Atmospheric pressure plasma treatment of textiles using non-polymerising gases

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Surface modification of textiles by plasma treatment for imparting certain desired properties in terms of wettability, adhesion promotion, surface energy improvement and host of other characteristics has been the subjects of interest to researchers in the last few years. The plasma technology for textiles has emerged from conceptual embryonic stage to growth stage, where considerable research is yet to be carried out to translate the potential into industrial reality. This review aims at reporting the current status of the atmospheric pressure plasma technology in surface treatment of textiles, its effect on certain properties and the techniques used for characterisation of plasma-treated textile materials. The review paper also covers the studies carried out so far on the effect of atmospheric pressure plasma generated from non-polymerising gases like helium, argon, air, oxygen and nitrogen on the surface properties of both natural as well as synthetic textiles along with the changes in chemical and morphological characteristics of plasma-treated textile material using different qualitative and quantitative characterisation techniques, such as measurement of wicking height, contact angle, surface energy, SEM, AFM, FTIR and XPS.

Keywords: Atmospheric pressure plasma, Non-polymerising gases, Surface modification, Surface characterization techniques

1 Introduction

Sir William Crooks suggested the concept of plasma as the ‘fourth state of matter’ in 1879. American chemist Irving Langmuir first used the term ‘plasma’ in 1928. Plasma contains the mixture of reactive species like free radicals, electrons and heavy particles, which makes it a unique and diverse media for surface modification. Plasma technology is a clean and dry process which offers numerous advantages over the conventional chemical processes and it is considered as more economical and ecological process¹. Due to diverse potentials and unique properties of plasma, it has been successfully used in different areas of electronics, tool making industries, automotives, medical devices and general plastics & films industries.

The structure and properties of textile materials are entirely different and are more complicated than those of plain metal or plastic surface. Although the surface of textile material contributes little to the total mass of the material, it is often responsible for the many end-use properties of textile products. The surface properties essentially play a decisive role in various textile manufacturing processes as well as it influences performance of the conventional and speciality textile products. Many properties of textiles like wettability, adhesion, printability, friction, static charge generation, shrinkage (in case of wool), water resistance, pilling resistance and soil resistance are governed to a large extent by the surface characteristics of the textile material. In other words, modifications in the surface characteristics can induce various desired properties/functionalities to the textile substrate.

Low pressure plasma techniques have been investigated and used for textiles and polymer surface modifications by several researchers²⁷. The low pressure plasma offers advantages, like uniform glow, low breakdown voltages, high concentration of reactive species and generation of non-thermal plasma⁸. But being a batch process, the low pressure plasma does not meet the requirements of continuous processing of textiles. Moreover, it requires creating and sustaining the vacuum/low pressure conditions, leading to limitations on machine productivity. Therefore, atmospheric pressure non-thermal plasma technology was evolved to fulfil the need of textile industry. The atmospheric pressure plasma (APP) technologies seem to be quite attractive alternative for
the textile industry. The APP technology offers several advantages over low pressure systems, like working at atmospheric pressure, continuous processing of material and possibility of integration with the existing textile processing set up.

Various technological and machinery aspects are involved in the atmospheric pressure plasma (APP) treatment of textiles. Different kinds of APP, i.e. corona discharge, dielectric barrier discharge (DBD) and atmospheric pressure glow discharge (APGD), are available for surface modification of textiles. APP has wide range of applications in textiles, ranging from surface etching to plasma polymerisation for speciality finishes. This review article, however, confines only to the surface modification of different textile materials using atmospheric pressure plasma generated from non-polymerising gases. Plasma treatment can bring changes in the surface chemistry and topography without altering bulk properties. Because of highly surface specific activity of plasma, it is essential to study the physical, chemical and morphological properties of the textiles after plasma treatment. The analysis of plasma-treated textile materials using different measurement and characterisation techniques like measurement of contact angle, surface energy, wicking properties, SEM, AFM, FTIR and XPS are discussed in details in this study. This paper also reports the developments, especially in the last 10 years, in the field of atmospheric pressure plasma surface modification of textiles using non-polymerising gases.

