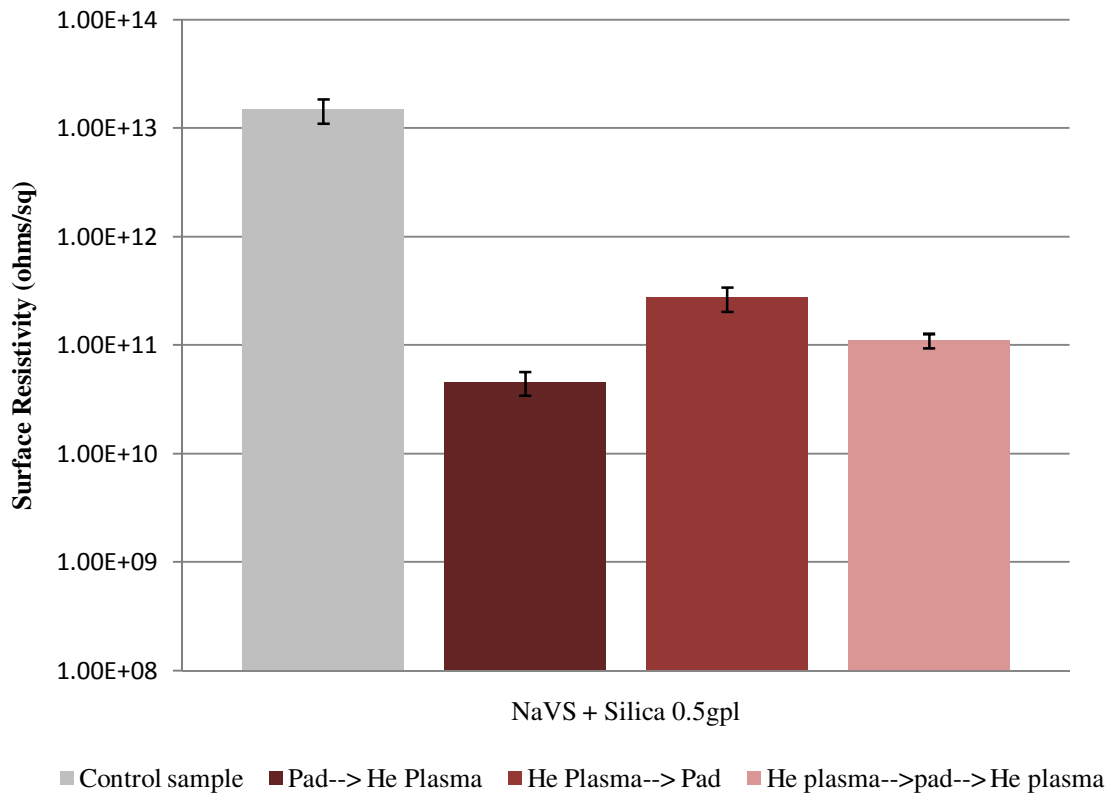
Figure 4.22 Comparison of treatment procedures with NaVS and helium plasma

When we look at the trends with AMPS in **Figure 4.21**, we find that all the treatment procedures are within less than a one order of magnitude of 10. This presents an interesting case in that, the three treatment procedures have more or less the same effect on the finish and the resultant resistivity properties. The changes are not big enough to cause noticeable difference in the performance of the fabric overall.

In **Figure 4.22**, the results of the treatment procedure with NaVS are shown. It can be seen that NaVS-treated fabrics seem to be a little more influenced by treatment procedure, than AMPS-treated ones. The differences in values in case of NaVS are a little more pronounced than AMPS. Although the treatment procedure that shows the lowest resistivity is the pad→ plasma treatment for NaVS, these changes are minute

from the industry-standards point of view and would serve to bring a very slight change to the functionality of the fabric.
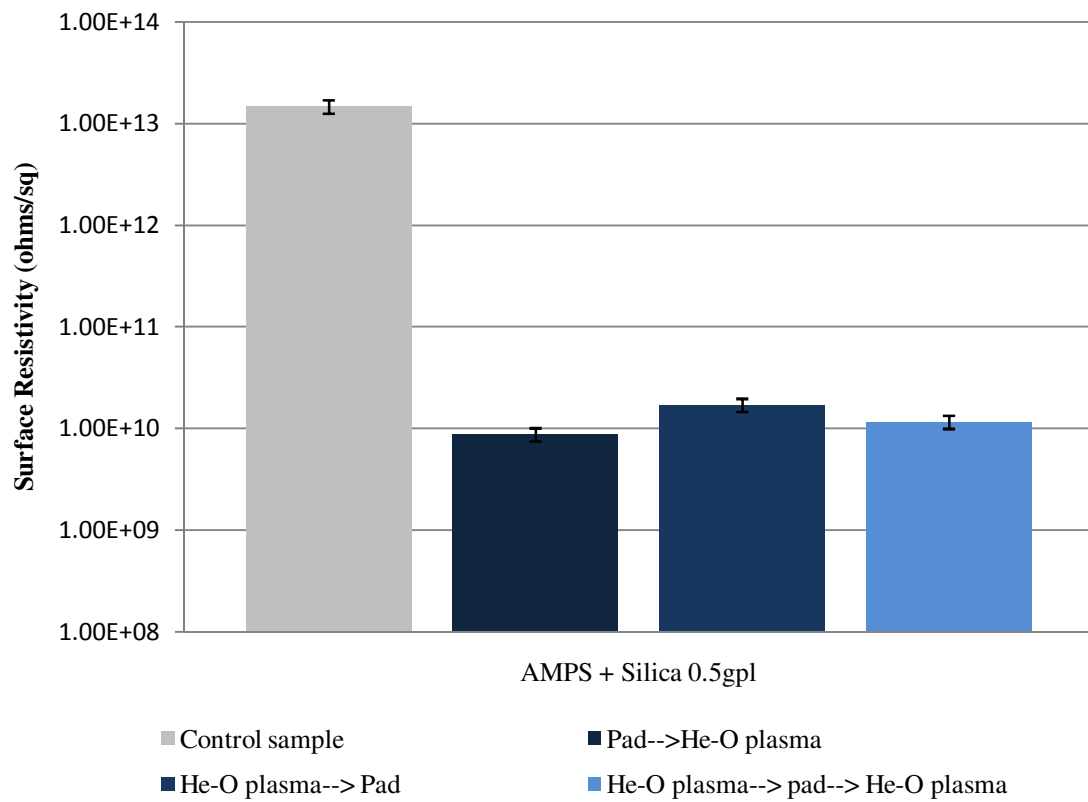
Figure 4.23 Comparison of treatment procedures with AMPS and helium-oxygen plasma

