

# **A REVIEW OF PLASMA TREATMENT FOR APPLICATION ON TEXTILE SUBSTRATE**

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## 1. Introduction to Plasma

Modern science preaches the existence of three states of matter, namely solid, liquid and gas. Most people, however, thanks to the advent of modern television displays, are vaguely aware that a fourth state known as plasma also exists.

In reality, plasma is more widespread in the universe than most people know. In fact it makes up most of the universe as it can be seen. The sun is a burning sphere of plasma and so are the stars and other celestial objects that can be seen in pictures of our universe. The display and sound produced every time there's a flash of lightening is also because of plasma.

Plasma therefore, isn't all that uncommon, and neither is it as hi-fi as plasma displays make it sound. Judging from its existence on the sun and other celestial bodies, it is automatically assumed that plasma is something intense and probably has something to do with extremes in temperature, pressure or even radiation. Fortunately, plasma exists in various forms, and a lot of it can be harnessed to study and possibly achieve desired outcomes on various substrates, including textiles.

Before going on into the uses of plasma, it's important to understand what it is. Simply put, plasma is nothing more than ionized gas. When the temperature of a gas is raised its molecules gain energy until a point reaches when the molecules gain enough energy to make the electrons in the gas leave the nucleus of the atom. The gas then exists in the form of charged ions electrons and neutral particles [1], the collisions of which release vast amounts of energy.

Since this project aims to study the effect of plasma on textiles, the immediate question that arises is whether the working temperatures of plasma are possible for application on textiles. The answer to this concern is cold plasma. But how can gas be provided enough kinetic energy to split the tremendous attractive forces between ions and electrons without raising the temperature?

There are many methods to achieve this. The general phenomena is that cold plasmas are only partially ionized gasses in a stable state. The plasma state can be achieved by heating (pulsed), applying a voltage, or injecting electromagnetic waves [1]. This state is stabilized by providing optimum conditions in which the rate of electrons leaving the ions equals the rate of electrons combining with the ions to form gas molecules. Without this equilibrium the plasma would either continue to gain temperature or wholly convert into gaseous matter.

One of the earliest works on plasma treatment of textiles [2] states that the most suitable method to create low temperature plasma for application on textiles is through electrical discharges. However, advances in recent years have led to developments that enable the creation of plasmas which are suitable for application on textiles with a variety of other means. Different manufacturers of equipment for plasma treatment have their own methods to achieve stable plasmas for application purposes.

The ability to harness plasma lies in controlling the parameters that make it suitable to achieve controlled outcomes on the required substrate. The next chapter will take a look at these parameters and what outcomes can be achieved with the use of low temperature or cold plasma.

## 2. Low Temperature Plasma

There are two types of plasma which can be used for application on textiles, namely vacuum pressure and atmospheric pressure. Since plasma can not be generated in a complete vacuum the name vacuum pressure is somewhat misleading and only refers to the low working pressures of such systems. Many authors, however, choose to classify vacuum pressure plasmas into sub categories of low and medium pressures [3, 4, 5]. The table below gives an idea of the working pressures of vacuum and atmospheric plasmas.

Pressure		Pressure Units			
		kPa	Torr (mmHg)	Atmosphere (atm)	Bar
Vacuum	Low	0 – 0.29	0 – 2.175	0 - 0.003	0 - 0.0029
	Medium	0.3 – 7	2.25 – 52.5	0.003 - 0.069	0.003 - 0.07
Atmospheric		101.3	760	1	1.103

*Table 2.1, Operating pressures of vacuum and atmospheric plasmas*

This text, due to very little difference between the sub classes of vacuum plasma will not differentiate between the two forms and discuss two main classes of plasma which are (near) vacuum pressure plasmas and atmospheric pressure plasmas.

Both these forms are suitable for application on textiles and progress continues to determine their effect on textiles. More work has, however, been documented on characterization of vacuum pressure plasmas as compared to atmospheric pressure plasmas [6].

Figure 2.2 [7] provides an idea of the variation in the existence of plasma as the current is increased. The regions marked as dark and glow discharge are normally suitable for surface modification. The corona region of dark discharges is used in atmospheric plasmas while vacuum pressure plasmas usually lie in the glow discharge region. Arc discharges, due to heavy bombardment of the cathode at high currents attain temperatures which are

too high for safe surface modification techniques [1]. This section will thus discuss vacuum and atmospheric plasmas which have been realized as suitable for application on textile substrate.

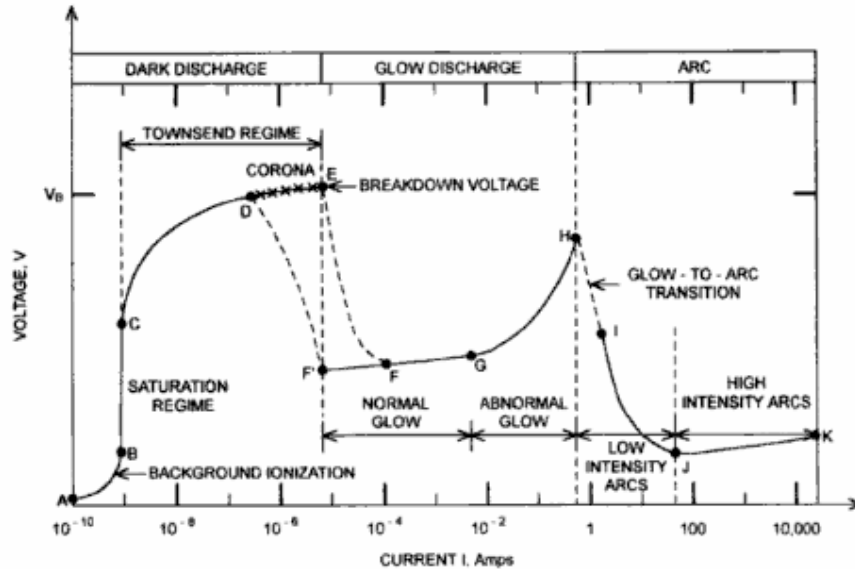


Figure 2.2, Voltage-current characteristics of the classical DC intermediate pressure electrical discharge tube [7]

## 2.1. Vacuum pressure plasmas

If a voltage is applied across a nearly evacuated gas chamber, under appropriate conditions, a plasma will ignite [1]. Changes in these conditions vary the effect and appearance of the plasma.