2 Plasma-textile Surface Interactions

To explore the potential applications of plasma in the textiles, it is essential to understand the interaction between the plasma constituent species and the textile substrate. The nature and extent of the effect of plasma on the substrate is largely dependent on the kind of interactions between the plasma particles and the textile substrate. When the exited and energetic plasma species (ions, radicals, electrons, and metastables) are bombarded on to the textile or polymer surface, they initiate various reactions. Generally, plasma can bring out two types of interactions with the surface. The first type includes chain scission on the surface which results in surface etching, cleaning or activation. The second type of interaction refers to plasma induced polymerization or grafting. The former is obtained using non-polymerising gases like helium, argon, oxygen, air and nitrogen. Plasma initiated polymerisation or grafting on the textile surface can be carried out by using various polymerising gases and precursors like fluorocarbons, hydrocarbons and silicone containing monomers. Figures 1(a) and (b) depict both types of interactions i.e. etching and grafting on the surface during the plasma treatment.

In both types of plasma-surface interactions, carrier gas plays a critical role. Usually inert gas like helium or argon is used as carrier gas for both etching and polymerising plasmas. However, helium is much preferred gas over the others because of its high energy metastable state and excellent heat conductivity. Surface modification of textiles using non-polymerising gases is dependent on the various parameters like discharge power, exposure time, nature of gas used and the nature of substrate. The type of gas used for plasma generation plays a key role as it can introduce different functionalities on the textile surface. Wrobel et al. have investigated the influence of different types of gases, viz. nitrogen, oxygen, air, carbon dioxide and ammonia, on the properties of plasma-modified polyethylene terephthalate (PET) fabric. It was reported that different gases in the plasma induced different kinds of morphological and chemical changes on the surface of PET fabric. Therefore, gas for plasma modification needs to be meticulously selected to get desired functional groups on the surface of textile substrate. Inert gases predominantly initiate surface activation by generation of free radicals on the surface by means of chain scission, whereas reactive gases like oxygen and ammonia can incorporate oxygen or nitrogen containing groups. These changes in the surface chemistry may lead to various applications such as improved adhesion, printability, biocompatibility, dyeability, etc. However, only surface characterisation is referred in the present review paper.

Different measurement techniques viz. wettability, contact angle & surface energy, and surface characterisation techniques like scanning electron
microscopy (SEM), atomic force microscopy (AFM) & X-ray photoelectron spectroscopy (XPS) are now widely used to investigate the chemical and morphological changes on the textile surfaces.

3 Effect of Plasma on Different Properties of Textiles

3.1 Wetting Properties

Application of plasma for wettability improvement of different textile substrates is recognised for many years. Etching, ablation, cleaning and activation of the surface usually result in improvement of the hydrophilic properties of textiles. Many researchers have successfully used plasma technology for the improvement in wettability, hydrophilicity and adhesion of textiles. Many times, contact angle measurements alone do not provide complete information about the wetting characteristics of textiles materials. It is difficult to measure contact angle, especially when a textile material is absorbent and have irregular structure with higher porosity. In such cases, wicking behaviour of textiles may provide information about the wetting properties of textiles.

3.1.1 Wicking Properties

Wicking properties of textiles can be expressed in terms of height of capillary rise measured for predetermined time or it may be expressed as time required for a test liquid to reach predetermined height. Measurement of the weight of liquid absorbed by the capillary mechanism may also be used to study the wettability of nonwovens.

Borgia et al. have carried out surface modification of natural and synthetic woven fabrics with dielectric barrier discharge. Polyester, nylon and wool samples were treated with the plasma generated from air, argon and nitrogen. Significant improvement in wicking properties of the plasma-treated samples was observed. For example, the water rise time for the polyester fabric decreased from 19s to 7s after plasma treatment. Similarly, improved wetting properties of nylon fabric were observed after plasma treatment. Furthermore, increase in plasma exposure time caused improved wettability for all the samples. Xu and Liu have used corona discharge for surface modification of polyester fabric. The effect of voltage on the capillary heights of polyester fabric is shown in Fig.2. It can be observed that the increase in discharge voltage leads to improved wicking properties. However, voltage higher than 10kV did not bring any further change in the capillary height, i.e. the degree of plasma action got stabilised at voltages higher than 10 kV.