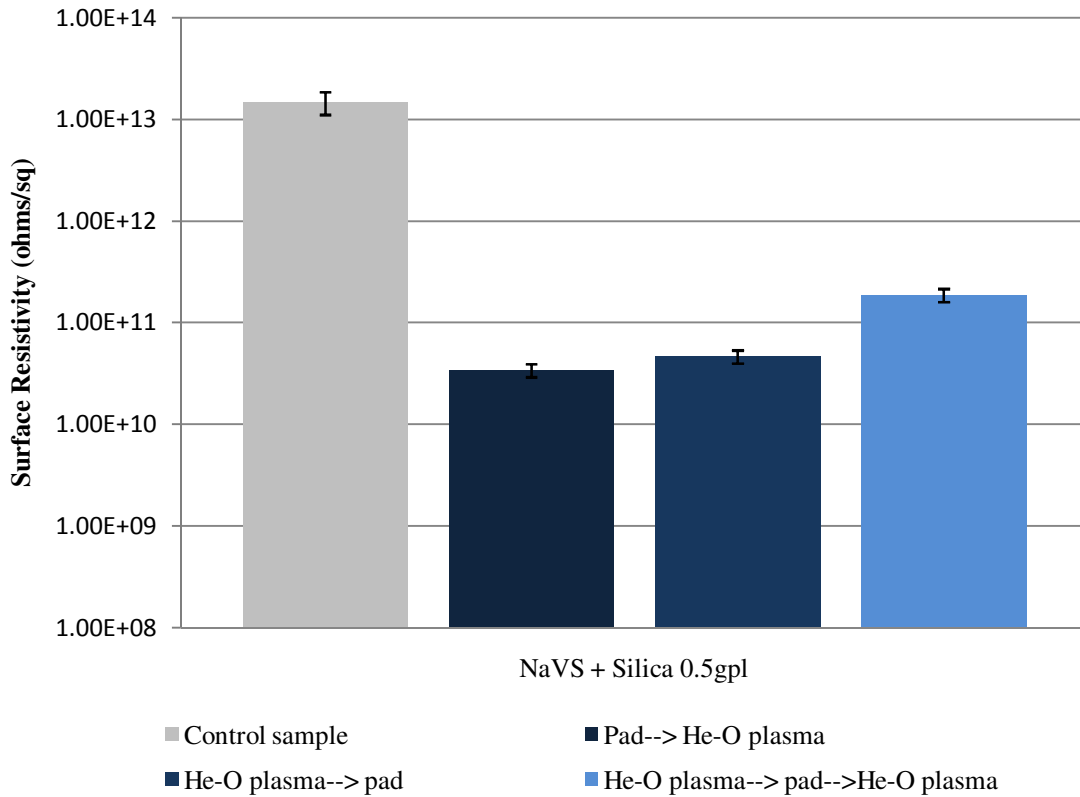**Figure 4.24 Comparison of treatment procedures with NaVS and helium-oxygen plasma**

Figure 4.23 and **Figure 4.24** represent the results obtained after the treatment of AMPS and NaVS with a helium-oxygen plasma mixture. Both figures present results that are similar to the results discussed with helium plasma. Now, it is seen here that the difference between individual plasma treatment procedures is very small (less than one order of magnitude).

It is therefore seen in this research that individual procedures seemed to affect the resistivity properties of the fabric in a way that can be considered insignificant. Treatment procedures therefore, might not have influenced results too much in this research.