Vacuum pressure treatments are generally used to achieve varying outcomes of textile substrate. These plasmas will either etch or form radicals on the surface of the processed material. Each of these terms is explained in more detail in section 3.

Vacuum pressure plasma systems have certain limitations adhered with them in terms of commercial application. The vacuum creating equipment adds to the cost of treatment and is expensive to run. Also, the operating pressure range allows only for batch processing of material to be possible.

There are certain advantages in terms of application such as etching and coating which can be performed better under low pressure plasmas. These advantages are discussed in more detail in section 3.

## **2.2. Atmospheric pressure plasmas**

As the name suggests, these systems process materials at atmospheric pressures thereby increasing the processing capabilities of the machine while reducing processing costs and loading times.

For atmospheric plasma treatment, corona or barrier discharges can be used. Corona sources contain inhomogeneous initial electric fields formed around pointed electrode elements. Barrier discharge sources are characterized by the presence of insulating layers on one or both electrodes, or in the gas-filled gap between the electrodes. Both these sources allow the production of large-area plasmas. Corona discharges have a strong filamentary character, whereas barrier discharges are significantly more homogeneous [1].

A more recent development in atmospheric plasma technology is the one atmosphere uniform glow discharge plasma [7]. This technique has been developed at the University of Tennessee, Knoxville.

Even though atmospheric plasma systems can be used for continuous treatment their application is limited due to the fact that such plasma only affects loose and surface fibers and lacks the capability of penetrating into the fabric structure. This is so because Corona plasma is essentially weak and operates at an inter electrode spacing of approximately 1mm [8]. Another drawback with atmospheric plasma is the liberation of ozone gas and nitrogen oxides at the workplace [9].

So far, the application of atmospheric plasma is limited to the extent of activation of surfaces while its low pressure predecessor is also capable of coating and etching as will be discussed in the next section. Different

manufacturers are developing innovative methods to incorporate greater functionality with the use of atmospheric plasma. Sigmatech USA is developing treatment units which will employ liquid precursors to apply nano layers on fabric through plasma treatment. This technology, however, is not yet commercial.

In spite of its drawbacks atmospheric plasma treatment has come up in recent years and holds the potential to develop further. Results so far have been promising and research continues to explore new dimensions for its application and improvement [10]. Latter sections in this text will shed light on papers which have explored the application of atmospheric plasma on different textile substrate.

Apart from the continuous application system that has been developed by Sigma Technologies International Inc, other companies have also looked into the technology and come up with patented innovations. Another system which is patented under the name of Plasmaair® uses a somewhat different form of plasma for treatment.

The next section looks into the application of plasma treatment and how it influences the characteristics of textiles.

### 3. Modes of action

When a surface is exposed to plasma a mutual interaction between the gas and the substrate takes place. The surface of the substrate is bombarded with ions, electrons, radicals, neutrals and UV radiation from the plasma while volatile components from the surface contaminate the plasma and become a part of it [11]. Whatever may be the final outcome on the surface, the basic effect that causes modification is based on the following phenomena.

#### A. Radical Formation

- i. Attachment of functional group
- ii. Deposition/polymerization

#### B. Etching

It is through the use of these in different combinations and on different substrate that the vast variety of outcomes which are possible through plasma treatment can be achieved. Figure 3.1 [12] illustrates the mechanism of plasma modification as discussed in this section.

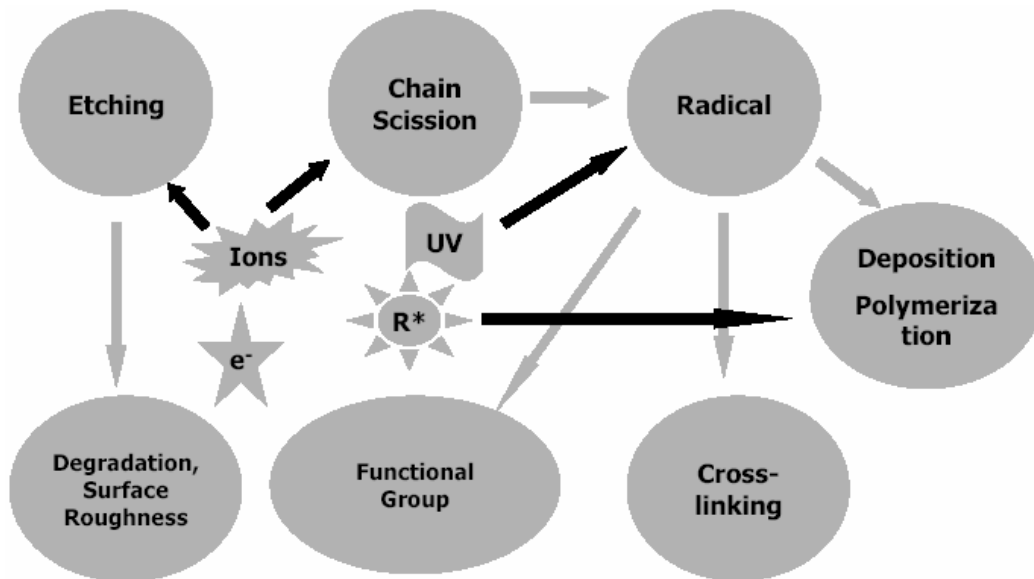


Figure 3.1, Mechanism of plasma-substrate interaction [12]

### **3.1. Radical formation**

Radical formation can lead to either the attachment of a functional group on the surface or the deposition of a complete layer through polymerization.