The study on the atmospheric pressure plasma treatment of polyester/cotton blended fabric has also shown significant improvement in the wicking height after plasma treatment. Plasma generated from mixture of helium and oxygen was used for the surface modification. Moreover, it was observed that the plasma process parameters, i.e. discharge power, treatment time, gas flow rates and inter-electrode spacing, have very significant effect on the efficiency of the treatment. Researchers have investigated the effect of plasma treatment on different textile substrates like polyamide/polyurethane (PA/PU), cotton, wool and PET. Improvement in the hydrophilic character after plasma treatment was also corroborated by the studies of Takke et al., Shin and Yoo and Ferrero.

The effect of DBD plasma on the nonwoven textiles was investigated by Morent et al. Polyethyleneterephthalate (PET) and polypropylene (PP) nonwoven samples were treated with plasma produced from air, helium and argon at medium pressure. Quantitative assessment of wettability after plasma modification was carried out using liquid absorptive capacity (W_A) method, where W_A is defined as the amount of water that a fabric has absorbed after immersion in distilled water. The W_A values of untreated PP and PET nonwovens were 106 % and 393% respectively. Higher energy density of the plasma yielded higher W_A values of 360 % and 730 % for PP and PET respectively. Plasma treatment can be immensely useful for the treatment of nonwoven textiles which are used as filtration media, battery separator and in geo-textiles, where the product needs to be wettable.

Although the foregoing studies indicate that plasma treatment imparts hydrophilic properties to natural as well as synthetic textile materials, it is necessary to
examine the durability of the hydrophilic effect. Kale and Palaskar\textsuperscript{22} have carried out studies on the effect of ageing on plasma-treated polyester/cotton blended fabric. The wicking height of samples was measured after storage period of one week, one month and three months. Significant decrease in the wicking height with the increase in ageing time was observed, indicating loss in wettability (Fig.3). Studies to improve the durability are imperative to make plasma technology suitable for use in commercial scale.

3.1.2 Contact Angle (CA) Measurement

The wetting properties of the solid can also be expressed by measurement of contact angle ($\theta$). When the value of $\theta$ is less than 90\textdegree, liquid is considered to be wetting a surface. If the $\theta$ is more than 90\textdegree, then it is considered as non wetting. A contact angle $\theta = 0$\textdegree indicates perfect wetting. Measurement of the contact angle at the solid–liquid interface has been used extensively for studying the surface properties of both solids and liquids\textsuperscript{30}. Geyter et al.\textsuperscript{31} have measured contact angle of plasma treated polyethylene (PE), using water and di-iodomethane as test liquids. It has been found that untreated PE shows contact angles of 101.7\textdegree with water and 55.6\textdegree with di-iodomethane, while plasma treated PE sample shows contact angles of 53\textdegree with water and 38.5\textdegree with di-iodomethane. There is a significant reduction in CA after plasma treatment, irrespective of test liquid used. Increase in plasma exposure time results in further decrease in contact angle. Guo et al.\textsuperscript{26} have reported the decrease in contact angle of air plasma treated woven polyester fabric. At discharge power of 300 watts, contact angle value of plasma-treated PET is reduced to 38\textdegree from initial value of 82\textdegree.

Pascual et al.\textsuperscript{32} have used corona discharge to improve the wettability of polyethylene. Contact angle was measured by using water, glycerol and diiodomethane as test liquids. The CA values of untreated PE were 93.50\textdegree, 79.90\textdegree, and 65.40\textdegree with water, glycerol, and diiodomethane respectively. Remarkable decrease in CA was observed after the plasma treatment, irrespective of test liquid used. Plasma treated PE exhibited CA values of 51.40\textdegree, 59.40\textdegree and 32.60\textdegree with water, glycerol, and diiodomethane respectively. They have comprehensively studied the effect of ageing on the contact angle of plasma treated PE. It was observed that after ageing for 21 days, plasma-treated samples showed significant increase in the CA values indicating loss in wettability. However, it is interesting to note that the values of CA even after aging for 21 days were lower than CA of untreated PE.