4.7. Effect of plasma types

Different plasma types can cause different reactions on the fabric by influencing the formation of different functional groups, as discussed in **Section 2.4.1**. This research made use of two different types of plasma gases: helium and helium-oxygen mixture. This section discusses the effect that both gases had on the surface resistivity properties of the fabric. For comparison, the resistivity results were taken for samples treated with the ionic monomers and 0.5 gpl silica with a 10 second plasma treatment time.
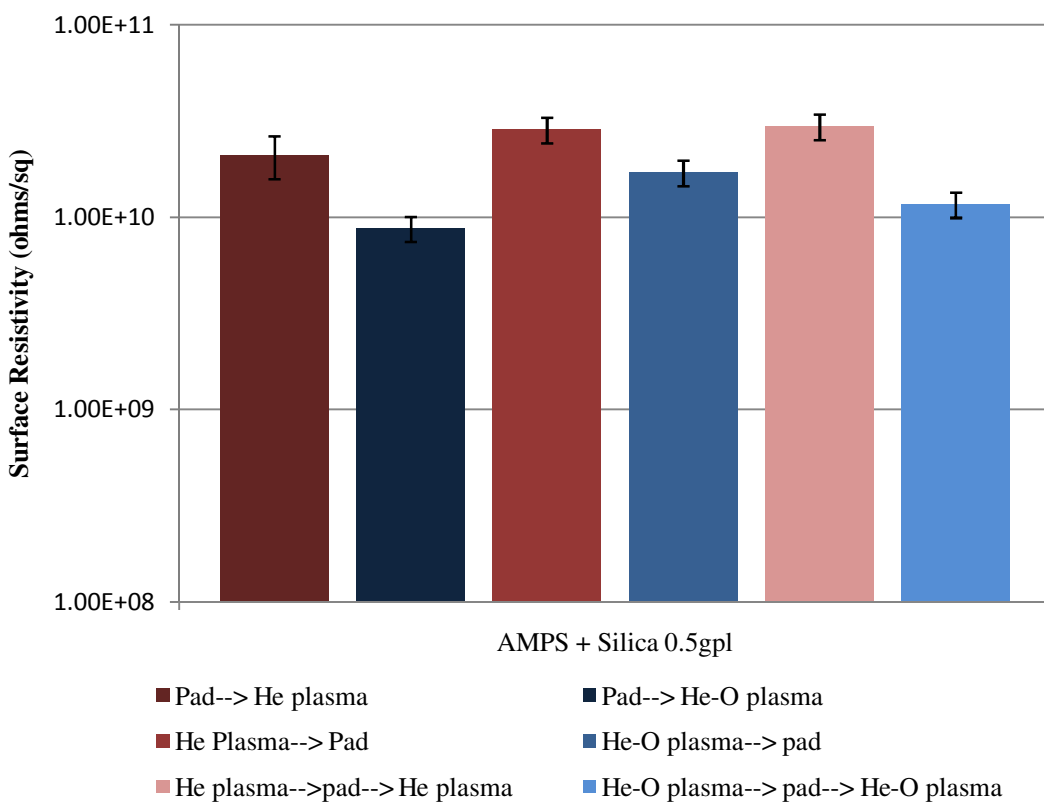
Figure 4.25 Comparison of helium plasma and helium-oxygen plasma over three treatment procedures for AMPS and 0.5 gpl silica nanoparticles
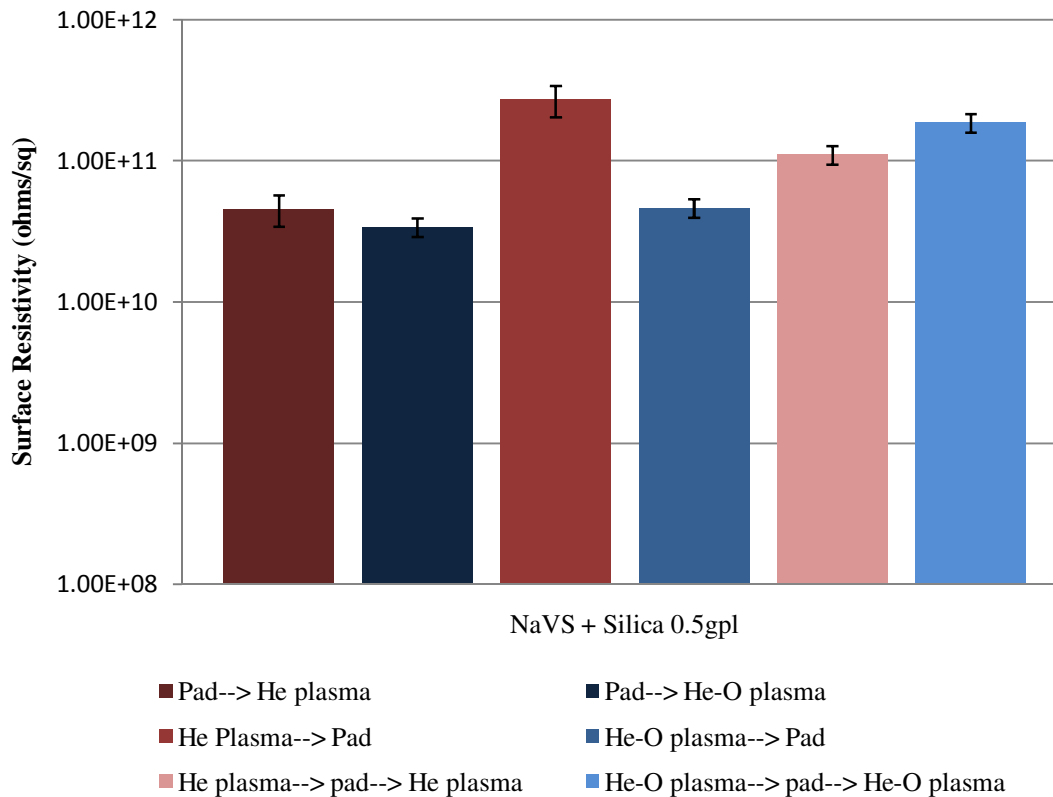
Figure 4.26 Comparison of helium plasma and helium-oxygen plasma over three treatment procedures for NaVS and 0.5 gpl silica nanoparticles

