Atmospheric pressure glow discharge plasma and its applications in textile

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Plasma, a partially-ionized gas generated by an electrical discharge or high temperature, is of different types and can be classified based on pressure, temperature, source of energy and type of gases. Cold plasma is generated by electric discharge at near-ambient temperatures and can be used for surface modification of textile substrates. This paper reports a brief review of the various plasma and their applications for textile modifications. For textile modifications, atmospheric pressure glow discharge cold plasma is more suitable because it can be designed for continuous treatment of textile. However, the main challenge in atmospheric plasma is to obtain a stable glow (filament-free) discharge over a large surface area suitable for the safe treatment of textile. At IIT-Delhi, uniform glow discharge plasma at the atmospheric pressure over large surface area has been developed by optimizing reactor design and process parameters. Using this plasma, polyester (PET) and nylon fabrics were treated for 10-60 s under different gases. The treatment significantly enhanced the water absorbency and surface energy of both the nylon and PET fabrics. In nylon-6, the properties imparted by plasma treatment did not change even after 25 days. However, in PET, the absorbency and surface energy were found to reduce slowly with time of storage. The samples did not degrade during plasma treatment and showed insignificant change in mechanical properties. The atmospheric pressure glow discharge plasma can effectively and safely be used to modify surfaces of textile substrates at reduced process and environment cost.

Keywords: Atmospheric pressure plasma, Glow discharge plasma, Nylon-6, Plasma treatment, Polyester

IPC Code: Int. Cl. D06M 10100, H05H

1 Introduction

Matter within the universe is most commonly found in the form of plasma rather than as a solid, liquid or gas. Plasma is partially-ionized gas normally generated by an electrical discharge at near-ambient temperatures. Plasma, often considered as the fourth state of matter, is composed of an ionized gas containing a mixture of ions, electron, neutral and excited molecule, and photons. This state of matter was first identified by Sir William Crookes in 1879, and named ‘plasma’ by Irving Langmuir in 1928. Man-made plasma has existed for millennia in the form of fire and recently, other types of man-made plasma have been prepared such as discharge under electric field. Unlike hot plasma which is used in metal industry, cold plasma can be used safely for textile modification. AC plasma (frequency: kHz, MHz & GHz) is generally used as it has several advantages over DC plasma. Over the past decade, many uses have been found for these plasma, whether they are coronas, non-equilibrium or thermal, for example in surface cleaning and adhesion promotion. Plasma has a high likelihood of surface interaction with organic substrates. This interaction may be physical, for example in the cleaning of organic contaminants from the surface; or the effect may be chemical, for example in the bonding of hydroxyl groups to the surface. In the treatment of textile substrates, the cleaning effect can modify wettability and dye uptake, and the free radicals can incorporate atoms which also change the surface, for example making a hydrophilic material into a hydrophobic one.

The main attraction of plasma in industrial processing is the avoidance of chemical effluents. Other advantages include: low cost, rapid reaction times, high cleaning efficiency, low consumption of gas due to physical effects, and the enclosed and dry nature of the process. Vacuum plasma having several advantages is not used in the industry as it is batch process and has high operation cost. These drawbacks of vacuum plasma can be overcome by atmospheric pressure plasma, and the system can be designed for continuous treatment of textile, therefore, it is gaining attention in the research community.

During the past decade, considerable efforts have been made to generate stable atmospheric pressure glow discharge plasma (filament-free) based on dielectric barrier discharge particularly over a large
The present study is aimed at designing and fabricating the atmospheric plasma reactor with stable glow discharge plasma over a large surface area, which is suitable for textile treatment. Nylon and PET fabrics have also been treated using this plasma to observe the effectiveness of this plasma to textile substrates.

2 Classification of Plasma

Plasma can be classified in various ways, such as

(i) On the basis of pressure in plasma chamber—Atmospheric pressure and low pressure plasma.
(ii) On the basis of degree of ionization and the temperature of electrons and ions—Hot and cold plasma.
(iii) On the basis of frequency of the power supply—DC and AC plasma (RF, Microwave, GHz Plasma).
(iv) Depending upon the electron affinity of the process gases used—Electropositive and electronegative gas plasma.

Any plasma reactor will be a combination of all of the above, e.g. one atmosphere glow discharge cold plasma is based on cold, AC and atmospheric pressure plasma.

2.1 Atmospheric Pressure and Low Pressure Plasma

2.1.1 Atmospheric Pressure Plasma

Atmospheric pressure plasma is used in a variety of materials processes. Traditional sources include transferred arcs, plasma torches, corona discharges and dielectric barrier discharges. In arcs and torches, the electron and neutral temperatures exceed 3000°C and the densities of charge species range from $10^{16}$ cm$^{-3}$ to $10^{19}$ cm$^{-3}$. Due to the high gas temperature, this plasma is used primarily in metallurgy. Corona and dielectric barrier discharges produce non-equilibrium plasma with gas temperatures between 50°C and 400°C. Higher voltages are required for gas breakdown at 760 torr and often arcing occurs between the electrodes. However, to prevent arcing and lower the gas temperature, several schemes have been devised, such as the use of pointed electrodes in corona discharges and insulating inserts in dielectric barrier discharges.

The advantages of atmospheric pressure plasma are: (i) continuous treatment can be given, and (ii) it is cost effective process. On the other hand, the disadvantages of atmospheric pressure plasma are: (i) difficulty of sustaining a glow discharge, (ii) higher voltages are required for gas breakdown, and (iii) difficult to form uniform plasma throughout the reactor volume.

Different types of atmospheric pressure plasma used are: corona discharge, dielectric barrier discharge and plasma jet.

Corona Discharge

A corona is a process by which a current, perhaps sustained, develops between two high-potential electrodes in a neutral fluid, usually air. Corona discharge usually involves two asymmetric electrodes, one highly curved (such as the tip of a needle or a narrow wire) and other of low curvature (such as a plate or the ground). The high curvature ensures a high potential gradient around one electrode for the generation of a plasma. Fig. 1 shows a schematic of a point-to-plane corona. The plasma usually exists in a region of the gas extending about 0.5 mm out from the metal point. In the drift region outside this volume, charged species diffuse toward the planar electrode and are collected.

