POLITECNICO DI TORINO
Repository ISTITUZIONALE

Atmospheric plasma treatments in converting and textile industries.

Original
Atmospheric plasma treatments in converting and textile industries / Sparavigna, Amelia Carolina; Wolf, R. A.. - (2008), pp. 1-112.

Availability:
This version is available at: 11583/2308916 since:

Publisher:
Lulu Enterprises, Inc.

Published
DOI:

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

30 May 2026

ATMOSPHERIC PLASMA TREATMENTS IN CONVERTING AND TEXTILE INDUSTRIES

Amelia Sparavigna
Dipartimento di Fisica
Politecnico di Torino, Torino, Italy

Rory A. Wolf
Enercon Industries Corporation,
Menomonee Falls, Wisconsin, USA

ISBN: 978-1-4092-1107-5
Editore: Lulu.com
Copyright: © 2008 A.Sparavigna and R.A.Wolf, Standard Copyright License
Lingua: English
Paese: Italia

There are many current and emerging adhesion issues which require an additional process to enhance interfacial surface properties. Materials which are non-polar, such as polymers, have low surface energy and therefore typically require surface treatment to promote adhesion. One way of increasing surface energy and reactivity is to bombard a polymer surface with ions. This is achieved by the surface treatment with plasma. Basically, a plasma treater ionizes a gas mixture in an electromagnetic field. The ionized gas is then discharged on the polymer surface, increasing the presence of chemical functional groups on it.

Among surface treatments, corona discharge is the most common method. Typically used for thin webs, corona treaters utilize air as working gas. For treating complex surfaces, atmospheric plasma glow discharge treatment is often the best approach. This plasma offers stable, more uniform and longer-lasting surface energy enhancement than corona discharge. In particular, plasma provides a critical advantage when processing steps are required for enhancing the properties of very low energy and reactivity surfaces, such as non-polar polyolefins.

Many materials, in fact, require surface treatments to adhere to inks and coatings. Promoting adhesion is made even more challenging with the use of water-based coatings, which have higher surface tension than solvent coatings and thus even less tendency to wet-out on a polymer surface. The aim of our book is a discussion about the use of corona discharge and emerging atmospheric plasma treatments in several applications within converter and textile industries.

Amelia Sparavigna
Rory A. Wolf

Index

1 Glow discharges	7
2 Plasma for the flexible packaging industry	19
3 Modifying the surface features of extruded films	27
4 Extrusion coating and lamination	35
5 Surface treatments for roto- and flexoprinting	43
6 Clear barrier films	53
7 Modifying the surface features with photografting	63
8 Hidden problems in surface treatments: Pinholing	69
9 Hidden problems in surface treatments: Ground rolls	75
10 The flexible future	83
11 Plasma treatment advantages for textiles	89
12 Plasma treatments of natural fibers	95
13 Plasma treatments of synthetic fibers	103
References	109

1

GLOW DISCHARGES

1.1 INTRODUCTION

A positive answer to the request of industry to improve production processes, with simultaneous and increasing respect to environment and worker/consumer health, comes from the glow discharges in atmospheric plasma reactors. These devices can confer to material surfaces the desired properties without affecting the bulk and with a low environmental impact, by reducing water and chemical consumption in production processing. Plasma treatments can effectively achieve modification of the intrinsically low surface energy of polymeric and natural fibers, and then subsequently, change of properties such as adhesion, wettability, printability and dye uptake.

The glow discharge in plasma reactors is regarded as an unusual phenomenon, but it is almost exactly the same as the glow discharges found inside fluorescent tubes, mercury vapor streetlights, and in plasma globes (Fig.1.1). A normal gas is composed of molecules: a high voltage can transform the gas into a glowing mixture of separate neutral molecules, ions and electrons. This mixture of particles is called a "plasma" and it fluoresces with light.

Industrial devices based on plasma have been around for many years in the converting industry, but plasma devices are relatively new for the textile industrial sector, traditionally driven by chemical processing. Low-pressure plasma systems, the oldest and more studied systems, are sometimes used to induce hydrophilic and hydrophobic effects on textiles. Requiring expensive vacuum equipment, they are not seen as a real advantage.

Since atmospheric plasma systems are well known and currently used in industries devoted to processing packaging materials, several industrial devices, from standard corona to the last 'afterglow discharge' systems, are then ready for use on textiles surfaces.