Fig.3—Effect of aging time on wicking height of P/C blended samples treated at different helium gas flow rates\textsuperscript{22}

It can be deduced that plasma treated surface does not completely lose its wetting properties even after long ageing period. The contact angle of oxygen-plasma treated fabrics made of cotton and wool was studied by Sun and Stylios\textsuperscript{25}. In contrast to above results, Sinha\textsuperscript{33} has found increase in the contact angle of plasma-treated jute fibre with water as a test liquid, while CA measured with other non-polar liquids such as toluene, acetone, dichloromethane, and bromo-naphthalene has shown decrease. This differential behaviour of contact angle using water and other non-polar liquids on jute perhaps requires further investigations.

From the above discussion, it can be inferred that plasma treatment significantly improves the wettability of a textile surface. However, the wettability imparted by the plasma treatment is prone to ageing. The morphological changes brought out by plasma treatment may not revert back due to ageing process. It is the surface chemical composition which gets altered during ageing period, leading to loss in wetting properties.

3.1.3 Surface Energy Measurement

Surface energy is dependent on the surface area and amount of electronic charge present at the surface. The origin of surface tensions arises from the existence of unbalanced intermolecular forces among molecules at the interface. Wetting behaviour of solids is largely related to their surface energies. Surface energies of solids determine the surface and interfacial phenomenon, including chemical reactivity, adsorption, desorption, wet processing and adhesion. For a solid to be wettable with a particular liquid, the surface tension of the solid ($\gamma_{\text{solid}}$), must be equal or greater than that of the liquid ($\gamma_{\text{liquid}}$).\textsuperscript{11}
Use of plasma for improving surface energy, especially of low surface energy textiles like polyethylene, polypropylene and polyester, is well established. Geyter et al.\textsuperscript{31} have investigated the effect of plasma treatment on the surface energy of polyethylene. Surface free energy of PE was increased to 56.2 mJ/m\textsuperscript{2} from initial value of 31.3 mJ/m\textsuperscript{2}. Moreover, the increase in the surface free energy was observed with the increase in plasma exposure time. The increase in the surface energy can be attributed to the introduction of oxygen-containing hydrophilic functionalities on the PE surface. Increase in surface energy of the textile material after atmospheric pressure plasma treatment was also corroborated by Leroux et al.\textsuperscript{34}. Similar kind of increase in surface energy has been corroborated by the studies of others\textsuperscript{35-38}. There are different methods available for measuring surface free energies of a solid. It can be derived from the contact angle data of different test liquids. Some researchers have used formic acid solutions of different concentrations for measuring surface energy after plasma treatment\textsuperscript{8,17}. In this method, a drop of formic acid solution is placed on the fabric surface. If drop is absorbed by the fabric within 5 s, the surface energy of the fabric is considered equivalent to surface tension of that liquid. Samanta et al.\textsuperscript{8} have used oxygen, air, argon and helium for the plasma treatment of PET. Considerable increase in the surface energy of PET from 40 dynes/cm to 71 dynes/cm was observed after plasma treatment for 60 s.

Pascual et al.\textsuperscript{32} have reported the effect of ageing on the surface free energies of the corona treated polyethylene. The environmental or storage conditions were found to have significant effect on the ageing process of plasma-treated substrate. The influence of relative humidity and temperature during the aging was studied with three different storage conditions, such as aging at room temperature, aging at 23\textdegree C/50\% RH, and ageing at 50\% C/40\% RH. The ageing process was accelerated by the temperature of the storage. Decrease in the surface energy during the ageing process can be attributed to the loss in surface functionalities due to re-arrangement of the polar groups. Plasma treatment with non-polymerising gases is not a permanent one and hydrophobic recovery takes place with successive ageing period. The stability of the new functional groups formed at the surface of textiles may not be good which results in their rearrangements.

3.2 Measurement of Zeta Potential

Zeta potential is the charge developed at the interface between a solid surface and its liquid medium. The net charge at the textile surface affects the ion distribution in the nearby region, which leads to increase in the concentration of counter ions. An electrical double layer is formed in the region of the particle-liquid interface.