Coronas are used for the activation of polymer surfaces, manufacture of ozone, scrubbing particles from air in air-conditioning systems and removal of unwanted volatile organics, such as chemical pesticides, solvents.

Dielectric Barrier Discharge

Dielectric barrier discharge (DBD) is also called ‘silent’ and ‘atmospheric pressure glow’ discharges. A schematic of this source is shown in Fig. 2. It consists of two metal electrodes, in which at least one...
The electrode is coated with a dielectric layer. The gap is of the order of several mm and the applied voltage is about 20 kV. DBD \(^7\) represents self-sustained non-equilibrium electrical discharges that are operated at approximately atmospheric pressure, typically between 0.1 bar and 1 bar. Because of the presence of dielectric barriers, this electrode configuration cannot be operated with DC-fields. Typically, they are operated with sinusoidal wave current, square wave current or pulse wave forms between the line frequency and RF frequency.

Two kinds of DBD can be distinguished. In the common form of the discharge, the plasma is composed of many short living micro-discharges (streamers), which are chaotically distributed over the electrode surface. Each micro-discharge consists of an almost cylindrical plasma channel, typically of about 100 μm in radius and spreads into a larger surface discharge at the dielectric surface(s).

In the second type, the plasma appears as a glow discharge and is initiated as a Townsend discharge. A large number of seed electrons are necessary to turn on the discharge through a Townsend breakdown. The main mechanism leading to the formation of these seed electrons depends on the lifetime of the gas metastables compared to the delay between two consecutive discharges and on the maximum ionization level which can be reached without transition to a filamentary discharge. Being non-equilibrium plasma, DBDs exhibit electron energies much higher than that of the ions and neutral species. Dielectric barrier discharges are sometimes confused with coronas, because the latter sources may also exhibit microarcing.

Dielectric barrier discharges have been examined for several material processes, including the cleaning of metal surfaces and the plasma-assisted chemical vapor deposition of polymers and glass films. However, since the plasma is not uniform, its use in etching and deposition is limited to cases where the surface need not be smooth.

**Plasma Jet**

Figure 3 is a schematic of an atmospheric pressure plasma jet. This new source consists of two concentric electrodes through which a mixture of helium, oxygen and other gases flows. By applying 13.56 MHz RF power to the inner electrode at a voltage between 100 V and 250 V, the gas discharge is ignited. The ionized gas from the plasma jet exits through a nozzle, where it is directed onto a substrate a few millimeters downstream. Under typical operating conditions, the gas velocity is about 12 m/s with the effluent temperature near 150°C. So far, this source has been used to etch polyimide, tungsten and silicon dioxide as well as to deposit silicon dioxide films by plasma-assisted chemical vapor deposition (CVD).\(^3\)

### 2.1.2 Low Pressure Plasma

Low pressure plasma has found wide applications in materials processing and play a key role in manufacturing semiconductor devices.\(^5\)\(^-\)\(^8\) The advantages of plasma are well known. They generate high concentrations of reactive species that can etch and deposit thin films at the rates up to 10 μm/min. The temperature of the gas is usually below 150°C, so that the thermally sensitive substrates are not damaged. The ions produced in the plasma can be accelerated toward a substrate to cause directional etching at submicron level. In addition, a uniform glow discharge can be generated, so that the materials processing proceeds at the same rate over large substrate areas.

In a weakly ionized gas at low pressure, the electron density ranges between \(10^8\) cm\(^{-3}\) and \(10^{13}\) cm\(^{-3}\). Under these conditions, the collision rate between electrons and neutral molecules is insufficient to bring about thermal equilibrium. Consequently, the electron temperature \(T_e\) can be one to two orders of magnitude higher than the neutral \(T_n\) and ion temperatures. However, as the pressure increases, the collision rate will rise to a point where effective energy exchange occurs between the electrons and the neutral molecules, so that \(T_e \approx T_n\). In this case, the electron density usually ranges from \(10^{10}\) cm\(^{-3}\) to \(10^{16}\) cm\(^{-3}\).

The advantages of low pressure plasma are: (i) they generate high concentrations of reactive species that can etch and deposit thin films; (ii) uniform glow is obtained; (iii) the temperature of the gas is usually below 150°C, so that the thermally sensitive substrates are not damaged; (iv) low breakdown
voltages; and (v) a stable operating window between spark ignition and arcing.

Low pressure plasma also has several disadvantages, like (i) vacuum systems are expensive and have high maintenance cost, and (ii) size of the object to be treated is limited by the size of the vacuum chamber.

2.2 Hot and Cold Plasma

Depending upon the temperature of ions and electron and the degree of ionization, plasma can be classified in two groups such as hot and cold plasma. Production in Universe is of hot plasma. Hot plasma occurs when the temperature of electrons and atomic and molecular species are extremely high. Ninety nine per cent of the matter in the universe is in the plasma state. Hot plasma is nearly fully ionized which is actually known as the ‘fourth-state of matter’. The Sun and the stars in the universe consist entirely of hot plasma, and the space within the stars of a galaxy is filled with plasma.

Cold plasma occurs when the atomic and molecular species are at ambient temperature, whereas the electrons are at high temperatures. A small fraction of the gas molecules (e.g. 1%) is ionized. It has already found uses in a variety of manufacturing processes. For example, flat-screen televisions use cold plasma to radiate light and create images. Cold plasma can be used to treat surfaces (e.g. oxidation, functionalization) or to deposit specific coatings onto organic and inorganic substrates. Cold plasma can produce ozone as its secondary offspring. Most important, cold plasma is used to finely etch channels on integrated circuits — the chips inside our desktop and laptop computers that made the computer and internet age possible.