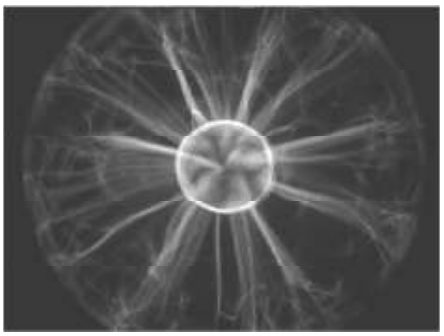

Figure 1.1 In a plasma ball, a transformer collects charges on a central spherical electrode. They jump off the sphere to get away from the other charges and gas inside the plasma ball glows where the electricity passes through the gas atmosphere.

1.2 COLD PLASMA

M. Faraday proposed to classify the matter in four states: solid, liquid, gas and radiant. Researches on the last form of matter started with the studies of H. Geissler (1814-1879): the new discovered phenomena, different from anything previously observed, persuaded the scientists that they were facing with matter in a different state. Sir W. Crookes took again the term ”radiant matter” coined by Faraday to connect the radiant matter with residual molecules of gas in a low-pressure tube.

Sufficient additional energy, supplied to gases by an electric field, creates plasma. For the treatment of polymeric films or fabrics, cold plasma is used, where the ambient treatment atmosphere is near room temperature. It can be produced in the glow discharge in a vacuum process or in more recent atmospheric pressure plasma devices.

To define it, plasma is a partially ionized gas containing ions, electrons, neutral species and UV/visible radiation. The origin of all phenomena in plasma is due to electrons that possess a very high temperature. Electrons, due to their low masses, gain high kinetic energy from the electric field. If electrons do not have an effective thermal exchange with ions, the two systems, electrons and ions, are not in thermal equilibrium and will then exist with different temperatures. The temperature of ions corresponds to temperature of the gas in which plasma is

generated; hence the name "cold plasma" used for these plasmas.

Figure 1.2 From sharp electrodes, discharges go toward the surface. With a suitable geometry, it is possible to treat the surface of two- and three-dimensional objects.

When a sufficient high potential difference is applied between two electrodes placed in a gas, a breakdown among electrons and positive ions produces a discharge (Fig.1.2). Excitation collisions, followed by de-excitation, give the characteristic luminescence that is seen as the glow of the discharge. Due to the various collision processes in the plasma, a large number of different plasma species can be present: electrons, atoms, molecules, several kinds of radicals, several kinds of (positive and negative) ions, excited species, etc.
These different species can all be in interaction with each other, making the glow discharge plasma a complicated gas mixture. When materials are subject to plasma treatments, the subsequent and significant reactions are based on free radical chemistry. Plasma, especially glow discharge plasma, is efficient at creating a high density of free radicals by dissociating molecules through collisions and photochemical processes. The gas-phase radicals have sufficient energy to disrupt chemical bonds in polymer surfaces on exposure, which results in formation of new chemical species.

To sustain a glow discharge in direct current, electrodes must be conductive. In the simplest case, discharge is formed by applying a potential difference (of 100 V to 1 kV) between electrodes inserted in a cell filled with a gas at a pressure ranging from a few mTorrs to atmospheric pressure. When one or both electrodes are non-conductive (Fig.1.3), then an alternating voltage is applied to each electrode, usually in the range of radio frequency.

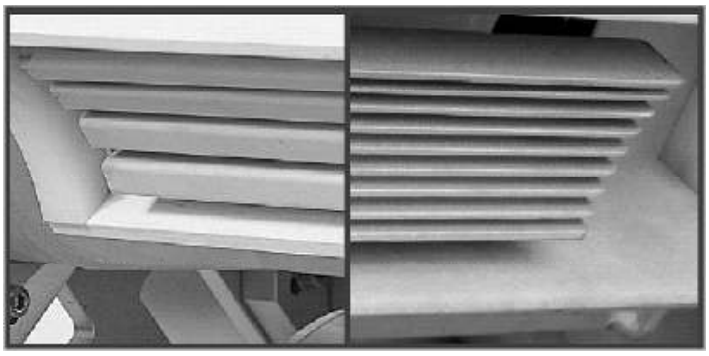

Figure 1.3 High voltage electrodes inserted in dielectrics (on the left), compared with metallic electrodes (on the right).