Guo et al.\textsuperscript{26} have studied the zeta potential of air plasma-treated woven PET fabric. The negative zeta potential was increased after plasma treatment which indicates the higher number of carboxyl groups at the fibre surface. The atmospheric air plasma-treated samples exhibited more number of carboxyl groups at the surface. Moreover, increase in the discharge power led to increase in the carboxyl groups. Wakida et al.\textsuperscript{39} have studied the zeta potential of wool and nylon 6 fibres treated with oxygen plasma. The zeta potential of the fibres was measured by the streaming potential method. The zeta potentials of both fibres increased the negative charge over the pH range measured. The plasma interaction with substrate causes polymer chain scission resulting in formation of reactive radicals and end groups such as carbonyl, carboxyl and hydroxyl groups. Chemical nature of the species formed at the surface of plasma-treated textiles can be known by zeta potential method.

3.3 Surface Morphology

3.3.1 Scanning Electron Microscopy

The scanning electron microscope (SEM) uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. When beam of electrons strike the surface of the specimen and interact with the atoms of the samples, signals in the form of secondary electrons are generated which give information about surface topography of the substrate\textsuperscript{40}.

Plasma treatment with non-polymerising gases leads to mechanisms like etching, cleaning and activation. Due to bombardment of highly energetic ions and radicals, ablation of atoms/molecules at the surface of textile fibre takes place, resulting in alteration in surface morphology. Zhongfu et al.\textsuperscript{41} have investigated the surface morphology of plasma-treated polyester fabric. Polyester fabric treated with argon-oxygen plasma exhibited rough surface morphology due to etching. The surface morphology of wool and cotton after plasma treatment has been studied by Sun et al.\textsuperscript{42}. The SEM micrographs of O\textsubscript{2}
plasma-treated wool and cotton fabrics revealed holes on the fibres surface. Tissington et al. have studied the morphology of polyethylene monofilaments. Fibriller structure of polyethylene resulted in the formation of pitted cellular structure. Longer treatment duration caused extensive pitting of the surface which resulted in improved adhesion due to mechanical keying effect. However, they have not studied changes in the surface chemistry and ageing effect after plasma treatment. Studies by other researchers have corroborated change in the surface topography after plasma treatment of different textile fibres like Jute, polyester, cotton and polypropylene.

Plasma treatment for scale removal and for anti-felting property of wool has been the subject of interest to many researchers. Xu et al. have investigated the morphology of weft knitted wool fabric after helium and He-O₂ plasma treatment. In case of both helium and He-O₂ plasma, SEM of fibre surface exhibited relatively smooth morphology due to removal of scales. The presence of moisture in the sample during the plasma treatment is very critical factor. The study of Xu et al. showed almost complete removal of scales in wool samples which were conditioned at 100% RH before plasma treatment. Moreover, lowest shrinkage ratio of 5.2% was obtained with wool fabrics conditioned at 100% RH. Similar kind of studies pertaining to the effect of moisture on plasma treatment of wool was also reported by Zhu et al. SEM photographs after plasma treatment (Fig.4) revealed that fibres with lower moisture regain exhibit little etching effect, whereas severe etching was observed in samples having higher moisture, leading to almost complete removal of scales. The chlorination is the conventional process for scale removal in wool. However, it creates pollution and environmental related problems. The plasma technology for scale removal seems to be a promising environment-friendly alternative to the chlorination process. However, application focused research is required in the plasma assisted scale removal of wool by comparing the conventional chlorination process and plasma process. Performance of the fabric treated with dry and environment-friendly technique like plasma needs to be evaluated. Commercial exploitation of plasma technology especially for wool seems to have promising future.

3.3.2 Atomic Force Microscopy

Atomic force microscopy (AFM) is a newly developed high resolution technique to study the surface morphology. It is possible to directly obtain three dimensional topographic images of the surface up to atomic level resolution. Preparation of samples such as heavy metal coating, involved in SEM and TEM, is not needed for AFM. AFM is capable of investigating surfaces of both conductors and insulators on an atomic scale.