2.3 DC and AC Plasma

AC discharges are preferred over DC-driven discharges in plasma systems for a number of reasons. First, as the frequency of AC increases, the energy transfer into the discharge becomes more efficient, especially at frequencies between ~100 kHz and 1 GHz, the RF regime. Also, in a DC discharge, charged particles from the plasma can accumulate on the substrate surface causing unwanted charging effects. By alternating the direction of the current flow sufficiently rapidly, these charging effects can be reduced. At RF frequencies, this alternation is sufficiently rapid to almost completely eliminate charging effects.

2.4 Electropositive and Electronegative Gas Plasma

Most of the etching plasma used in the semiconductor industry is formed from gases which readily form negative ions, i.e. electronegative gases. Plasma is usually classified into two different types depending upon the electron affinity of the process gases used. Process gases can be arranged roughly in the following order of increasing electronegativity:

\[
\text{Ar} \rightarrow \text{N}_2 < \text{CF}_4 < \text{CF}_2\text{Cl}_2 < \text{Cl}_2 < \text{CFCI}_3 < \text{SF}_6 < \text{CCl}_4
\]

Electropositive (EP) Plasma

These are discharges consisting mainly of species which do not form negative ions easily. Examples are all noble gases, such as Ar, He and some unreactive gases like N\(_2\). In this plasma, the number of positive ions is almost exactly equal to the number of electrons, although both are still much smaller than the number of neutrals.

Electronegative (EN) Plasma

By contrast, EN plasma contains a significant number of species which have a positive electron affinity. In these cases, the number of free electrons is significantly reduced as a result of capture by EN species to form negative ions. A typical reaction might be:

\[
e + \text{CCl}_4 \rightarrow \text{CCl}_4^- \rightarrow \text{CCl}_3 + \text{Cl}^-
\]

In CCl\(_4\) plasma, the number of electrons can be up to 100 times less than the number of positive ions, with overall charge neutrality being maintained by large numbers of negative ions. EN plasma requires higher power to sustain and is difficult to initiate. This make EN plasma unstable and often non-uniform. The electron temperature is also much higher than in EP plasma.

3 Glow Discharge Plasma

A glow discharge\(^{10}\) is a kind of plasma. It is an ionized gas consisting of equal concentrations of positive and negative charges and a large number of neutral species. In the simplest case, it is formed by applying a potential difference (of a few 100 V to a few kV) between two electrodes that are inserted in a cell (or that form the walls of the cell). The cell is filled with a gas (an inert gas or a reactive gas) at a pressure ranging from a few mTorr to atmospheric pressure.
Due to the potential difference, electrons that are emitted from the cathode by the omnipresent cosmic radiation are accelerated away from the cathode, and give rise to collisions with the gas atoms or molecules. As a result of this excitation, the ionization and dissociation take place. The excitation collisions give rise to excited species, which can decay to lower levels by the emission of light. This process is responsible for the characteristic name of the “glow” discharge.

3.1 One Atmosphere Uniform Glow Discharge Plasma (OAUGDP)

The OAUGDP is produced by applying a kilohertz electric field between two parallel plates. The electric field required to initiate the OAUGDP is 8.5 kV/cm for air, well below the DC electric field for sparking. Both electrodes may be covered with quartz, Pyrex, alumina or glass insulating plates, the thickness of which is between 1 mm and 3 mm. The exposed samples are placed on the lower electrode. The OAUGDP is obtained for a wide range of experimental conditions. The working gas is entered from one side and flows out through the other side. OAUGDP reactor is uniform without filamentary microdischarges, if the proper combination of gap distance, RF driving frequency and rms voltage is selected to maintain ion trapping. The OAUGDP technology is simple, cost effective and suitable for online treatment of fabrics and films.

3.2 Homogeneity and Stability of Dielectric Barrier Discharge

During the past decade, considerable efforts have been made to generate stable atmospheric pressure plasma using a dielectric barrier discharge technique. Especially the atmospheric pressure glow discharge (APGD) technique using a dielectric barrier discharge has been intensively studied. Yokoyama et al. achieved stable glow plasma at an atmospheric pressure and the stability of atmospheric pressure plasma has been improved in various ways such as varying power sources, electrode materials and modifying of electrode designs. In general, the gas temperature increases with the increase in gas pressure and the glow discharge is easily transformed to arc discharges at atmospheric pressure. However, the glow to arc transition is suppressed using dielectric barriers in the DBD process and stable glow discharge plasma can be generated at atmospheric pressure. Gas temperature is also sustained at room temperature due to the generation of short nanosecond current pulse at atmospheric pressure.

Trunec et al. carried out glow discharge at atmospheric pressure in neon gas (99.99 % purity). It was found that with raising the voltage of power supply, first the dielectric barrier discharge is ignited in neon. The discharge is filamentary, but the filaments are diffused, not so clearly bounded as at DBD in argon. They also found that the APGD can be stabilized by the neon flow with flow rate of 0.7-1.2 liter/min. At a lower flow rate the discharge can be unquiet but it is still homogeneous. Beside these they found that if admixture of argon (1%) is added to neon, the APGD change to dielectric barrier discharge and the filaments are observed. Similar effect was also observed with a small admixture of nitrogen (1%), i.e. the APGD changes to DBD.

It has been shown that DBD can be homogeneous, if the frequency of power supply is higher than 1 kHz and if helium or argon with a small admixture of acetone is used. In 1993, Okazaki et al. proposed a new method for the stabilization of homogeneous DBD at atmospheric pressure with 50 Hz power supply in any gas. This was done by inserting a fine metal mesh between the metal electrode and dielectric layer.