Figures 4.25 and **4.26** show comparative results of surface resistivity obtained when samples were treated with helium plasma, and helium-oxygen plasma. The effect of different gases is pronounced in the case of AMPS. Helium-oxygen plasma treatment for 10 seconds brought down the resistivity of the samples. However, in case of fabrics treated with NaVS, the pattern is quite erratic. In **Figure 4.26**, we see that the difference in resistivities for the experimental design II (pad→ plasma→ dry) is a little less than one order of the magnitude of 10, which is significant in terms of the effect of just using different gases. This effect has explanations in literature (Fridman, 2008; Shishoo, 2007), which state that different gas plasmas have the ability to induce different functional groups on the surface of the polymer substrate. Treatment with oxygen-

containing plasma tends to result in the formation of polar groups on polymer surfaces, significantly increasing the wettability characteristics of the polymer and adhesion to different organic compounds (Fridman, 2008).

4.8. Static dissipation of untreated and treated fabrics

Resistivity measurements discussed above are indirect method. In order to further confirm the results from the resistivity tests conducted on the fabrics, tests in static dissipation were carried out on select fabrics. The static dissipation tests were carried out by building up charge on the fabric by contacting against a Teflon piece. After a certain number of contacts, the time in which the charge decayed was recorded. In this experiment, the lower the charge decay time, the better the antistatic properties of the treated fabric. **Figures 4.27 – 4.31** illustrate a certain trend which will be discussed in this section.
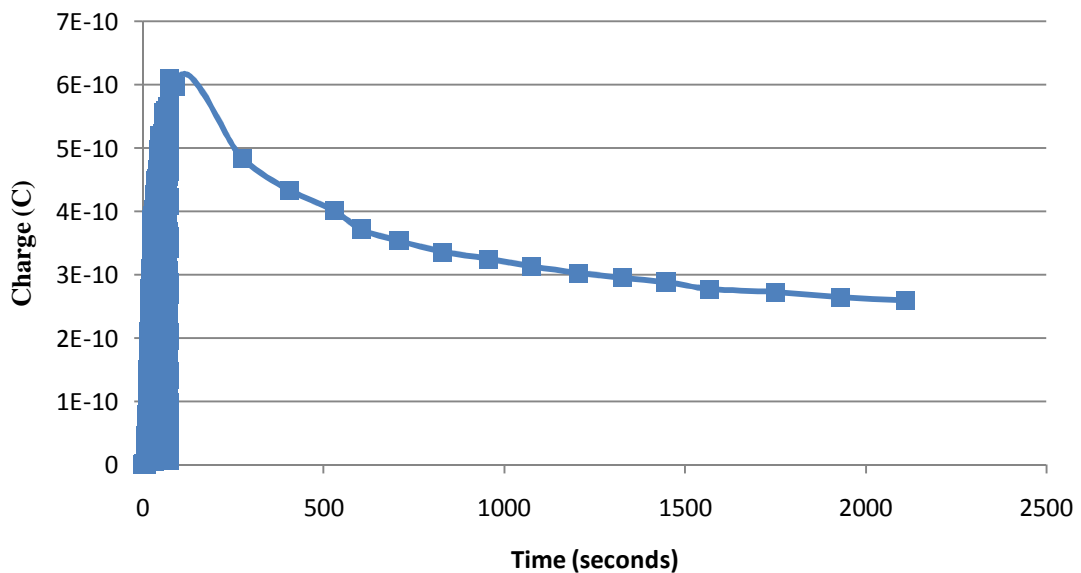
Figure 4.27 Charge decay curve of an untreated sample after charging for 50 contact cycles
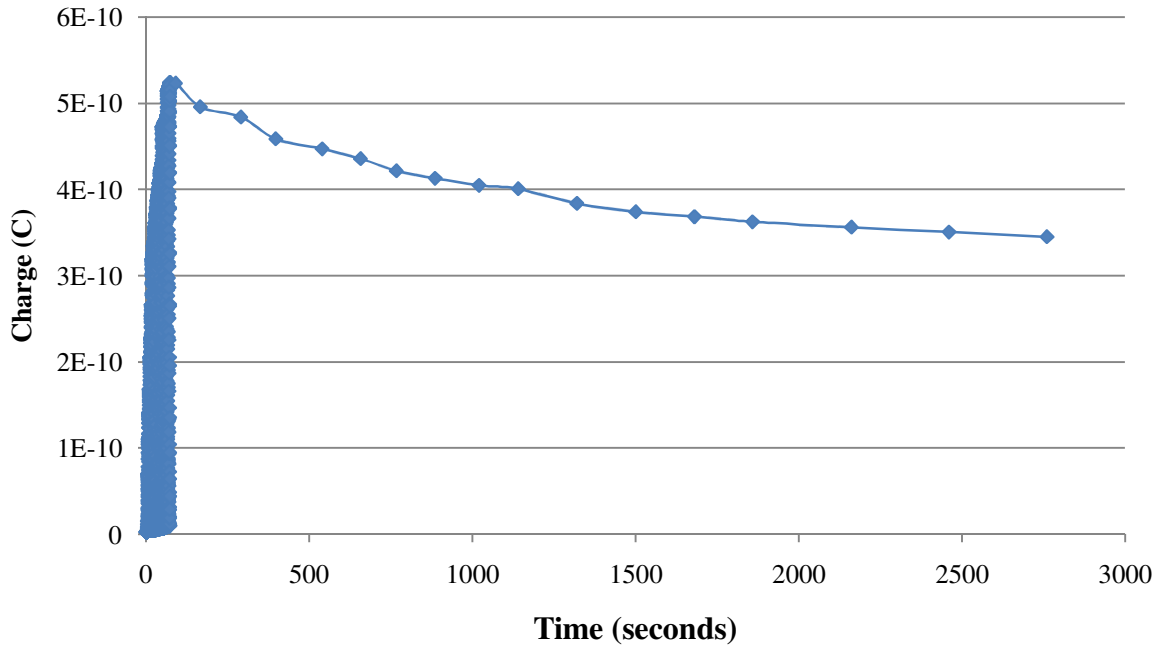
Figure 4.28 Charge decay curve of a sample treated with NaVS/1 gpl silica/ pad→ dry→helium plasma method, after 50 contact cycles
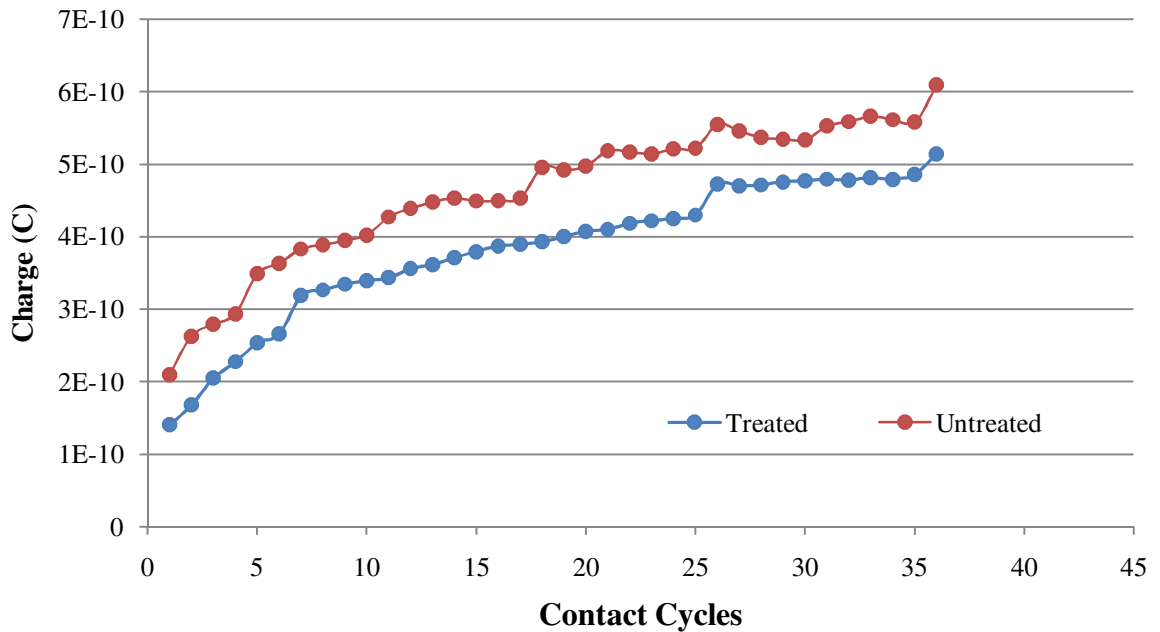
Figure 4.29 A comparison of accumulated charge after 50 contact cycles in raw and finished fabrics

It can be seen from comparing **Figure 4.27** and **Figure 4.28**, that the untreated polyester cotton fabrics tend to dissipate away charge faster than the sample treated with NaVS/silica. The half-life is close to 1000 seconds for the untreated fabric, and is greater than 3000 seconds for the fabric treated with a combination of NaVS and silica nanoparticles and helium plasma. However, it is seen from **Figure 4.29**, in a comparison of static charge accumulated, that the treated samples tended to accumulate less charge than the untreated fabric.