Concerning gas pressure, the glow discharge can operate in a wide range of pressures. In the case of a low- pressure operating gas, the volume of the discharge can be rather expanded. Operating at atmospheric pressure, that is, in the case of an atmospheric pressure glow discharge (APGD), the linear dimension over which the discharge develops is reduced. The typical dimension is 1-2 mm, reducing the characteristic length of the discharge chamber.
Stable APGDs used for technological applications have been developed, differing with respect to the structure of electrodes, carrier gas and operating frequency. Typically, APGD systems are characterized by having one electrode covered with a dielectric with the discharge operating in alternating voltage. The type of discharge gas used determines the stability of the glow discharge. Helium gives rise to a stable and homogenous

glow discharge, whereas nitrogen, oxygen and argon require higher voltage for ionization and can cause the transition to a filamentary glow discharge. However, it is still possible with a change in the electrode geometry to obtain a somewhat homogenous, yet somewhat filamentary, glow discharge.
According to J. Reece Roth (see his book *Industrial Plasma Engineering*, IOP, 2001), two main classes of atmospheric pressure plasmas are obtained with the dielectric-barrier discharge (DBD) and with the atmospheric plasma glow discharge (APGD). Sometimes DBD are also known as "corona treaters".
DBD devices are well known in the packaging industry, where they are used to increase the wettability of polymeric films. They are strongly related to the APGDs, which operate with an a.c. voltage of 1-100 kV at a frequency of few Hz to MHz. We can consider APGDs as those devices having uniquely homogenous and uniform discharges across the electrodes, whereas the DBDs produces discharges with micro-discharge filaments and considerably less uniform.

1.3 FROM VACUUM TO ATMOSPHERIC PRESSURE.

Russian researchers were the first to develop a full, industrial scale roll-to-roll vacuum reactor with plasma in the glow-discharge family. They succeeded to reach a large scale in fabric width plasma reactors, applying in the building of the vacuum chambers the technologies developed for space missions. Such reactors can treat any type of fabric and are only limited in the amount of material that can be treated in one batch (i.e., the fabric roll diameter must be limited, due to the chamber dimension and to mechanical problems with roll-to-roll systems). Such reactors have also been built in Western Hemisphere, sometimes duplicating the Russian experience. The main drawback of the system is the need for a vacuum chamber, a rather expensive part of the equipment.
Continuous atmospheric plasma treaters are currently being used in the printing processes of packaging films where the surface treatment is achieved with a film velocity reaching 100 m/min. or even greater. In textile industries, such high velocities are not required, then an atmospheric plasma treater mounted directly on the loom is not necessary.

In fact, atmospheric plasma treaters can be easily integrated into textile finishing lines. For this reason, vacuum technology is regarded as being non-competitive. Extra requirements such as the ability to treat full width textiles of at least 2m wide, and higher processing speeds at 20 m/min are more economically addressed by atmospheric plasma treatment systems.
In Fig.1.4, a schematic diagram for film treatments with a DBD system is shown, in the usual set-up to increase wettability. From a supply reel, the film passes through the glow discharge, driven by the rotating drum.

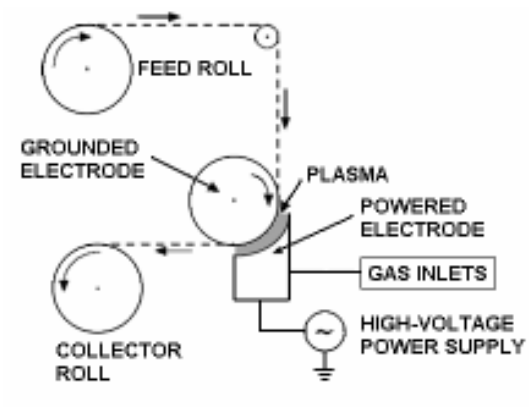

Figure 1.4 Taken from a feed roll, the film undergoes a DBD treatment between a grounded rotating drum and a high voltage electrode. Gas can be used in treatment.