3.3 Breakdown Voltage

To ignite plasma, the breakdown voltage for the gas must be exceeded. This voltage depends on the electrode spacing \(d\) and the pressure \(p\) as follows:

\[
V_b = \frac{B(p \cdot d)}{\ln[A(p \cdot d)] - \ln[\ln(1 + 1/\gamma_{se})]}
\]

where \(A\) and \(B\) are the constants found experimentally; and \(\gamma_{se}\) the secondary electron emission coefficient of the cathode. Breakdown voltage \(V_b\) increases rapidly with pressure at constant electrode spacing. For example, the breakdown voltage for argon is estimated to be 2500 V at 760 torr and with a 5 mm gap distance. A narrow gap is necessary to achieve a reasonable breakdown voltage at atmospheric pressure. Fig. 4 shows the dependence of the breakdown voltage on electrode spacing and pressure.

3.4 Effect of Frequency

The electric fields in the one atmosphere glow discharge plasma reactor are only a few kilovolts per centimeter; values are usually too low to electrically...
break down the background gas. The most desirable uniform one atmosphere glow discharge plasma is therefore created when the applied frequency of the electric field is high enough to trap the ions between the two parallel plates, but not so high that the electrons are also trapped.

If the frequency is so low that both the ions and the electrons can reach the boundaries and recombine, the plasma will either not initiate or form a few coarse filamentary discharges between the plates. If the applied frequency is in a narrow band in which the ions oscillate between the two plates, they do not have time to reach either boundary during a half period of oscillation. If the more mobile electrons are still able to leave the plasma volume and impinge on the boundary surfaces, then the desirable uniform plasma is produced. If the applied frequency is still higher so that both electrons \((e)\) and ions \((i)\) are trapped in the discharge, the discharge forms the filamentary plasma. Thus, for uniform glow discharge plasma, the driving frequency should lie between the limits, as shown below:

\[ \frac{eV_{\text{rms}}}{\pi m v_c d^2} \leq v_o \leq \frac{eV_{\text{rms}}}{\pi m v_{\text{rms}} d^2}, \text{ Hz} \]

where \(m\) is the mass; \(v_c\) the collision frequency of species of interest; \(V_{\text{rms}}\), the \(\text{rms}\) voltage applied to the plates; and \(d\), the distance between electrode plates.

### 3.5 Comparison of Plasma Sources

Table 1 shows breakdown voltages and densities of charged species for the different plasma sources. The plasma jet has a lower breakdown voltage compared to that of low pressure discharge plasma, whereas the other atmospheric pressure plasma has breakdown voltages above 5 kV. Except for the transferred arc and plasma torch, all the plasma exhibit electron densities in the same range as a low pressure discharge. However, in the corona and the dielectric barrier discharge, the plasma is restricted to a small region of space and is not available for uniformly treating large substrate areas.

### 4 Advantages of Plasma Treatment of Textiles

Plasma treatment is essentially a surface treatment and does not affect the bulk properties of the fibre, which allows the fabric to retain strength after treatment. Plasma treatment can be used for all kinds of organic fibres because the modification is carried out by breaking the bonds of the polymer chains on the surface. Since the reactive sites (radicals) produced on the surface can be reacted with reactive gasses or monomers, a variety of surface effects can be generated. Also, this process eliminates liquid-solid interaction, therefore, the process is an environment friendly and cost effective alternative to traditional chemical processing for carrying out chemical modifications of fibers, yarns and fabric surfaces. For example, soil resistant, flame retardant, dye and permanent press treatments can all be accomplished without creating toxic effluents and at times several effects can be generated in one single step.

A proper configuration of plasma reactor can provide versatile and uniform treatment of the textile substrates. Atmospheric, plasma treatments can be integrated into the production line to reduce pollution and energy consumption.

#### 4.1 Mechanism of Surface Modification

Both vacuum and atmospheric pressure plasma achieve their surface treatment effects as a result of the interaction of one or more active species from the plasma with the surface of interest. These active
species are more chemically reactive and more energetic than the species associated with conventional chemical processing. Such species may include:

(i) Ultraviolet photons which are capable of breaking chemical bonds, and photons in the visible parts of the spectrum which can produce a positive surface charge by the photoelectric.

(ii) Charge particles are a second major class of active species from plasma; they include electron that either recombine on the surface or build up a surface charge; ions that may be produced by ionization events, attachment or charge exchange in the plasma; and free radicals or other charge molecular fragments such as OH resulting from plasma chemical reactions.

(iii) A third major class of active species is neutral particles which can include very reactive atoms such as monoatomic fluorine, oxygen or other atomic fragments; atoms or molecule in excited atomic states; and highly reactive molecular fragments, including monomers produced in the plasma. Most of these active species are rarely present or much less dense in ordinary chemical reactors, and their high energy levels make possible surface treatment effects that can be achieved only with difficulty, if at all, with conventional chemical processing.

The process of plasma surface modification on textile substrates can be divided into three distinct mechanisms due to the presence of different species as mentioned above.

4.1 Surface Modification Using Inert Gas Plasma

Ablation/etching—The ability of plasma processing to break down weak covalent bonds in a polymer through bombardment with high-energy particles is known as ablation. This affects the outermost molecular layers of the substrate exposed to the plasma which evaporates as small volatile fragments. Desizing of cotton and antifelting of wool are some examples.

Surface Cross-linking—Cross-linking is the setting up of multiple chemical links between the molecular chains of polymers. Plasma processing with inert gases can be used to crosslink polymers and produce a stronger and harder substrate microsurface.

4.1.2 Surface Modification using Reactive Gases and Molecules

The replacement of surface polymer groups with chemical groups from the plasma is called activation. During activation, the plasma breaks down weak bonds in the polymer and converts them to highly functional groups such as carbonyl, carboxyl, hydroxyl, etc. in the presence of active species such as reactive gases and other small organic compounds.

4.1.3 Surface Modification using Polymerizable Monomers

In this case, a thin polymer layer may be formed on the substrate surface through polymerization of a monomer. The monomer is directly polymerized on the surface activated by plasma treatment. This is known as grafting through plasma. Grafting can be carried out in situ, where the monomer gas is introduced within the plasma zone or carried out subsequently, where the activated surface is exposed to polymerization conditions in the presence of a reactive monomer such as vinyl monomer after the plasma treatment. Depending on the selection of the gas, monomer and process parameters, these thin coatings can be deposited/grafted with various properties or physical characteristics.