Figures 4.30 and **4.31** illustrate the dissipative properties of fabrics that were treated with only ionic monomers, followed by plasma treatment. In this case, the experiments were carried out with only 20 contact cycles as opposed to 50. **Figures 4.30** and **4.31** are therefore no indication of the maximum charge that was accumulated, but present insights into the discharging behavior of the treated fabrics.
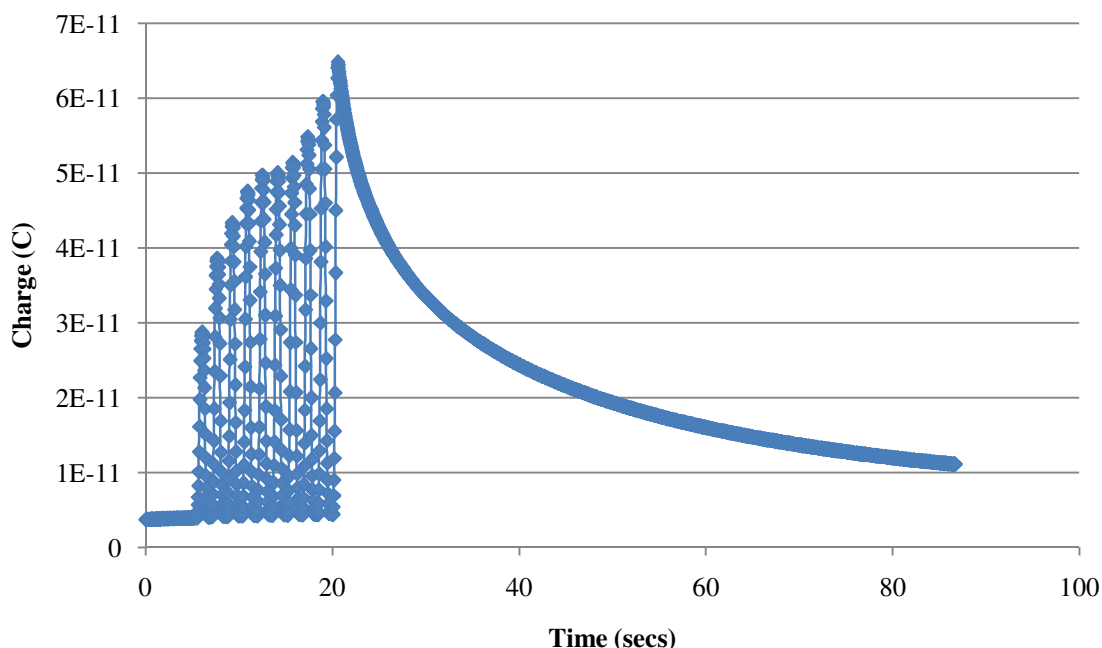
Figure 4.30Charge decay curve of a sample treated with AMPS/ no silica/ pad→ dry→ helium plasma treatment
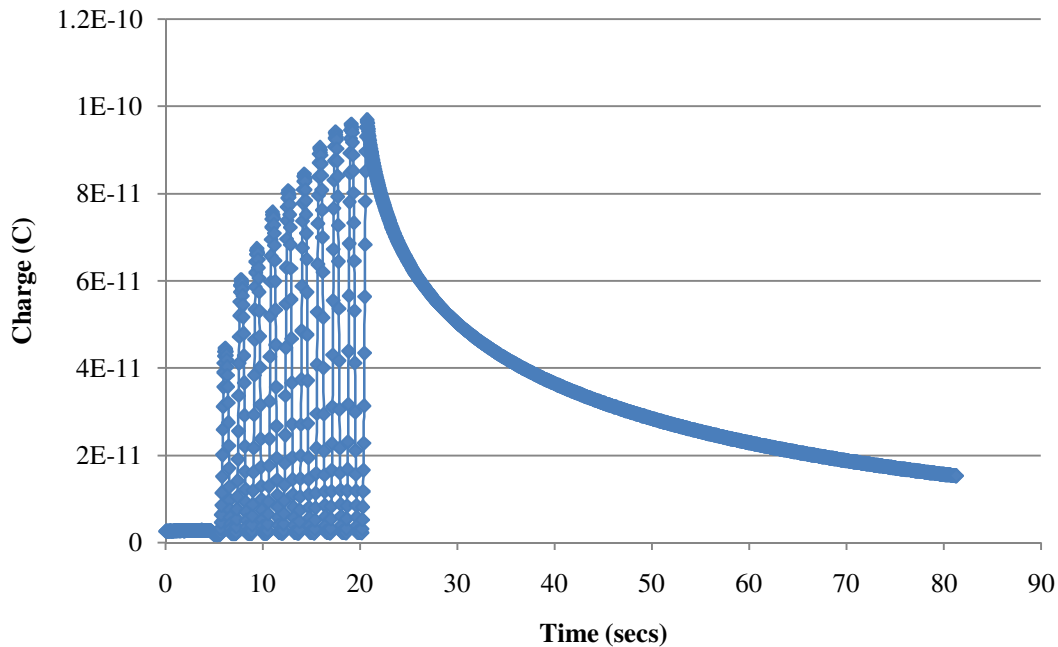
Figure 4.31 Charge decay curve of a sample treated with NaVS/ no silica/ pad→ dry→helium plasma treatment

It can be clearly seen from **Figures 4.30** and **4.31** that the accumulated charge decays very quickly. The half-life of the fabric treated with AMPS is a mere 8 seconds, and that of the NaVS treated fabric is close to 10 seconds. These results are much better than the results obtained for untreated fabric samples, as also the fabrics treated with silica nanoparticles. Now these results are interesting, because although the resistivity values measured for the treated fabrics (with or without silica nanoparticles) are always lower than untreated fabrics, as discussed in **Section 4.2.1**. However, it is seen that the charge dissipation characteristics are vastly different. Lowered resistivity values correspond to lower levels of accumulated static charge, but the capacitance, or the ability to hold charge, is an unknown quantity. However, it is not known at this juncture whether the static dissipation half life characteristics would be affected by lower silica nanoparticle

concentrations, or type of treatment procedure and this presents scope for further investigation and research.