Vacuum plasma technology is considered to be the most mature, almost perfect, plasma technology available for surface treatments. However, many DBD systems are currently used for packaging production and new APGD devices available.
The driving force in the packaging industry for the development of atmospheric plasma sources is the unavoidable requirement of a continuous, roll-to-roll technology. Production processes in the textile industry are essentially non-continuous and so this drag force is lacking. The textile industry is now in the fortunate position to use well-known and rather inexpensive technologies relative to vacuum plasmas, for several applications. Let us note that the quality of atmospheric plasma devices will continue to

be improved, whereas research on vacuum reactors can be considered at the final point and new applications for textile industry can scarcely come from this area.
In the case that environment respect is a priority, a plasma treatment system can replace an existing wet processing step. Examples are treatments for improved wetting and adhesion properties, such as advantages for dyeing, coating and making composite materials.
An evident advantage can be experienced in those cases where plasma treatments completely replace an existing wet process. Even in cases where only a reduction of water consumption is obtained (but that there is a real cost of supplying water), plasma technology becomes more cost effective every day. Reduction of the amount of chemicals needed in wet treatment, better exhaustion of chemicals from the bath, and shortening of the wet processing time can help compensate for a financial investment in plasma treatment. Reduction of the needed wet processing temperature, which in turn saves thermal energy, adds a more efficient use of energy due to plasma treatment.
All of these points are true for vacuum reactors and atmospheric plasma devices. One must carefully compare the performance/cost ratios with each choice. A full width vacuum plasma reactor which has been designed for the treatment of textiles is considerably more expensive than the commercial atmospheric reactors currently available. It will obviously depend on the application of the reactor, and how many years it will take for this difference in investment cost to be recovered.

1.4 PLASMA PROCESSES

The bombardment of plasma onto the surface of a material exposed to it produces several effects that we call plasma processes. Plasma processes can be conveniently classified into four overall processes: *cleaning, activation, grafting* and *deposition.*
In a *cleaning process*, inert (Ar, He) and oxygen plasmas are used. The plasma-cleaning process removes, via ablation, organic contaminates such as oils and other production releases on the surface of most industrial materials. These surface contaminants as polymers, undergo abstraction of hydrogen with free radical formation and repetitive chain scissions, under the influence of ions, free radicals and

electrons of the plasma, until molecular weight is sufficiently low to boil away in the vacuum.
Activation plasma process is a process which happens when a surface is treated with a gas, such as oxygen, ammonia or nitrous oxide and others, that does not contain carbon. The primary result is the incorporation of different moieties of the process gas onto the surface of the material under treatment. Let us consider the surface of polyethylene, which normally consists solely of carbon and hydrogen: with a plasma treatment, the surface may be activated, anchoring on it functional groups such as hydroxyl, carbonyl, peroxyl, carboxylic, amino and amines. Hydrogen abstraction produces free radicals in the plasma gases and functional groups on the polymeric chain (Fig.1.5).

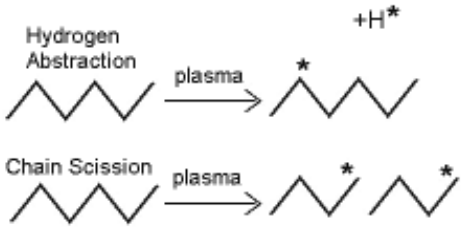

Figure 1.5 Free radicals formation by means of plasma action. Plasma can abstract hydrogen from the polymeric chain or can split chains.

Almost any fiber or polymeric surface may be modified to provide chemical functionality to specific adhesives or coatings, significantly enhancing the adhesion characteristics and permanency. Polymer surfaces, in such a manner active, provide greatly enhanced adhesive strength, representing an improvement in the production of flexible packaging.
Plasma can also produce a material *deposition*: when a more complex molecule is employed as the process gas, a process known as plasma-enhanced chemical-vapor deposition (PECVD) may result. For instance, when methane or carbon tetrafluoride is employed, the gas undergoes fragmentation in the plasma, reacting with itself to combine into a polymer. Selecting the process conditions, pinhole-free chemically unique films, may be deposited onto surfaces of materials within the plasma reactor. PECVD coatings alter in a permanent way the

surface properties of the material onto which these have been deposited.
In *grafting*, an inert gas such as argon is employed as process gas, many free radicals shall be created on the material surface. If a monomer capable of reacting with the free radicals is introduced into the chamber, the monomer shall become grafted. This is a procedure for low-pressure plasma treatment but grafting can be obtained with atmospheric plasma processing too. Typical monomers are acrylic acid, allyl-amine and allyl-alcohol (Fig.1.6).
By means of the plasma processes some properties of the surface can be changed to obtain several applications. First of all, surface wetting changes. Polymeric surfaces are usually not wettable and adhesion is poor. After plasma treatment the surface energy increases and wettability and adhesion enhancements are produced.