Shin et al. have reported mean surface roughness (Ra) from AFM images of He/O₂ plasma-treated PET nonwoven at different exposure times varying from 0s
to 90s. The mean roughness recorded for untreated sample was 0.805 nm, which then increased to 1.305 nm after exposure for 90 s. Koo et al. have studied the surface roughness of the cellulose triacetate treated with argon plasma. It was observed that smooth structure of untreated cellulose triacetate has gradually changed into irregular structure after plasma treatment. Increase in the treatment time led to increase in the surface roughness value. Processes like etching, re-deposition, and cross-linking which occur during plasma treatment affect surface morphology and lead to micro-roughness.

The effect of air plasma treatment on the PET fibre surface topography was investigated by Wei et al. using tapping mode AFM images. Significant changes in the original topography of the PET fibres were observed after plasma treatment. Similar kind of alteration in the surface topography of plasma-treated PET is reported by Ricardi et al. (Fig. 5). Surface morphology and roughness of aramid fibres after oxygen plasma treatment was studied by Wang et al.

Oxygen plasma caused increase in the surface roughness value (Ra) of aramid fibres from 153.8 nm to 329.1 nm after 20 min of treatment.

Plasma treatment is basically a surface treatment. Therefore, many times topographical changes occur at very limited depth on the fibre surface, which cannot be detected or quantified by SEM. In such cases, AFM is a very useful tool. However, due to irregular structure of textiles AFM may not always yield accurate results due to non-uniform surfaces. Therefore, technique for assessing surface morphological changes requires to be selected depending upon the nature of substrate.

3.4 Surface Chemical Analysis

3.4.1 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is the most widely used surface analysis technique for plasma modified surfaces and plasma enhanced deposited thin films. The XPS is also known as ESCA (electron spectroscopy for chemical analysis). It is very powerful surface analysis technique where chemical characterization near the surface region up to 1-2 nm can be determined. In the XPS, X-rays hit the sample and produce photoelectrons whose energy is measured. The XPS technique is highly surface specific due to the short range of the photoelectrons that are excited from the solid. The energy is specific to each element and can be used to identify all the elements present in the outer 10 nm of the surface.

Guo et al. have investigated the effect of atmospheric air-plasma treatment on surface chemistry of PET woven fabrics. The XPS analysis revealed oxidation of the fibre surface, leading to formation of hydroxyl, carboxyl and carbonyl groups. Increase in the O/C atomic ratio was reported after the plasma treatment. Shin et al. have reported the increase in O1s/C1s ratio of nonwoven PET surface after He/O2 plasma treatment. The XPS analysis revealed increase in the O/C atomic ratio progressively from 0.37 to 0.46 as plasma exposure time was increased (Fig. 6).

Morent et al. have reported similar kind of increase in the O/C atomic ratio of plasma-treated PP and PET nonwovens. The O/C ratio of PP and PET nonwoven after plasma treatment is found to be PP—2.4 (untreated) & 17.5 (plasma treated); and PET—31.0 (untreated) & 47.7 (plasma treated). They have also determined the effect of ageing on O/C ratio. The O/C atomic ratio decreased with increasing ageing time until a plateau value was reached. However, the plateau value of the O/C ratios after ageing was considerably higher than the O/C ratios of the untreated textile samples. The effect of ageing on the O/C ratio of plasma treated surface was also studied by Riccardi et al. and Pascual et al. The oxygen content of the plasma-treated surface decreases during aging period. Wang et al. have found that surface-oxygen concentrations in plasma-treated fibres are higher than that in the untreated one.

Fig. 5—AFM images of (a) untreated and (b) plasma treated PET
Change in surface chemistry of wool was studied by Xu et al. with XPS technique. They have determined the concentration of C, O, N and S on the surface of wool fabric after treatment with pure helium and He-O₂ plasma. Decrease in the carbon and nitrogen contents and increase in O₁s content have been observed after plasma treatment. Sulphur is present in the cystine linkages of wool fibre. In He/O₂ plasma treated wool samples, sulphur content decreased significantly. However, helium plasma treated samples did not exhibit substantial change in S and N contents. This reveals that oxygen plasma leads to more severe oxidation of surface than pure helium plasma. Decrease in the sulphur content of plasma-treated wool is also reported by Kan et al. Removal of scales as seen in SEM images of plasma-treated wool might have contributed in lowering the amount of sulphur which is present in the cystine linkage of wool scales.