4.9.Rinse testing to determine fastness

In order to properly evaluate the antistatic finish, it was also necessary to subject the samples to a rinsing test evaluation in order to determine how well the finish would withstand everyday rinsing and laundering. However, it was decided that the conventional test methods proposed by the AATCC would be harsh and therefore, a preliminary rinse, under running water, was deemed fit for this research. Samples containing 0.5gpl silica were rinsed, dried and evaluated for any loss in their antistatic properties. A summary of some results is shown in **Figures 4.32** and **4.33**.
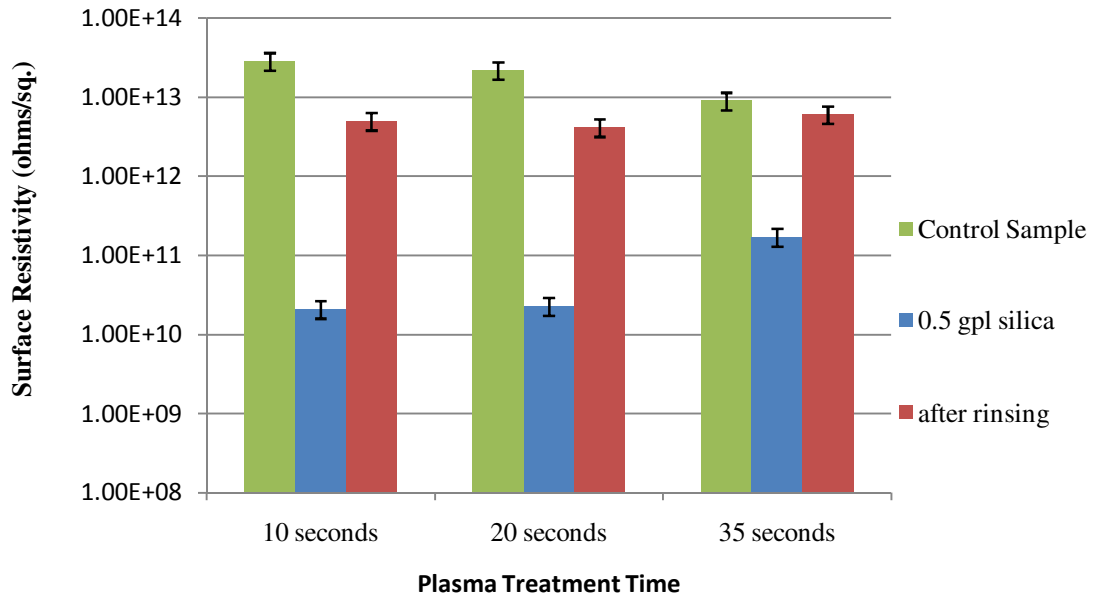
Figure 4.32 Rinse test results for AMPS/silica prepared by the pad→dry→helium plasma method
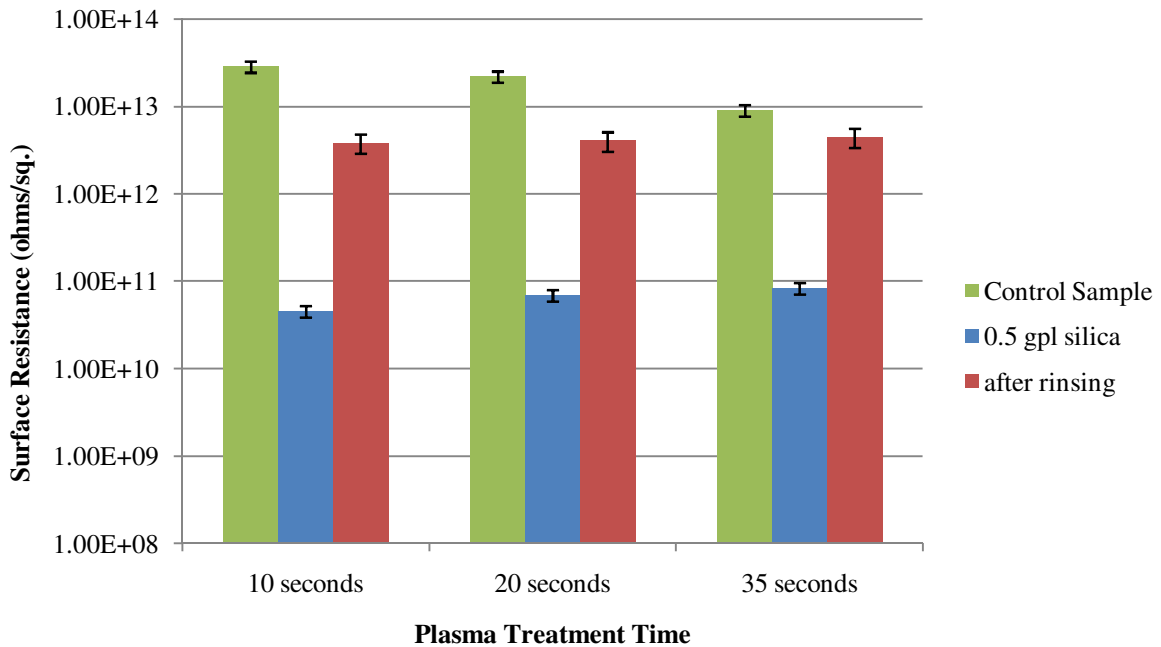
Figure 4.33 Rinse test results for NaVS/silica prepared by the pad→dry→helium plasma method