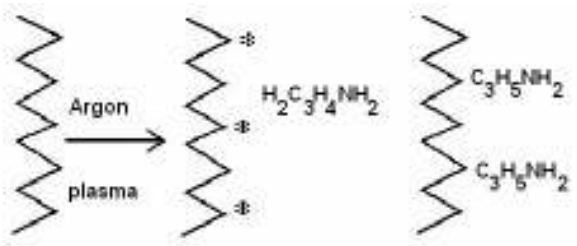

Figure 1.6 Grafting of a monomer on the surface: argon plasma produces radicals on the chain and monomers are grafted on the surface.

Whether it is an adhesive-bonded coating or a painted or printed decoration and markings, plasma surface treatment can provide significant improvement. The strength of an adhesive coating is enhanced by several factors: removal of contaminants, an increase in the surface energy of the substrate and consequently in wetting, and the formation of chemically reactive sites for the adhesive or ink that covalently bond. Covalent bonds provide stability because bonds are scarcely affected by aging, ultraviolet-light exposure or other environmental effects.

Plasma can provide improvements when gas employed as well as plasma parameters are optimized for each material and adhesive class. Several materials have been treated to increase bond strength until a bond permanency. In most instances, the loci of failure shifts with plasma treatment from adhesive-bond failure to cohesive failure, either within the adhesive layer or the substrate being bonded.

Fluoropolymers are typically considered as materials to which quality adhesive bonds are impossible. Hydrogen plasma, often in conjunction with a co-process gas, has been found to be particularly effective. Plasma processes employing hydrogen cause dehydrohalogenation along the fluoropolymer backbone to which the co-process gas can subsequently covalently attach.

Depending on the gas employed, plasma treatment may render the surface very hydrophilic, oleophobic or hydrophobic. The hydrophilic feature can be controlled very well. Oleo- and hydrophobic features are readily achieved in plasmas containing fluorine. If a fluoro-alkane such as tetrafluoromethane or hexafluoroethane is utilized as process gas, fluorine will be substituted for abstracted hydrogen on the surface of the substrate, reducing its surface energy.

Plasma-induced grafting offers another method of providing specific reactive sites to normally inert polymers. When an unsaturated monomer such as allyl-alcohol or allyl-amine is introduced into the reaction low-pressure chamber after the plasma is extinguished and prior chamber ventilation, it will add to the free radical, yielding a grafted polymer. If plasma in vacuum chamber is used, the treatment must be considered as a batch treatment. On-line atmospheric systems can be used too. Plasma systems of all sizes and degrees of automation are now available, from manually loaded batch systems as small as a microwave oven to fully automated systems treating automotive instrument panels.

To summarize, we can tell that cold gas plasma processes offer an efficient and reliable means to alter surface properties of all materials without affecting the bulk properties of the treated material. Reengineering the surfaces by introducing functional groups in a controlled and reproducible manner, greatly enhances adhesive permanency and reliability. The nature of cold gas plasma surface modification leads itself on precise

control and process repeatability. In the vast majority of applications, plasma surface treatment employs innocuous gases, enabling the manufacturing engineer to avoid corrosive chemicals and solvents.

In the following chapters we will discuss the role of atmospheric plasma treatment in improving the converting technology and the possible application of plasma to textile industries. A suggested reading on plasma and plasma technologies is the mentioned book by J. Reece Roth. A list of research papers on the subject of plasma in textile industries is placed at the end of this book.

2

PLASMA FOR THE FLEXIBLE PACKAGING INDUSTRY

2.1 INTRODUCTION

Flexible packaging is experiencing a technological revolution aimed at increasing consumer's convenience, enhancing his protection, and delivering new solutions for a host of challenges throughout the manufacturing and distribution chain.

High performance film structures, package configurations and applications, and printing technologies continue to drive flexible packaging into existing as well as completely new markets. While corona and flame surface pre-treatments are traditional finishing treatments of flexible packaging structures for graphic and coating enhancements, there are now evidences of print adhesion performance benefits using atmospheric plasma treatment (APT) technology in APGD devices.