#### **3.1.1. Attachment of functional group**

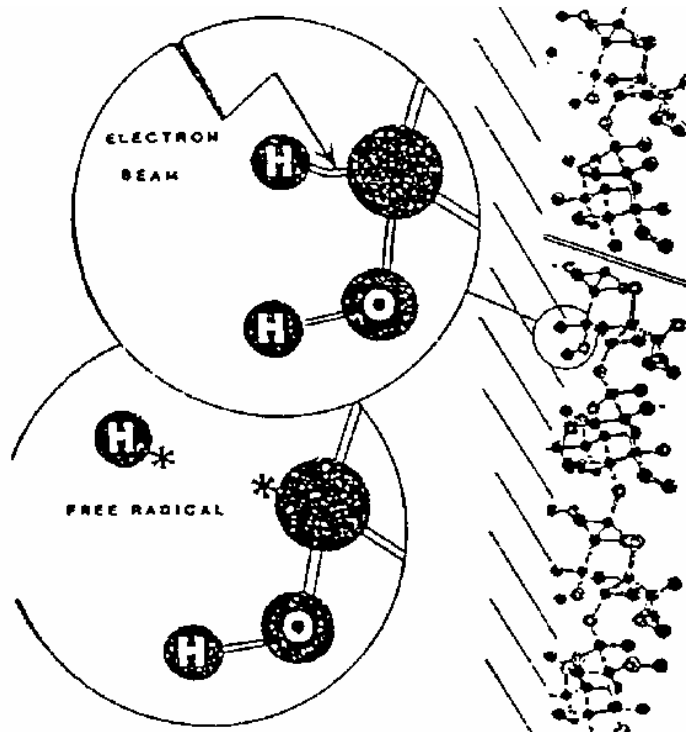
The process refers to the activation of surfaces of polymers by attaching different active species on the surface. The chemistry of attachment of functional groups on polymer surfaces by electron beam plasma has been somewhat explained by Sotton and Nemoz [13].

The paper explains that the phenomenon, irrespective of the substrate involves two steps:

- i. Initiation of radicals in the fiber material.
- ii. Attachment of ionized groups to the initiated radicals.

Functional groups such as carbonyl, hydroxyl or carboxyl can be grafted onto the surface to increase the polar characteristics of a surface and achieve high hydrophilicity [7]. This application is discussed further section 4.

Figure 3.2 shows how an ion beam creates a free radical on the surface of the polymer. This free radical is able to interact with the activated species in plasma to form the surface functional group.



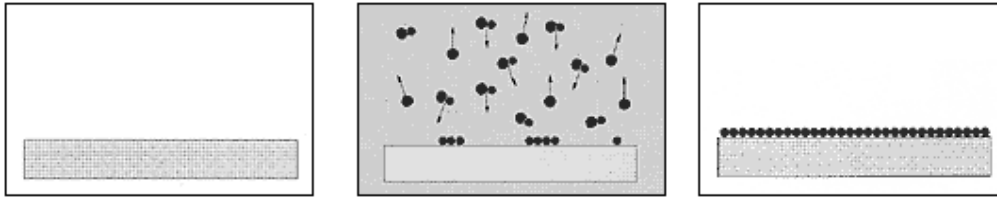
*Figure 3.2, Activation by electron beam [13]*

Once the surface is activated with free radicals, the final outcome depends on the groups these radicals react with. They can achieve cross linking or later react with oxygen present in air to form peroxides [11] or any other group depending on the species present in the surrounding.

### **3.1.2. Coating, deposition or polymerization**

Coating and layering are synonymous terms for applying films on textiles substrate by using plasma activated gasses. The term nano-layering is used when the thickness of the applied layer is measurable in nanometers.

As discussed earlier, so far only low pressure plasma can be used for application of coatings while atmospheric plasma systems have so far not been commercially developed to achieve this outcome.



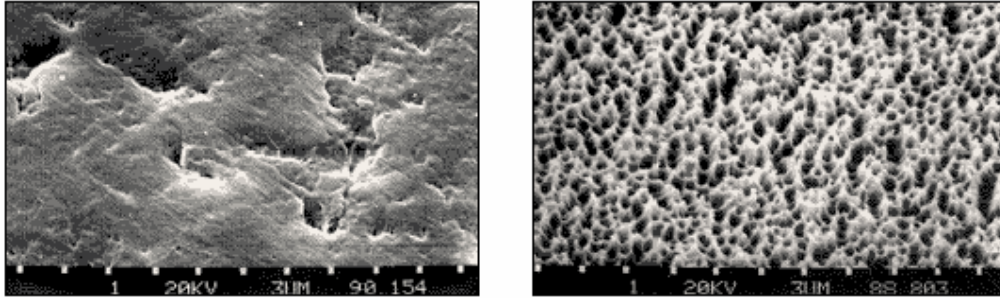
*Figure 3.3, Substrate before (left), during (centre) and after (right) coating with plasma treatment [14]*

It turns out that the process of coating also involves the activation of surfaces by radical formation. Once activated, the surface is covered with a layer of polymer which forms a coating as it polymerizes on the surface. The thickness and behavior of the formed layer depends on various processing parameters such as gas composition and flow rate, energy flux, electric power characteristics, proximity to the target film surface, and exposure time [15].

Plasma technologists use different terminology to discuss the varying outcomes that can be achieved through plasma treatment. The outcomes that have been achieved on different textile substrate in light of the above discussed phenomena will be discussed in section 4.

### **3.2. Etching**

The process of etching can be explained through the name itself. The surface of the polymer under treatment is literally etched or scraped out or with the aid of a reactive process gas. The material is then vaporized and sucked off to be removed from the surface.