4.2 Plasma Modification of Textile

Some of the effects or characteristics that have been shown by cold plasma treatment on textile substrates include crease-resistant finishes, reduced felting of wool, antistatic finishes, improvement of wetting, enhancement of dyeability or printability, enhancement of UV-protective, flame-retardant finishes, hydrophilic and hydrophobic finishes, cleaning of surfaces such as desizing, scouring and bleaching.

Plasma treatment is surface oriented. In natural fibers, such as wool and cotton, the hydrophobic layer on the surface is oxidized and partially removed (desizing). The specific surface area is significantly increased during plasma treatment, which is clearly demonstrated by means of atomic force microscopy. Again, due to the surface-directed activity of the plasma, the tenacity of the fibers is hardly influenced. The chemical and physical surface modification results in decreased shrinkage behaviour of wool top.

Specific surface area of cotton also increases with oxygen plasma treatment. In hydrophobic materials such as polypropylene, plasma treatment significantly increases the hydrophilicity of the surface and surface modifications are sustained for a long time. The effect of inert gas plasma on various textile substrates is summarized in Table 2.

The modification of surfaces depends upon the type of gases used for plasma. Reactive and inert gases in
presence of organic compounds are able to bring about permanent chemical change on the surface of the substrate. Some of the studies on such modifications are given in Table 3. The treatment of cotton with organic compounds, such as hexamethyldisiloxane (HMDSO) and hexafluoro-ethane plasma, leads to a smooth surface with increased hydrophobization. The material becomes highly hydrophobic, while its water vapour transmission is not influenced.

Plasma treatment is also used for improving adhesion of reinforcing fibers to a matrix polymer. Plasma treatment of high performance fibres, such as PBO, kevlar, carbon, PET, etc. for composites was found to increase the total surface free energy of the fibres. The interfacial shear strength of such composites increases significantly on plasma treatment. Interaction between fibre surface molecule and the matrix might improve because of the increase in the total surface area and change in chemical characteristics of the surface of the fibre.

Dyeing properties of fibers, such as wool and PET, may be improved with plasma treatment. The treatment appears to modify the surface of the endocuticle or the cell membrane complex, contributing to accelerated dye diffusion in wool. In other fibres, the improvement in wettability in dyebath improves dyeing characteristics, and the increase in surface roughness imparts darker appearance to the dyed fabrics.

Modification of textile substrates using plasma polymerization and grafting are summarized in Table 4.

Several monomers such as hydroxyl ethyl methacrylate (HEMA), acrylamide (AAm), N-isopropyl acrylamide (NiPAAm), acrylic acid (AA), 2-methoxethyl acrylate (MEA), 2-hydroxyethyl acrylate (HEA), etc. have been grafted in situ in plasma or subsequently to plasma treatment for imparting effects such as improved hydrophilicity or dyeability. 1,1,2,2-tetrahydroperfluorodecyl acrylate (AC8) has been used for flame retardancy, while perfluoroacrylates have been used for water repellency effects.

The application of a repellent coating to disposable surgical garments has been reported, where the cotton fabrics were treated with fluorinating gas (hexafluoroethane) for making it high-comfort, water-repellent. It was found that the plasma treatment would provide an effective barrier to aqueous contamination as long as a threshold of surface fluorination was reached.

A more powerful method of designing new hybrid materials involves the combination of inorganic and organic structural units in the precursor compounds used for plasma polymerization. Nanocomposite hybrid plasma polymer coating obtained from such precursors allows a wide range of possible combinations and variations of inorganic and organic groups or structural elements and tailoring, which makes them superior to commonly used organic coating materials. The properties, aimed at many, include chemical resistance, abrasion resistance, antistatic, antireflective, barrier properties and corrosion protection.
Table 3—Surface modification with reactive gases and molecules in plasma

<table>
<thead>
<tr>
<th>Plasma treatment</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric pressure glow plasma; gas: air; on nylon and PU melt blown and electrospun fibers.</td>
<td>The surface energy increased to &gt; 70 dynes/cm by 5 s of plasma exposure; did not degrade significantly up to 120 s treatment.</td>
</tr>
<tr>
<td>Vacuum plasma; gases: dichloromethane; on cotton and PET fabrics.</td>
<td>Moisture content and dyeability were enhanced without affecting other properties.</td>
</tr>
<tr>
<td>Vacuum: 70 W; gas: oxygen; on PBO, Kevlar and carbon fibers.</td>
<td>Total surface free energy of PBO increased from 43.3 mJ/m² to 61.1 mJ/m² (by 41%) with treatments for 5 min and the interfacial shear strength of a model PBO/epoxy composite increased from 34.7 MPa to 44.7 MPa (or 29%). Similar results for other fibers.</td>
</tr>
<tr>
<td>Vacuum; gas: oxygen; on wool substrate.</td>
<td>Level of shrink resistance could be significantly enhanced on application of polymers to wool fabric after a 2 min treatment.</td>
</tr>
<tr>
<td>Atmospheric glow plasma; gases: He, Ar, air, carbon dioxide and other gases; on PP melt blown.</td>
<td>Increase in wettability.</td>
</tr>
<tr>
<td>DBD plasma; gas: hexafluoroethylene/H₂; on nomex fibres</td>
<td>Plasma is used to apply a diffusion barrier layer to the surface to improve the resistance to 85% H₂SO₄ (20 h at room temperature).</td>
</tr>
<tr>
<td>Vacuum plasma; gases: oxygen and hexafluoroethane; on cotton fabric.</td>
<td>Provided an effective barrier to aqueous contamination.</td>
</tr>
<tr>
<td>Atmospheric pressure glow discharge and dielectric barrier discharge plasma; gas: air; on PTPE.</td>
<td>The atmospheric pressure glow discharge results in more uniform and effective than dielectric barrier discharge.</td>
</tr>
<tr>
<td>Atmospheric pressure; gases: Ar fluorocarbon mixtures; on technical textiles.</td>
<td>A small percentage admixture of hydrogen to Ar/C₂F₄ resulted in increased deposition rate. Plasma-post-treatment in etching gases can be used to decrease the surface tension.</td>
</tr>
<tr>
<td>Atmospheric pressure; gas: N₂ &amp; vinyl triethoxysilane; on PET substrate.</td>
<td>Hybrid organic–inorganic precursor resulted in better barrier properties against oxygen gas in comparison to an organic precursor due to organic and inorganic networks formation.</td>
</tr>
<tr>
<td>Atmospheric pressure; gases: helium/argon or acetone/argon; on wool and PET fabric and film.</td>
<td>Wettability increased with increased treatment time. The helium/argon plasma treatment more effective than the acetone/argon plasma.</td>
</tr>
<tr>
<td>Atmospheric pressure; gas: air; on Nylon-6,6 film.</td>
<td>Surface contact angle decreased rapidly from 83.5° to 35°.</td>
</tr>
<tr>
<td>Atmospheric pressure; gases: N₂, H₂, NH₃ and mixtures; on HDPE and PP plates.</td>
<td>Increase in surface energy was observed. From the XPS analysis, the bonds C–H, C–C, C–N, C–O–C and C–O–H were found in the surfaces of the treated samples.</td>
</tr>
</tbody>
</table>