The XPS studies of plasma-treated samples done by other researchers have also suggested an increase in oxygen content. Wong et al. have reported the changes in surface chemistry of plasma-treated linen. After exposure to oxygen and argon plasma, it led to lower C₁s and higher O₁s intensities. The type of functional groups incorporated also depends on the nature of gas used. Ward et al. have reported incorporation of amide groups into the surface of cotton after treatment with ammonia plasma. The NH₃ plasma irradiated fabric exhibited modest increase in the dry crease recovery; however no increase in wet crease recovery was observed.

The XPS technique provides quantitative and qualitative data about the interaction of plasma with a substrate. Different functional groups can be incorporated in the textile or polymer surface with use of various gases like oxygen, ammonia, nitrogen, CO₂ and fluorine. However, role of atmospheric air entrapped in the fabric structure cannot be neglected in the atmospheric pressure plasma modification of textiles. Researchers need to investigate the effect of factors like entrapped air, impurities present in the substrate and porosity of textiles on the ultimate properties.

3.4.2 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared (IR) spectroscopy is a chemical analytical technique which measures the absorption of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Plasma treatment with non-polymerising gases can impart different functionalities to the surface of textile substrate. Changes in the surface of plasma-treated textile material can be detected with the use of FTIR.

Pascual et al. have done the FTIR-ATR analysis of untreated and plasma-treated LDPE (low density polyethylene). The peaks corresponding to polar groups of hydroxyl, carbonyl and ester were observed after plasma treatment. FTIR spectra of samples after ageing showed decrease in the intensity of characteristic peaks. Geyter et al. have treated PE film with a dielectric barrier discharge (DBD) operating in air. In the ATR-FTIR spectra, large peak at 1737 cm⁻¹ was observed after plasma treatment which can be attributed to C=O stretching of ketones, aldehydes and carboxylic acids.

Kale and Palaskar have carried out the surface chemical analysis of oxygen plasma treated polyester/cotton blended fabric using ATR-FTIR. The effect of inter-electrode spacing on the surface chemistry of the samples was studied. Gradual intensification of the peak at 1600 cm⁻¹ was observed in FTIR spectra of samples treated at narrower spacing, which was attributed to enol form of the β-ketone. Pandiyaraj and Selvarajan have reported higher absorption intensity in the FTIR spectra of low pressure air-plasma treated grey cotton fabric than that of untreated fabric. The formation of new peaks corresponding to hydroxyl and carboxyl stretching vibrations was reported in their study. FTIR analysis performed by Malek and Holme have evidenced incorporation of oxygen containing group in the oxygen plasma treated cotton. Cai and Qiu have investigated the effect of oxygen/helium atmospheric pressure plasma on the desizing of PVA. The ATR-
FTIR spectra of PVA films after plasma treatment showed enhanced peaks of alcohol (O-H stretch), aldehyde (C=O stretch) and carboxylic acid (COOH stretch).

FTIR analysis of argon plasma treated jute fibres carried out by Sinha\textsuperscript{33} has shown decrease in the phenolic and secondary alcoholic groups, resulting in development of hydrophobicity. Usually, increase in the hydrophilic character is expected after the argon plasma treatment. Further research is required in the plasma treatment studies of jute fibres with more advanced characterisation techniques to understand the mechanism between the plasma and the substrate.

Plasma treatment is a surface treatment and the depth of effect achieved in the plasma treatment is approximately up to 10 nm or less. On the other hand, sampling depth of ATR-FTIR techniques is many times too large to detect structural alteration after plasma treatment\textsuperscript{56}. This is why, most of the times XPS is preferred over the FTIR for surface characterization of plasma treated fabrics. Geyter \textit{et al.}\textsuperscript{31} have compared the XPS and FTIR techniques for surface characterization of dielectric barrier discharge treated polypropylene. Their study showed that ATR-FTIR analysis can only give qualitative information about the change in surface chemistry, whereas XPS can provide quantitative chemical analysis.