*Figure 3.4, PTFE: Untreated (left), Treated (right) [16]*

The principle behind etching can also be used to perform other tasks such as cleaning. On textiles, the removal of sizing material is one such application [18]. This form of treatment is discussed in more detail later in section 4.1.1.

The common misconception with etching is that it can only be used for surface roughening. This however, is not the case in reality. Though effects on specific materials are discussed in section 4, there is scientific evidence to support the fact that etching can effectively reduce the surface area or achieve surface smoothing by etching out peaks on polymer surface thus leaving the surface flat or smoother than that of the untreated sample [17].

#### **4. Application by substrate**

This section deals with the various different types of treatment outcomes that can be achieved on textile substrate by application of plasma. The discussion here is focused the main fibers which are in used in the textile namely cotton, wool, polyester, nylon, poly propylene, linen and rayon.

The achievable outcomes on each substrate have been discussed in light of published research with aid of the possible modes of application mentioned in the previous section. In some cases a combination of these has also been used and discussed accordingly.

The text will cover results for both, atmospheric and vacuum pressure plasmas wherever possible. As mentioned earlier most of the literature published to date is based on studies conducted at vacuum pressure. In this discussion, attempts have been made to include as much of both forms of treatment as possible.

##### **4.1. Cotton**

Cotton being the most widely used amongst natural fibers has gone through quite a bit of experimentation in terms of plasma treatment. Experimentation on cotton has been recorded using different treatment parameters to achieve a very vast range of outcomes.

No matter what the outcome on cotton, the underlying principle is generally similar. Most of the papers talk about increase in wettability of the fabric or increase in fiber roughness. As a result of these changes there are effects on processing throughout the production line, be it pretreatment, dyeing or finishing.

In this section therefore, the discussion on cotton is based on the chemical/morphological changes that occur in the fibers under different variables and types of plasma treatment.

#### 4.1.1. Desizing [18]

Atmospheric plasma has been used to remove PVA sizing material from cotton fibers. It has been noted that in contrast with conventional treatment which requires hot water for effective removal of size, plasma treated cotton could be completely rid of PVA sizing material with a simple cold water wash.

Analysis reveals that the treatment enhances removal of PVA sizing material by two ways. Firstly the treatment breaks down the chains of PVA making them smaller and more soluble. X-ray photoelectron microscopy results reveal that plasma treatment introduces oxygen and nitrogen groups on the surface of PVA which owing to greater polarity increase the solubility of PVA. Of the two gas mixtures that were studied, the results also indicate that O<sub>2</sub>/He plasma has a greater effect on PVA surface chemical changes than Air/He plasma. The table below shows the relative intensities of the chemical composition of PVA films treated with atmospheric pressure plasmas.

Treatment	Element %		
	C	O	N
Control	87.4	11.9	0.6
Air/Helium Plasma, 5 min	87.5	12.9	1.0
Oxygen Helium Plasma, 5 min	81.5	16.2	2.3

*Table 4.1, Relative intensities of the chemical composition of PVA film treated with atmospheric pressure plasmas [18]*

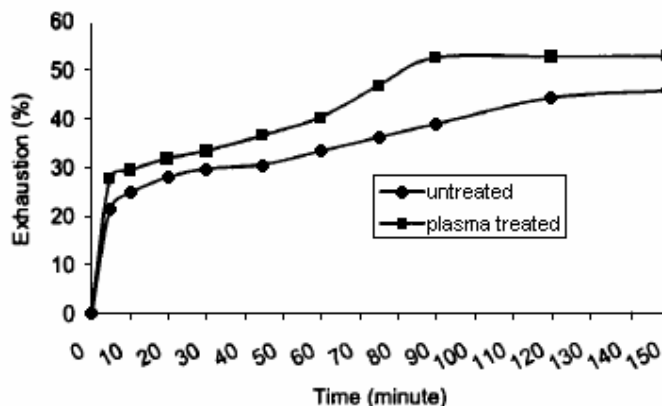
#### 4.1.2. Scouring and Dyeing [19]

The scouring and dyeing behavior has been shown to improve with O<sub>2</sub> plasma treatment under low pressure conditions. The results for scourability are shown in table 4.2.

Samples	Residual oil, fat, wax (%) on cotton
Greigh	100
Greigh + plasma 1 min	92.98
Greigh + plasma 1 min + scouring 5 min	49.68
Greigh + plasma 1 min + scouring 10 min	31.32
Greigh + plasma 1 min + scouring 15 min	24.84
Greigh + plasma 1 min + scouring 20 min	16.22
Greigh + plasma 1 min + scouring 25 min	12.29
Greigh + plasma 1 min + scouring 30 min	9.98
Greigh + plasma 1 min + scouring 35 min	9.60
Greigh + plasma 1 min + scouring 40 min	8.01
Greigh + scouring 40 min	13.15

*Table 4.2, Residual oil, fat and waxes on plasma treated cotton [19]*

The graph below shows the difference in exhaustion rates in plasma treated and untreated cotton fabrics.



*Figure 4.3, Exhaustion rate of dyestuff on plasma treated and untreated cotton [19]*

The paper reports that the enhanced treatment of the fiber is due to two reasons.

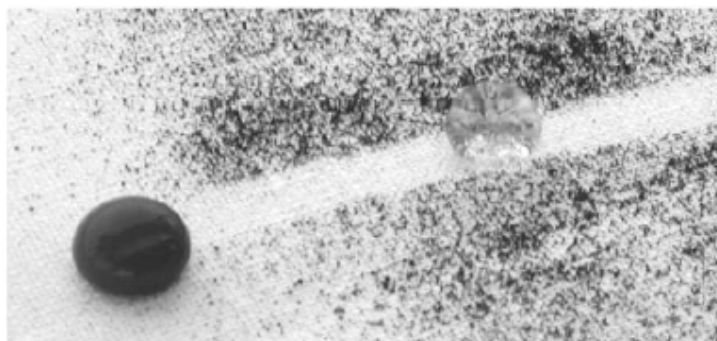
The attachment of surface polar groups increases the wettability of the cotton thus improving the scouring and adsorption of dye. Better adsorption consequently leads to better treatment. SEM observation of the cotton fibers reveals that the plasma treated fabric has holes on the fiber surface which serve as entry sites for dye molecules leading to better dyeing rates.