Table 4—Surface modification with polymerizable monomers

<table>
<thead>
<tr>
<th>Plasma treatment</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Vacuum plasma; gas: Ar monomer: acrylonitrile; on PP fabric.</td>
<td>PPAN (plasma polymerized acrylonitrile) surface grafted PP fabrics exhibit improve water absorption and dyeing properties.</td>
</tr>
<tr>
<td>Vacuum of 0.2 mbar; gas: Ar; monomer: perfluorooctylate; on cotton/PET fabrics.</td>
<td>Treatment for 1 min gave water repellent properties.</td>
</tr>
<tr>
<td>Vacuum; gas: Ar; monomer: acrylic acid; on PET fabric.</td>
<td>Increase in wettability, soil ing resistance and colour strength of polyester fabric was better by argon post-plasma polymerisation of acryl ic acid compared to in situ polymerization.</td>
</tr>
<tr>
<td>Atmospheric pressure; gases: He/O₂; monomer: organosilicone; on PET fabric.</td>
<td>Antireflection layer causes increase in colour intensity of the polymerized PET surfaces.</td>
</tr>
<tr>
<td>Vacuum; gas: Ar; monomer: fluoroacrylate in presence of vinyl crosslinking agents; on Nylon-6.</td>
<td>Fire retardant coating; 50% decrease in peak value of rate of heat release.</td>
</tr>
<tr>
<td>Vacuum; pretreatment with Ar/O₂ followed graft polymerization by acrylamide, acrylic acids and acrylates; on celluloses, acetates, and acrylic substrates.</td>
<td>Direct grafting of perfluoroalkyltrichlorosilanes, on activated PE occurs much more readily compared to monochloro-substituted silanes.</td>
</tr>
<tr>
<td>Atmospheric pressure; on PE for 10s.</td>
<td>Contd—</td>
</tr>
</tbody>
</table>
Table 4—Surface modification with polymerizable monomers—Contd

<table>
<thead>
<tr>
<th>Plasma treatment</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum; gases: Ar, O2, N2; monomers: glycidyl methacrylate, 2,2-diphenyl-1-picrylhydrazyl; on cotton fabric for 60-300 s.</td>
<td>Plasma induced grafting yield with different gases and their mixture is compared.(^{38})</td>
</tr>
<tr>
<td>Vacuum; gases: air, Ar and O2; monomer: acrylic acid; on PET and polyamide fabric for 1-90 min.</td>
<td>In situ plasma polymerization of acrylic acid resulted in improved wettability, dyeability and soil resistance.(^{29})</td>
</tr>
<tr>
<td>Vacuum; gases: air, Ar and O2; monomers: acrylate containing phosphorus; on PAN fabric for 15 min.</td>
<td>The LOI value of PAN (18.5) increases by 4-8 units when treated with the flame retardant phosphate and phosphonate monomers.(^{30})</td>
</tr>
<tr>
<td>Vacuum; gas: Ar; monomer: 1,1,2,2-tetrahydroperfluorodecyl acrylate; on PAN fabric for 10 min.</td>
<td>Graft-polymerization of monomer in direct contact with the substrate surface required much smaller amounts of fluorinated reactant to achieve water and oil repellency.(^{41})</td>
</tr>
<tr>
<td>Vacuum; gas: O2; monomer: 1,1,3,3-tetramethyldisiloxane acrylate; on N-6 film for 20 min.</td>
<td>Rate of heat release decreased by 30%. Many different properties such as flame retardancy, damping, film deposition or hindering of additive diffusion out of the host matrix can be achieved using this in a single stage treatment.(^{30})</td>
</tr>
<tr>
<td>Vacuum; gas: Ar; monomer: acrylic acid; on PE for 1-4 min.</td>
<td>Considerable increase in surface free energy and wettability was observed within 1 min of plasma treatment.(^{42})</td>
</tr>
<tr>
<td>Vacuum; gas: oxygen; monomer: acrylic acid; on PP.</td>
<td>Etching + plasma polymer coating provided enhanced electrochemical properties.(^{43})</td>
</tr>
</tbody>
</table>

Biological molecules display remarkable functions that the developers of new materials are eager to harness. A European consortium is exploring an original approach for coating the surface of almost any material with active biomolecules. The idea is to use cold atmospheric pressure plasma to deposit the biomolecules together with a thin polymer coating. Potential applications are wide ranging.