In case of the fabric samples treated by the pad→dry→plasma method, it was seen that the surface resistivity of the rinsed samples was higher than the surface resistivity of the unwashed samples. In treatment with both monomers, AMPS and NaVS, the rinsed samples had resistivities that were at least a 100 times higher than the samples that were not washed.

Similarly, all the samples, that were treated under different concentrations of silica nanoparticles, over different times and different gases, show the same trend as observed (data not shown). It becomes clear that the finish fastness on the substrate is limited and is irrespective of the type of treatment procedure, gas used or concentration of silica nanoparticles.

CHAPTER 5: CONCLUSIONS

An antistatic finishing technology was developed by introducing low-cost silica nanoparticles with ionic monomers onto fabric surfaces through atmospheric plasma treatment. The research presented insights into the behavior of silica nanoparticles and plasma treatment technology. The experiments were successful, with the antistatic finish being obtained on the surfaces of the fibers. The studies that were conducted investigated the effects of nanoparticle concentrations and plasma treatment times on the efficiency of the finishes. Two different types of gases were used for plasma treatment.

Silica nanoparticles help reduce the surface resistivity of the fabric being tested. Silica nanoparticles, used in conjunction with ionic monomers are beneficial in terms of imparting antistatic properties, in that, the resistivity values were within the limits of the prescribed industrial standard. It was observed that as the concentration of the silica particles increases in the dispersion, the resistivity of the treated fabrics decreases first, and then increases. The optimal concentration of silica that yielded the best results was 0.5 or 1 gpl, depending on the treatment procedure.

Atmospheric plasma treatment has a marked effect in reducing the surface resistivity of the treated fabrics. This is indicated in the difference of almost two orders of the magnitude of 10, between the resistivities of fabrics treated with plasma and free radical initiators. Plasma treatment gave better results than the use of a free radical initiator (in this case, potassium persulfate). Plasma treatment tends to affect changes on the substrate surface both physically and chemically, and thus, could prove to be more effective than conventionally used polymerization initiators.

Plasma treatment times have an inverse effect on the efficacy of the finish on the substrate. The surface resistivity of the fabrics increased as the plasma treatment times increased. The best results were obtained with samples treated for time duration of 10 seconds.

The results obtained by using two different plasma gases for treatment showed that the combination of AMPS with helium-oxygen plasma gave slightly better results than the combination of AMPS and helium plasma, but the same could not be observed with NaVS in all cases. The resistivity difference between the treatments with different plasma types, observed in case of AMPS was almost ten times, or one order of the magnitude of ten

The finishes were not durable to laundering, indicated by the increase in resistivity of the rinsed samples. The rinsed samples showed resistivity values that were higher by almost two orders of magnitude, which can be considered significant. Although the finishing durability results are not on par with the industry standards, the research presents a step forward in helping the understanding of the effects of plasma treatment and nanotechnology on the antistatic behavior of textiles.

CHAPTER 6: RECOMMENDATIONS FOR FUTURE RESEARCH

The most important aspect of any future research would be the optimization of process and performance of this antistatic finish. The research showed a drop in the surface resistivity of the polyester cotton blend fabrics at silica concentrations of 0.5 gpl and monomer concentration of 10 gpl. However, more research needs to be carried out to investigate the optimum concentration of silica in the dispersion that will induce the lowest resistivity in the fabric. The optimum concentration ratio of the monomer to the silica nanoparticles also needs to be investigated, so that an empirical measure can be introduced. Different nanoparticles such as TiO_2 and ZnO can be tested on the fabric surface, to find out if they induce better antistatic properties.

Plasma treatment could also be carried out using different gases, as different gases are capable of introducing different functional groups to the treated surface. Experimentation with monomer plasma should be done to study the effectiveness of directly impregnating the monomer onto the fabric surface.

More investigation into the static charge dissipation properties would help us understand the discharging behavior of the treated fabrics and thus help us understand their overall effectiveness as an antistatic finish.

The same research can be carried out on different types of textiles, with the most recommended ones being of the hydrophobic variety (e.g., polypropylene). It is also important that such investigations be carried out on dyed textiles. This will help improve our understanding about any possible interactions with the dye molecules resulting in a color change, or loss or gain in fastness properties. This research would be

of importance from the point of view of introducing this technology to textile facilities as part of a series of finishing treatments.

Another area that can be worked on is the introduction of both plasma technology and nanotechnology into the field of conventional antistatic finishing. Possible investigations would include, but not be limited to, the use of plasma technology to induce polymerization on substrates and the addition of silica nanoparticles to conventional antistatic finishes with the aim of achieving a more durable finish.

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