The ablation effect of the plasma which is characterized by holes in [19] could have added to the surface area of the fiber which coupled with the enhanced wetting due to the attachment of surface polar groups provided better wetting and hence cause a possible enhancement of dyeing rates.

#### **4.1.3. Hydrophobization [20]**

By varying the application gasses, plasma treatment can be used to achieve the completely opposite effect of those discussed so far in this text. Treatment of cotton fabric with hexamethyldisiloxane gas can be used to smooth the surface of the fibers and is capable of increasing the contact angle on the fiber till up to  $130^\circ$ . Similarly, by using hexafluoroethane plasma, a strong effect of hydrophobization can be achieved by introducing fluorine groups on the surface of the fibers. Neither of these methods reduces the water vapor transmission ability of cotton.

The image below shows a water droplet removing dye particles dispersed on cotton fabric.



*Figure 4.4, Water drop-induced dye removal from a plasma-treated cotton fabric [20]*

Plasma treatment can also be used to achieve the lotus effect on cotton fabrics. The underlying principle is etching of the fiber to create nano sized peaks and then covering them with a hydrophobic layer using an appropriate gas such as hexafluoroethane.

Though the text discussed [19] doesn't mention the pressure conditions under which the plasma was applied, earlier chapters in this text discuss the limitation of atmospheric plasma for layering on textile substrate. As research on the development of atmospheric plasma treatment systems continues and innovations come about, systems are now being developed that use liquid precursors for plasma coating under atmospheric pressure (see section 2.2).

#### 4.1.4. Mechanical properties [21]

This section sheds light on the tensile, sheer, bending, compression and surface properties of cotton along with fabric hand values.

The effect reported is based on the increase in inter fiber friction thus enhancing the coefficient of friction between the fibers. As a result the cohesive forces between the fibers greatly increase and enhance the holding property of the fabric.

Tensile linearity which can be attributed to fabric stiffness and tensile energy of the fabric which denotes the force required to stretch the fabric, increase in both warp and weft while the tensile resilience which is the recovery of the fabric once a stretching force is removed and extensibility/stretch (EMT) of both show a decrease. Table 4.5 shows the recorded readings.

Shear Property	Cotton			
	Control	O <sub>2</sub>	Control+Wet	O <sub>2</sub> + Wet
Shear Rigidity (gf/cm.degree)				
Warp	0.779	0.781	0.653	0.771
Weft	0.729	0.783	0.671	0.763
Average	0.754	0.882	0.662	0.767
Shear hysteresis at 0.5° (gf cm <sup>-1</sup> )				
Warp	10.4	11.14	0.653	18.66
Weft	9.95	10.26	0.671	14.39
Average	10.18	10.7	0.662	16.53
Shear hysteresis at 5° (gf cm <sup>-1</sup> )				

Warp	60.7	50.55	0.653	48.63
Weft	57.1	50.15	0.671	52.8
Average	58.9	50.35	0.662	50.72
Elongation EMT (%)				
Warp	5.34	5.19	10.13	9.65
Weft	5.46	4.22	8.22	7.58
Average	5.4	4.71	9.18	8.62

*Table 4.5, Results of tensile properties of cotton fabrics [21]*

## **4.2. Wool**

More experimental study of plasma treatment has been conducted on wool as compared to any other fiber and some authors have claimed that certain processing of wool with low temperature plasma treatment does meet industrial requirements [22].

Some concepts such as that of shrink proofing or anti-felting are unique to wool fibers and have been discussed in this section along with others which are similar to other fibers.

### **4.2.1. Shrink resistance [20, 22]**

Shrinkage in wool fibers occurs due to the directional coefficient of friction in the fibers because of the presence of scales on the fiber surface. The frictional forces coupled with the hydrophobic effect due to the presence of a hydrophobic epicuticle curl the fibers towards the root.

Plasma treatment of wool fibers has shown to reduce this curling effect by etching off the exocuticle that contains the disulfide linkages which increase cross linking and contribute towards shrinkage. This procedure also enhances wettability by etching off the hydrophobic epicuticle and introducing surface polar groups. The increase in surface area of the fiber, recorded with atomic force microscopy, is increased from  $0.1\text{m}^2/\text{g}$  to  $0.35\text{m}^2/\text{g}$ . These physico-chemical changes decrease the felting/shrinkage behavior of wool from more than  $0.2\text{g}/\text{cm}^3$  to less than  $0.1\text{g}/\text{cm}^3$  [20].

Table 4.6 shows results from [22] draw a similar conclusion as the case mentioned earlier.

Wool fabric	Relaxation dimensional change in area shrinkage (%)	Consolidation dimensional change in area shrinkage (%)	Felting dimensional change in area shrinkage (%)
Untreated	6.90	9.22	12.28
LTP treated	0.80	1.07	1.46

*Table 4.6, Results of dimensional changes (lengthwise) of wool samples [22]*

Anti shrinkage results can be enhanced if the wool fiber is coated with a resin through plasma nano-layering to achieve results which are comparable with modern aqueous treatments such as acid aqueous chlorine solution treatment or reduction with sulfite. However, it must be remembered that the physio chemical changes brought about by plasma treatment offer additional advantages such as increasing dyeing kinetics, an enhanced depth of shade, and an improved bath exhaustion [20].