In another study,\(^{44}\) blood compatibility of blood contacting materials has been enhanced using vacuum plasma in presence of silicon containing organic monomers vapours. Silicone-like films were deposited by feeding RF glow discharge plasma with silicon-containing organic monomers vapours. Films having composition of Si, C, H, O, were utilized to coat active carbon particles in blood filters and PP hollow fibres membranes in blood oxygenators.

As has been summarized above, a large amount of information is available in the literature on the plasma treatment of textile. However, most of it is on the vacuum plasma or DBD discharge. Relatively, less literature is available on the diffused glow discharge plasma operating at atmospheric pressure. Development of stable, filament-free one atmospheric pressure glow discharge plasma over a large surface area is still challenging, and only a few research groups around the world have been able to demonstrate the stable and true glow plasma. In this paper, attempts have been made to successfully build glow discharge plasma at the atmospheric pressure in variety of gases from helium to air. A plasma reactor has been developed for continuous treatment of textile substrates. Plasma-treated fabrics have been observed to undergo surface modification under plasma treatment. The comparative effect under different gases on hydrophilicity and surface energy of these materials has not been reported in the literature. Also, a systematic study on the stability of changes brought about by the plasma treatment has not been reported in the literature. In this paper, a systematic investigation on the behaviour shown by nylon-6 and PET fabrics has been reported under different gases and for different treatment time.

5 Materials and Methods

5.1 Plasma Reactor Unit

**Plasma Chamber**

Plasma reactor comprising two aluminium electrodes with commercial glass plates as dielectric material was used. The design allowed the distance between the two electrodes to be varied from a few millimetres to a few centimetres. The fabric in the plasma chamber was fed continuously with the help of a feed and a take-up roller. The time of the treatment could be varied by adjusting the speed of the fabric in the range of 13.5-81.0 cm/min. The plasma was generated using a power supply with variable output of up to 25 kV and frequency of up to 30 kHz.
Stabilization of Plasma

Plasma was stabilized by optimizing electrode design, thickness of dielectric material, discharge gap and gas flow. Initially, this was done over a small surface area (1.13 cm²) and finally over a large surface area of 67.5 cm².

5.2 Textile Substrate and Plasma Treatment

Nylon-6 fabric of 62.34 g/m² and polyester fabric of 81.5 g/m² were used. Nylon and polyester fabrics were washed with 2 gpl Lissapol D soap solution at boil for 30 min and dried in air for overnight. The fabric of width 5 cm was treated in a continuous manner in the stable glow discharge plasma at frequency -9-10 kHz and voltage ~17 kV under Ar, He, air and oxygen environment. The treatment time was varied from 10 s to 60 s.

5.3 Test Methods

5.3.1 Mechanical Strength

Mechanical strength and elongation of the fabrics were measured by Instron (Model 4202). Crosshead speed was 100 mm/min and the sample size was 75mm × 40 mm.

5.3.2 Absorbency

Water absorbency of the polyester and nylon fabrics was measured by gravimetric in-plane wicking tester developed at IIT-Delhi. In this tester, the fabric sample of 5 cm × 5 cm was used.

5.3.3 Etching Loss

Etching loss was calculated using analytical weighing balance with an accuracy of 0.0001 g model Explorer-Dhaws. Fabric was first dried at 105 °C for 30 min (W₁), and then plasma treated for 60 s under helium. Thereafter, the sample was again dried at 105°C for 30 min (W₂).

Percentage of etching loss was calculated by the following formula:

\[
\% \text{ Etching loss} = \frac{(W₁ - W₂)}{W₁}
\]

5.3.4 Surface Energy

Surface energy of the fabrics was measured by using formic acid solutions of different concentrations. A drop of formic acid solution (of a particular concentration) was placed on the fabric and if the drop was absorbed by the fabric within 5 s, the surface energy of the fabric was considered equivalent to the surface energy of the liquid.

6 Results and Discussion

6.1 Effect of Process Parameters on Quality of One Atmospheric Pressure Glow Discharge Plasma

6.1.1 Distance between two Electrodes

The maximum gap between the two large size electrodes could be kept at around 10 mm to start the plasma discharge under He atmosphere. On increasing the gap further, plasma could not be generated even on applying very high voltages, and only a discharge sound could be heard. For other gases, such as argon and nitrogen, the maximum gap for generating plasma was less than 10 mm. However, the gap of less than 3 mm between the two dielectric plates was necessary for generating the glow plasma.

6.1.2 Effect of Frequency

Plasma could not be generated between the two electrode plates at a very low frequency (~1 kHz) of the applied electric field. Intermediate frequencies in the range of 7-15 kHz gave uniform plasma. At high frequencies, only filamentary plasma could be produced as shown in Fig.5.

6.1.3 Effect of Voltage

Voltage has very significant effect on plasma generation particularly at the atmospheric pressure because normal atmosphere requires high breakdown voltage. Breakdown voltage depends on the nature of the gas used, the active electrode area and the distance between the two electrodes. It was observed that the higher voltage gives better uniformity of plasma. The higher voltage is preferred because it is also known to give higher concentration of radicals in the plasma. Much lower voltage was required to generate uniform glow plasma in He gas compared to air/N₂ or argon gas. The relative voltage required to generate uniform glow plasma under different gases was as given below:

Air ~ O₂ > N₂ > Ar > He

6.1.4 Stabilization of Plasma Over a Large Surface Area

Proper dissipation of heat generated due to plasma is one of the most important factor in generating uniform glow discharge plasma over the large surface area of 67.5 cm². Therefore, electrodes were designed to allow easy circulation of atmospheric gases. The discharge gap was kept at 1-3 mm. Uniform glow discharge plasma could be produced at significantly higher gas flow rate and voltage compared to that
6.2 Characteristics of Plasma-treated Nylon and PET Fabrics

6.2.1 Mechanical Strength

Mechanical strength of polyester and nylon fabrics was measured after plasma treatment in different gases for 60 s. The breaking load of the treated samples was compared with untreated samples. The average breaking load of nylon fabric reduced from ~60 kg to 58.56 kg in He plasma. The decrease in breaking load was higher in other gases. The maximum strength loss of 15% was observed in Ar plasma (Fig. 7). Reduction in mechanical strength was insignificant in the first 30 s of the treatment time. Similar trend was observed in the case of polyester fabric. In this case, the percentage loss in strength was about 13% with 60 s of treatment in Ar. The loss in strength of treated polyester fabrics was found to be similar to that of nylon in case of helium plasma.