The APT process was developed for treating a wide range of materials and has unique advantages over the presently used technologies of corona, flame, and priming treatments for flexible packaging applications.

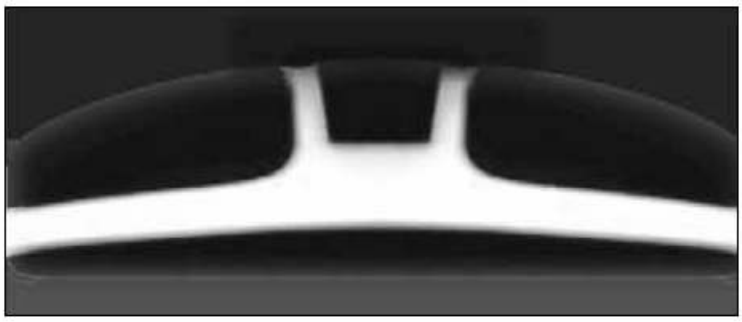

Figure 2.1 A homogeneous discharge between the two electrodes of an APT system.

The APT system (Fig.2.1) allows the creation of uniform and homogenous high-density glow discharge plasma at atmospheric pressure and at low temperature utilizing a broad range of inert and reactive gases. This process works on material surfaces in a way, which is similar to the vacuum plasma treatment process. APT production equipment testing has been successfully performed for the treatment of various materials, including polypropylene, polyethylene, polyester, Tyvek®, polyamide, and poly-tetrafluoroethylene.
The surface energies of the treated materials increased substantially (without any backside treatment or pinholing), thereby enhancing their wettability, printability, and adhesion properties.

2.2 APT PROCESSING POLYMERS

The APT process consists of exposing a polymer to a low-temperature, high-density glow discharge (i.e., plasma). The resulting plasma is a partially ionized gas consisting of large concentrations of excited atomic, molecular, ionic, and free-radical species.
Excitation of the gas molecules is accomplished by subjecting the gas, which is delivered within an open station design, to an electric field, typically at high frequency. Free electrons gain energy from the imposed high frequency electric field, colliding with neutral gas molecules and transferring energy, dissociating the molecules to form numerous reactive species. It is the interaction of these excited species with solid surfaces placed in opposition to the plasma that results in the chemical and physical modification of the material surface. The effect of plasma on a given material is determined by the chemistry of the reactions between the surface and the reactive species present in the plasma.
At the low exposure energies typically used for surface treatment, the plasma surface interactions only change the surface of the material; the effects are confined to a region only several molecular layers deep and do not change the bulk properties of the substrate. The resulting surface changes depend on the composition of the surface and the gas used.
Gases, or mixtures of gases, used for atmospheric plasma treatment of polymers can include nitrogen, argon, oxygen, nitrous oxide, helium, water vapor, carbon dioxide, methane,

ammonia, and others. Each gas produces a unique plasma composition and results in different surface properties. For example, plasma-induced oxidation, nitration, hydrolyzation, or amination can increase the surface energy very quickly and effectively. Depending on the chemistry of the polymer and the source gases, substitution of molecular moieties into the surface can make polymers very wettable. The specific type of substituted atoms or groups determines the specific surface potential.

For any gas composition, in APT, three surface processes simultaneously alter flexible packaging substrates, with the extent of each depending on the chemistry and process variables: ablation, crosslinking, and activation. In the ablation process, the bombardment of the polymer surface by energetic particles (i.e., free radicals, electrons, and ions) and radiation breaks the covalent bonds of the polymer backbone, resulting in lower-molecular-weight polymer chains. As long molecular components become shorter, the volatile oligomer and monomer by-products vaporize off (ablate) and are swept away with exhaust.

Crosslinking is done with an inert process gas (argon or helium). The bond breaking occurs on the polymer surface. But since there are no free-radical scavengers, it can form a bond with a nearby free radical on a different chain (crosslink).

The plasma bombardment is also able to create a micro-roughness on a polymeric film. This micro-etching usually does not modify the mechanical bulk properties of the film but strongly increases surface adhesion. Moreover, plasma does not burn pinholes in the film structure that corona treaters sometimes do if spots of high moisture or some other extra conductive material are present on the film. Corona strong shorts through the spot can cause a small hole through the substrate.