#### **4.2.2. Dyeing**

The dye exhaustion rate of plasma treated wool has been shown to increase by nearly 50%. It has been shown that O<sub>2</sub> plasma treatment increases the wettability of wool fabric thus leading to a dramatic increase in its wicking properties. Also the disulphide linkages in the exocuticle oxidize to form sulphonate groups which also add to the wettability [23]. The etching of the hydrophobic epicuticle and increase in surface area also contributes towards the improvement in the ability of the fibers to wet more easily.

The graph below [19] shows that plasma treated wool can achieve 90% exhaustion in 30 minutes as compared to 60 minutes for untreated samples while the time required to achieve maximum exhaustion is reduced to 50 minutes as compared to 90 for untreated wool.

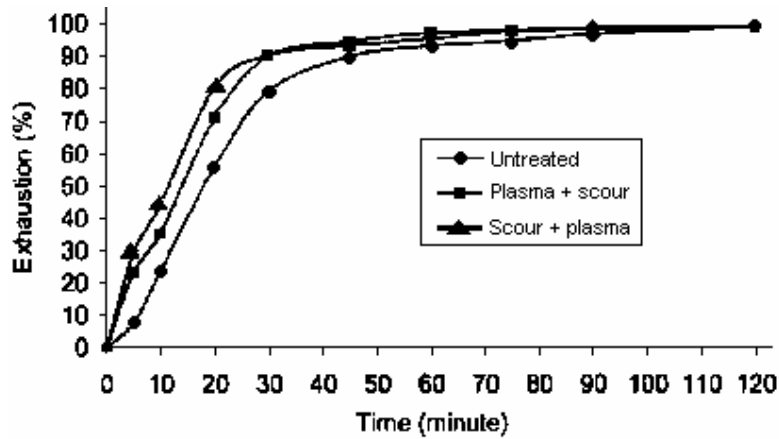


Figure 4.7, Exhaustion rate of dyestuff on plasma treated and untreated wool [19]

Plasma treatment of wool can result in different maximum exhaustion percentages with application of different dye classes. Studies have shown that oxygen plasma treatment does not significantly increase exhaustion of acid and chrome dyes but has a significant effect on the maximum exhaustion when wool is dyed with reactive dyes [24]. A possible explanation to this behavior is that the dye exhaustion of reactive dyes probably increases due to the increase in sulphonate groups on the fiber surfaces.

#### 4.2.3. Mechanical properties

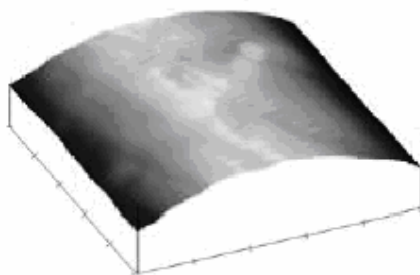
The mechanical properties, air permeability and thermal properties of woolen fabric treated with low temperature plasma with oxygen gas for different times were studied [25]. The low stress properties were classified according to the Kawabata Evaluation System (KES-F). The experiments revealed that etching enhanced inter fiber and yarn friction thereby affecting the properties of the fabric. Changes in the morphology of wool could have caused entrapment of air within the fiber/yarn matrix which had an impact on the thermal properties of the fiber [21]. Also, increase in fabric thickness due to the treatment reduced the air permeability of the fabric. The results are summarized in table 4.8.

KES-F properties		Plasma treatment time (minutes)				
		0	5	10	20	30
Tensile	WT (gf.cm/cm <sup>2</sup> )	11.61	12.72	12.75	12.79	12.84
	RT (%)	64.07	59.59	59.39	59.15	58.97
	EMT (%)	9.54	8.39	8.34	8.28	8.20
Shearing	G (gf/cm.degree)	0.71	1.30	1.32	1.35	1.38
	2HG (gf/cm)	0.60	2.00	2.05	2.06	2.08
	2HG5 (gf/cm)	1.75	5.55	5.58	5.60	5.63
Bending	B (gf.cm <sup>2</sup> /cm)	0.111	0.139	0.140	0.143	0.146
	2HB (gf.cm/cm)	0.038	0.083	0.087	0.089	0.095
Compression	To (mm)	0.659	0.709	0.712	0.716	0.718
	Tm (mm)	0.531	0.557	0.559	0.563	0.568
	WC (gf.cm/cm <sup>2</sup> )	0.08	0.08	0.08	0.09	0.09
	RC (%)	46.63	19.21	19.16	19.08	19.02
	EMC (%)	19.42	21.44	21.48	21.52	21.55
Surface	MIU	0.213	0.369	0.372	0.375	0.380
	SMD (micron)	3.88	4.20	4.32	4.43	4.53
Air permeability	R (kPa s/m)	6.79	7.70	7.75	7.82	7.90
Warm/cool feeling	qmax (W/cm <sup>2</sup> )	0.155	0.128	0.124	0.120	0.113

*Table 4.8, Low-stress mechanical properties, air permeability and warm/cool feeling of LTP-treated wool fabric [25]*

### 4.3. Polyester

Polyethyleneterephthalate is the most frequently used synthetic fibers for textiles. Experimentation on the fiber has yielded interesting results on the fiber. Figure 4.9, shows and AFM image of the surface of unmodified polyester fiber [26].



*Figure 4.9, Atomic force microscope image showing the surface of untreated PET fiber [26]*

#### **4.3.1. Dyeability**

Research proves evidence that the dyeability of polyester can be enhanced by plasma treatment. The effect of low pressure, pseudo discharge using nitrogen under different pressure (0.06, 0.1 and 0.2 torr), current (1–6 mA), and exposure times (15–600 s) was investigated in [4].

The results showed that the optimum parameters that recorded the highest water absorbency and best color were an exposure time of 15 s coupled with a pressure of 0.1 torr and current of 5 mA [4].