Similar kind of comparison between XPS and FTIR was also carried out by Mercx\textsuperscript{27} on air and ammonia plasma treated polyethylene terephthalate. Though XPS revealed the oxidation and amination of PE surface, IR spectroscopy did not show any signs of either oxidation or amination due to air or ammonia plasma. Usually, shallow penetration is more prevalent in case of plasma generated by non-polymerising gases. In such cases, XPS would provide better sensitivity for surface chemical analysis than FTIR. However, in case of plasma polymerisation, where continuous deposition of plasma polymer takes place at longer depths, FTIR is also very important surface analysis tool to understand the mechanism of plasma polymerisation.

3.5 Mechanical Properties

Cioffi \textit{et al.}\textsuperscript{58} have conducted tensile tests on monofilaments of radio frequency plasma treated PET. Oxygen and argon plasma treatment resulted in a decrease in the average tensile strength as compared to the untreated fibres. Moreover, higher tensile strength reduction was observed for longer treatment times. Similar kind of decrease in the fibre tenacity and modulus after argon plasma treatment was corroborated by the study of Sinha\textsuperscript{33}.

Wong \textit{et al.}\textsuperscript{32} have studied the effect of low temperature plasma on weight loss of linen. The oxygen plasma treated samples showed increase in weight loss with the increase in both discharge power and treatment time. Shin \textit{et al.}\textsuperscript{25} found that He/O\textsubscript{2} plasma treated PET nonwoven fabric shows higher weight loss with increased plasma exposure time. Hwang and McCord\textsuperscript{59} and Bhat \textit{et al.}\textsuperscript{60} have also showed similar increase in % weight loss at higher plasma exposure time. Matthews \textit{et al.}\textsuperscript{61} have thoroughly investigated the mechanism of etching for PET treated with He and He-O\textsubscript{2} plasma. It was observed that weight loss gradually increases with exposure time up to saturation value. Further increase in exposure time led to re-deposition of previously etched film material. The weight loss of plasma treated PET samples was determined by Vesel \textit{et al.}\textsuperscript{62}.

In their study, the etching rates of 12.9 nm/s and 3.3 nm/s were obtained after oxygen and nitrogen plasma treatment of PET respectively.

Kan and Yuen\textsuperscript{63} have revealed that low temperature oxygen plasma treatment on wool influences mechanical properties as well as properties like air permeability and thermal properties. Morent \textit{et al.}\textsuperscript{29} have shown that the efficient hydrophilization of nonwovens could be achieved without affecting the mechanical properties. The tensile strength of rayon yarns after air–O\textsubscript{2}–He and air–He plasma was measured by Cai \textit{et al.}\textsuperscript{64}. They have reported that atmospheric plasma treatments did not have a negative effect on the tensile strength of the viscose fabric. It can be inferred that mild plasma treatment does not affect the tensile properties of textile material. However, higher discharge power or longer treatment time during plasma treatment may lead to loss in tensile properties due to excessive etching.

4 Conclusion

Atmospheric pressure plasma treatment can modify the textile surfaces in variety of ways and can impart desired functional properties to the textile substrate. Treatment of textiles with plasma generated from non-polymerising gases improves wettability, hydrophilicity and adhesion. It brings about chemical, physical and morphological changes in the textiles. Plasma treatment offers unique advantages of being dry and environment-friendly process. However, like other industries, plasma has not found the same
success in the textile sector, due to involvement of multiplicity of factors. While science and technology of plasma is well understood, its industrial application in textile is still a challenge. Furthermore, one of the hurdles in commercialising the plasma process is the ageing factor of plasma treated material, leading to gradual loss in the imparted properties. Unlike non-porous polymer films or metallic materials, specific properties of textiles like large surface area, and irregular and porous structure make plasma treatment more challenging. Helium is usually preferred as carrier gas over the others, however its cost and requirement in large quantities poses a hurdle of its use on commercial scale. However, future of plasma technology lies in its potential for innovation, value creation, and environmental sustainability.

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