Activation is a process where surface polymer functional groups are replaced with different atoms or chemical groups from the plasma.

As with ablation, surface exposure to energetic species abstracts hydrogen or breaks the backbone of the polymer, creating free radicals. In addition, plasma contains very high energy UV radiation. This UV energy creates additional free radicals on the polymer surface. Free radicals, which are

thermodynamically unstable, quickly react with the polymer backbone itself or with other free-radical species present at the surface to form stable covalently bonded atoms or more complex groups (Fig.2.2).

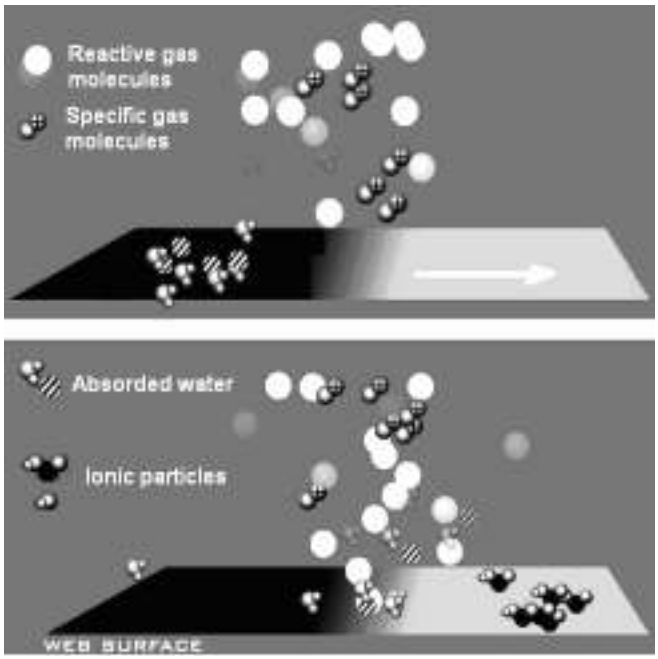

Figure 2.2 The two images show how plasma adds functional properties to a moving web surface. Reactive gases are accelerated or diffuse toward the surface under the influence of external fields. Low molecular weight materials such as water, absorbed gases and polymers fragments are knocked off the surface to expose a clean, fresh surface. At the same time a percentage of the reactive components in plasma with sufficient energy bond to the freshly exposed part of the film, changing the chemistry of the surface and imparting the desired functionality.

Application of atmospheric plasma to finished films has been theorized and practiced to provide specific functionality to the base film substrate adequate for improved adhesion relative to

the corona treatment process. Since atmospheric plasma contains highly reactive species within high-density plasma at atmospheric pressure, it is proven to significantly increase surface energy and to create polar groups on the surface of polymers so that strong covalent bonding between the substrate and its interface (i.e., inks, coatings and adhesives) takes place.

2.3 IMPROVING PRINT ADHESION

The flexible barrier packaging must have the fundamental property to protect the quality but also to enhance the appearance of some of world's most recognized consumer brands. A secured prints on the product packaging will guarantee consumer's and producer's requests. Experimental designs are now providing evidence of strong printing adhesion using APT technology. As data suggest, the opportunity exists for converters of flexible packaging to successfully achieve interface adhesions with untreated (no corona pre-treatment), low slip films.

There are five primary variables, which are thought to affect printing adhesion, namely: 1) the substrate, 2) the substrate pre-treatment, 3) the surface post-treatment power density (power setting relative to the discharge assembly length, line speed, and power level), 4) the surface treatment chemistry (the type and proportion of chemistries used) and 5) the ink chemistry. Here, we shall see a design to improve printing adhesion on a PVdC-coated PET film. The levels used in this design are found in Table 1.

Variable	**APT**	**Corona**	**Control**
Substrate	23 µm PET	23 µm PET	23 µm PET
Pre-treatment	None	None	None
Power density	10 $W/m^2/min$	10 $W/m^2/min$	
Post-treatment surface tension	54 Dynes/cm	46 Dynes/cm	40 Dynes/cm
Treatment chemistry	Helium/Oxygen	None	None
Ink chemistry	Water-based	Water-based	None

Table 1 - Variable levels utilized in experimental design.