Again, the phenomena behind the increased dye uptake are the same. The increase in surface area due to optimized etching and induction of polar groups through grafting increases the wettability of the fibers thus allowing better adsorption and consequently absorption of dyestuff. The exponential decrease in absorbency due to increased exposure time which has been explained in the cited text as an occurrence due to plugging of surface pores due to melting of the top most layer of the fabric has been explained better in [27]. The text states that the decrease could be due to surface smoothening with long term treatment, owing to the creation of plasma induced charges on the surface which reduce etching efficiency due to repulsive forces. Or it could also be because of the inability of the plasma to etch the crystalline regions of the fiber.

Research by El-Nagar [4] shows that plasma treatment does not cause significant deterioration of the fibers after treatment and has thus concluded that plasma treatment is a suitable method to improve dyeability of polyester by enhancing the wettability of the fibers and the method is industrially applicable.

#### **4.3.2. Hydrophobization [3]**

Polyester fibers, by nature, exhibit a hydrophobic character with an absorbency of about 0.5%. This study aimed to achieve the Lotus Effect on polyester fabric by replication the surface structure of lotus leaves on fabric through plasma treatment.

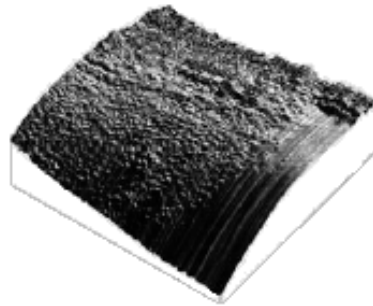
Studies were conducted with low pressure plasma under variable pressures, exposure times, treatment equipment and gasses. Results indicate that higher treatment times and lower pressures yield rougher surfaces with many small peaks which are ideal for the required purpose.

However, during the second phase of applying a thin hydrophobic layer on the peaks, the initial effect is lost as the coating covers the peaks, leaving the surface smooth. The hydrophobic effect of which is produced is still not lost and there is a slight increase in the average contact angle. Gasses such as  $CF_4$  or  $SF_6$  can be used to create this hydrophobic effect by introducing fluorine groups on the surface [27]. The formation of a nano layer using  $SiO_2$  plasma ranging from 10- 100 nm has been recorded in [26]. More work needs to be done to ensure that a fine enough hydrophobic film is formed so that it doesn't cover the peaks on the surface.

#### **4.3.3. Mechanical properties**

The mechanical properties of polyester have been shown to be affected in a way similar to wool and cotton due to the increase in surface roughness [28]. The figure below is an AFM image showing the surface roughness induced

due to plasma gas etching [26]. An additional effect which occurs with polyester is the enhanced ability of the fiber to prevent static build up due to the increased water adherence properties because of surface polar groups [28].



*Figure 4.9, Atomic force microscope image showing the surface of PET fiber after 60s treatment with O<sub>2</sub> Plasma [26]*

#### **4.4. Polypropylene**

Polypropylene is one of the most rapidly growing synthetic fibers for a variety of uses, including technical textiles. Most of the experimental work conducted on poly propylene relates to enhancing their wettability by surface activation using oxygen plasma [6, 20, 29, 30]. The general indication is that application of plasma with different gasses such as O<sub>2</sub>, Ar, He, He-O<sub>2</sub> can reduce the contact angle of water on fiber surfaces and lead to an increase in the wettability of the fibers due to the increase in oxygen and decrease in carbon groups on fiber surfaces. Tests performed with both, atmospheric and low pressure plasma have yielded satisfactory results, thus the method is industrially applicable.

Corona treatment after melt spinning of polypropylene fibers is capable of reducing the static buildup on the fibers by enhancing the wettability of the fibers [31]. The method can be used to replace application of temporary anti static finishes on the fiber surface which is needed during the initial processing period.

#### 4.5. Other fibers

Studies on other fibers have yielded similarly positive results to achieve various forms of functional modifications and finishes.

Papers have been published on treatment of silk to achieve a hydrophobic finish with successful results indicating an increase in the contact angle on Thai Silk to upto  $140^{\circ}$  using  $\text{SF}_6$  plasma [32]. Similar studies on acrylic fiber products for outdoor application have also yielded successful results indicating possible industrial application of atmospheric plasma. Plasma treated acrylic fiber has also shown better resistance to wear and UV radiation and more work is underway to explain this [33].

Low temperature plasma treatment of linen has shown to modify the surface morphology of the fibers similar to that of cotton to enhance the mechanical behavior of the fibers and also increase water absorbency due to a dramatic increase in surface oxygen, consequently polar groups [34].

A comparative study of plasma treated melt spun and electrospun polyurethane and nylon fabrics [35] shows that the electrospun fabrics bear a measurable strength loss after one atmosphere uniform glow discharge plasma treatment for over 10 seconds. However, since the areal mass normalized strength of the electrospun fabrics is 10 fold of that of the melt spun micro fibers, the strength loss can be regarded as insignificant. The results revealed that plasma one atmosphere uniform glow discharge treatment increased the surface energy of the substrate as well as the contact angle.

Studies on blended fabrics, 67/33 Cotton/Polyester [10] have been conducted to investigate the effect of plasma on bleaching, mercerization and dyeing. Results indicate the atmospheric plasma treatment does not have a significant effect on the whiteness properties of the fabric but is capable of enhancing dye uptake by various degrees for different dyes such as VAT, reactive and even pigment adhesion.

Research on plasma treatment of textiles is now heading towards the study of different fibers for varying applications and is no longer just focused on the principle fibers that dominate the textile industry. Ching-luan Su [36] has studied the effect of plasma modification on the performance of carbon absorbents in textiles.

The evolution of plasma treatment will be a subject of interest across the textile world and it will be of interests for, industrialists and researchers alike, to keep an eye on the direction it takes in future.