6.2.2 Etching Loss

Etching loss was determined for both nylon and polyester fabrics after plasma treatment in helium for 60 s. The fabric weight did not decrease significantly after the plasma treatment. The loss in weight was usually < 0.2 wt% for most samples, except for a few samples where it was ~1 wt%.

Fig. 5 — Atmospheric pressure filamentary plasma obtained at high frequency (~25 kHz).

Fig. 6 — Stabilized atmospheric pressure glow discharge plasma over a large surface area required for plasma generated over a small surface area. Figure 6 shows glow discharge plasma under He gas over a surface area of 67.5 cm².

6.2.3 Surface Energy

The change in surface energy of the polyester fabrics upon plasma treatment is shown in Figs 8 and 9. Surface energy of the as-processed (not washed, NW) polyester fabric was about 40 dynes/cm. This changed to ~ 59 dynes/cm for the washed fabric (without plasma treatment). Upon plasma treatment, the surface energy improved significantly to a value greater than 71 dynes/cm. Since the methodology used for measuring surface energy could not be used for determining values greater than 71 dynes/cm, the effect of treatment gases on the ultimate value of
surface energy could not be estimated. All gases gave the maximum measurable values of surface energy for a treatment time of 60 s. Since air was the most convenient and inexpensive gas among all other used, the effect of treatment time on the surface energy of the PET fabric was determined in air plasma. The surface energy values for the treatment time 10 - 60 s are shown in Fig. 9. A treatment time of 10 s was found to be sufficient for bringing out the maximum measurable change in the surface energy (71 dynes/cm) of the PET fabric.

Figure 10 shows the changes in surface energy of nylon-6 fabric on plasma treatment using different gases. For nylon fabric, the surface energy was measurable in the range of 43.5-71 dynes/cm using formic acid method. This is because the higher concentrations of formic acid needed for measuring surface energies lower than 43.5 dynes/cm were found to affect (shrink) the nylon fabric. Argon, air and helium resulted in maximum measurable value of surface energy in 60 s of treatment time. However, in oxygen plasma, the value achieved was lower at around 53 dynes/cm. Figure 11 shows the effect of treatment time on the surface energy of the fabric in He plasma. Unlike the case of PET fabric, the surface energy of nylon fabric increased slowly from 50 dynes/cm to 63 dynes/cm when treatment time was increased from 10 s to 60 s. The changes in the surface energy of the PET and nylon fabrics on plasma treatment may be attributed to the transformation of the hydrophobic surfaces due to the generation of hydrophilic groups.

6.2.4 Absorbency

Figure 12 shows the water absorbency of the plasma-treated PET fabrics under different gases. Compared to the prewashed samples (i.e. without treatment, PW), the treated samples showed a
significant increase in the rate of water absorbency. However, there is no significant effect of the type of gas used during the treatment. This is in agreement with the same surface energy values obtained for various PET fabrics treated with different gases. On the other hand, type of gas used during plasma treatment had definitive effect on the nylon-6 fabrics. The rate of water absorbency was found to be best in air plasma treated samples followed by those treated with He and Ar (Fig. 13). Surface energy values for all the three samples were found to be above the maximum measurable values. Oxygen, as expected based on its surface energy value, showed the least increase in the rate of water absorbency.

Time of treatment also had a significant effect on the rate of water absorbency as shown in Fig. 14. The untreated nylon sample had a very low absorbency. It took more than 90 s to fully wet the fabric, whereas treated samples had high absorbency. Sample treated for 10 s in helium plasma could wet the fabric to saturation within 10 s. With higher treatment time, the absorbency improved significantly as shown in the figure.

6.2.5 Stability

The stability of the surface modifications achieved in nylon and PET fabrics through plasma treatment was studied in terms of variation in surface energy or rate of water absorbency with storage time and number of wash cycles. Figure 15 shows change in the rate of water absorbency with number of days of storage in nylon fabric. As it evident from the figure.
Fig. 16 — Decay of water absorbency of plasma-treated (60 s He) nylon-6 fabrics with number of washes.

Fig. 17 — Decay in water absorbency of plasma-treated (He, 60 s) PET fabric with storage time.

the absorbency does not change even after 8 days of storage. However, on washing, there was a small drop in absorbency after every wash. Even after 7 washes, the absorbency in plasma-treated nylon fabric was significantly higher compared to the untreated prewashed sample (Fig. 16). Surface energy of the plasma-treated nylon fabric did not appear to change even after 25 days.

On the other hand, the stability of the changes brought about in PET fabric was relatively poor. There was a significant drop in the rate of water absorbency just after 2 days of storage (Fig. 17). Similarly, the surface energy also reduced significantly after each wash except for the first (Fig. 18). After seven washes, the surface energy of the plasma-treated PET fabric reduced to that of the prewashed untreated sample.

7 Conclusions

Atmospheric pressure barrier discharge plasma reactor was fabricated in-house. The effect of various parameters on the quality of plasma was evaluated and the parameters were optimized to generate uniform glow discharge. Though glow discharge could be generated in different gases (such as air, Ar and oxygen), helium was found to give the best glow discharge properties among all. The plasma reactor was used to treat PET and nylon-6 fabrics in a continuous manner and a systematic investigation was carried out under various gases. The surface energy and water absorbency were found to improve significantly under all gases without any detrimental effect on the mechanical properties of the fabrics. However, the effect brought about by plasma treatment in nylon-6 fabrics were found to be more stable with respect to storage time and washing cycles than PET fabrics.

References