## **5. The role of plasma treatment in sustainable development**

In light of the application processes discussed in this text, plasma technology holds tremendous potential to develop processes which can limit the environmental impact of textile processing and contribute towards sustainable development. Savings with plasma treatment can be due to a variety of factors but mostly relate to conservation of water and energy as plasma treatment leads to dramatic reductions in the use of both. This section will discuss how the use of plasma treatment relates to environmental impacts.

Physical etching of textile substrate can be used to create nano sized peaks on the surface of the fiber. This coupled with nano-layering of a hydrophobic fluoro carbon compound can be used to create the famous lotus effect on textile which makes surfaces of hydrophilic fibers effectively hydrophobic while still leaving it breathable [20]. Conventionally these treatments are performed by pad/dry/cure treatments which utilize large amounts of water and also require heat to cure the applied chemical [1, 11, 20].

In contrast plasma treatment can achieve the same effect by applying a gas such as oxygen for etching and a fluorocarbon in gaseous state for nanolayering by using comparatively very little electrical power and also performing the same action in much lesser time [20].

Though these finishes can not yet produce results of the same scale as conventional wet treatment, research in the field promises that results will improve in the future and will ultimately lead to the replacement of the conventional method of hydrophobization [10].

Anti felt treatment of wool which normally requires the application of harmful chlorine based chemical on the surface of the fibers to degrade the epicuticle and exocuticle to increase the hydrophilicity of the fibers and remove their directional scales can be done using a plasma gas treatment such as O<sub>2</sub>. This leads to the elimination of the wet treatment and also avoids the use of environmentally non friendly chlorine based chemicals. This treatment,

coupled with a resin coating can achieve results similar to conventional wet treatments [20, 22].

In some cases, plasma treatment alone can not lead to the elimination of wet processing from any process in particular. However, it is still capable of contributing towards environmental preservation through a variety of means. Research indicates that surface modification is capable of improving the wettability of fibers by inducing polar groups on the surface [18, 19, 24]. This can lead to dramatic savings in wet processing in terms of processing times which contribute towards energy savings, less chemical consumption, better dye uptake which leads to less chemical in discharged waste water and lower temperature requirements for certain processes.

Desizing of plasma treated fabrics has shown that by introducing polar groups on the surface of cotton with O<sub>2</sub> plasma the fabric can be desized in water at room temperature rather than the 90° C bath conventionally required. This can lead to energy savings because heating of the bath will not be required [18]. Also the introduction of polar groups effectively reduces the time required for scouring by about 45% from 40 to 25 minutes to achieve similar results [19].

Plasma treated fibers also show quicker and higher exhaustion of dyestuff leading to less processing times and lesser amounts of chemical in waste water, thus leading to more efficient use of energy resources and less hazardous waste in discharged water [19]. These benefits and higher shade depths for some classes of dyes such as reactive on wool promise more efficient use of dyes and auxiliaries so that hazardous wastes in discharged water such as heavy metals, unexhausted dyes, residual surfactants and other wetting agents are kept at a minimum [24]. The benefits of plasma treatment therefore are multi fold and no research work has been purely conducted to measure this amazing potential held by the technology.

Plasma treatment, however, does have certain draw backs. The treatment tends to produce harmful gasses such as ozone and nitrogen oxides during operation [9]. This happens due to the formation of free radicals and nascent

oxygen during the treatment, which react with atmospheric gasses to form harmful by products. In some cases, contaminations from the substrate such as sulphur from the cystine links in wool can react with atmospheric oxygen to form oxides of sulphur [23]. It is thereby recommended that plasma treatment systems are installed in well ventilated areas to ensure that they pose no health risks for the workers working in the surrounding environment.

Some companies are now making plasma systems which employ an inert gas such as Argon as the main plasma gas rather than atmospheric air. An inert gas doesn't react with contaminations to produce hazardous air pollutants thus their generation is kept at a minimum by utilizing the active component such as  $O_2$  in limited quantities and only for the specific application.

Plasma treatment holds tremendous potential for application in the field of textiles because of the types of finishes it can incorporate on textile material. However, at present treatment is expensive due to high equipment costs and the finishes incorporated are in many cases not comparable with current wet treatments.

With heavy investments being made in the technology in countries from the developed world [1] and enormous amount of research being conducted in the field, because of its potential and ability to conserve the resources of our planet, plasma treatment can be seen as a technology that has a strong future in the textile industry, both as a tool for providing unique functional finishes on textiles with the added advantage of non-aqueous treatment as well as a tool to use the planet's resources more efficiently and effectively.

## **6. Conclusion**

This work has managed to provide an insight into plasma treatment of textile substrate. There are numerous factors in this project which have only been brushed from the surface that can be worked on in detail.

A study of equipment for plasma treatment will certainly be able to provide a better insight into the technology and has not been included in this text owing to the limited scope of the project and lack on initial understanding of the subject but is a very good area to look into after acquiring fundamental knowledge in the field.

Numerous manufacturers of plasma equipment have a lot of knowledge and information to offer. Innovations carried out at companies should be closely followed to keep at par with the developments in this rapidly advancing field.

Another challenge has been to get access to instruments for test treatment. Quaid-e-Azam University, Islamabad does have plasma treatment equipment. However, the specifications of the equipment could not be determined and testing carried out as the initial enthusiasm shown by professors at the QAU labs, prematurely died out.

It might be possible to now look into textile treatment with plasma in light of the material compiled so far and explore the possibilities of conducting research on the application of plasma on textiles in Pakistan.

This study has managed to shed light on research being conducted across the world and does provide an overview of the methodology behind surface modification and functionalization of materials with plasma. However, with new applications being developed and published regularly it has been a challenge to keep at pace with latest developments and include all of them in this study.

Research on Plasma treatment can so far safely conclude that the technology seems to carry promise with its benefits of cost reduction, energy savings and application outcomes only limited by imagination.

It would not be practical at this point to suggest the adoption of plasma treatment to the local textile industry but this is an important field in terms of research and seems to hold a promising future for textile processing.

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