The trial runs were performed on Enercon's Bare Roll Corona Treatment Station, as well as its Plasma3™ Atmospheric Plasma Treatment System, resident on its same pilot line.
For all runs, two PVC-coated polyester films were post-treated, one in the APT system with a Helium/Oxygen plasma, the other by means of a corona treater. Another sample constitutes the control reference and was not treated. The samples were then printed with aqueous ink (Flint Ink) using a laser-engraved anilox roll to 300 lines per inch (lpi). The printed image provided solid (100%) ink coverage. The calculated ink transfer (thickness) to the film, based upon this cell volume, is approximately 1.9 microns.
Friction/peel testing equipment conforming to test standards was used as the adhesion standard for testing the printed polyester film. Results in terms of the averages of twenty test iterations are presented in Figure 2.3 below.

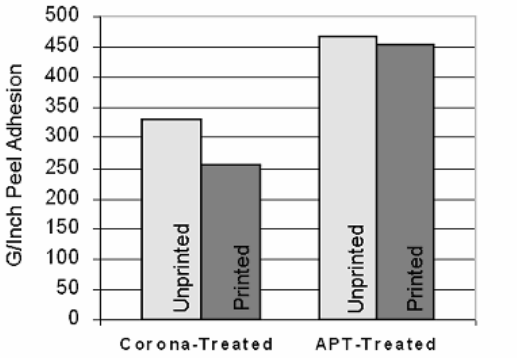

Figure 2.3 Average peel adhesion for printed and unprinted polyester film, after treatment with a power density of 10 W/m^2/min.

The peel adhesion data indicated that at a power density of 10 W/m^2/min, printed APT-treated polyester surpassed peel adhesion results registered by printed corona-treated polyester by a margin of seventy-eight percent. The four percent decline in ink peel adhesion between unprinted and printed APT-treated base material suggests that the formation of strong covalent atomic bonds on a cleaned and uniform, homogeneously micro-etched surface may account for improved anchorage of inks.

To determine the impact on peel adhesion under conditions where the surface tension created by both corona and APT were the same, the protocols were repeated and reported in Figure 2.4. This condition was established by reducing the power density of APT to 7 W/m^2/min to achieve the same post-treatment surface tension of 46 dynes/cm.

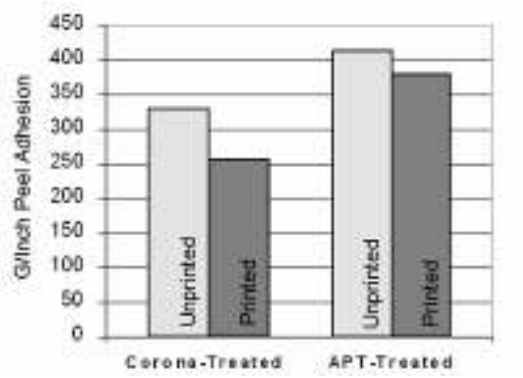

Figure 2.4 Average peel adhesion for printed and unprinted polyester film, when surface tension is 46 Dynes/cm.

This set of peel adhesion data indicates that at a surface tension level of 46 dynes/cm printed APT-treated polyester maintained a significantly higher peel adhesion performance over printed corona-treated polyester, in this analysis by nearly fifty percent. This fact suggests that covalent bonds most likely contribute to improved ink adhesion.

The analysis provides evidence that the flexible packaging converters utilizing aqueous inks on polyester based structures may experience improvements in ink adhesion by employing APT-based surface treatment systems.

3

MODIFYING THE SURFACE FEATURES OF EXTRUDED FILMS

3.1 INTRODUCTION

When it becomes necessary to change the surface features with proper treatments in the extrusion film line, a number of different problems are involved. Factors including budget, available space, and specific application criteria all contribute in choosing of the better solution. Because of these variables, it's understandable that the film extruders often decide their line set-ups of the surface treatment section with rather different approaches. Not all of the configurations create an optimum scenario for surface treating success.

3.2 BLOWN FILM EXTRUSION – AN EXAMPLE

The blown film process involves extrusion of a plastic through a circular die, followed by the "bubble-like" expansion. Several advantages of manufacturing film by this process include the ability to regulate the film width and thickness by control of the volume of air in the bubble, the output of the extruder and the speed of the haul-off. Moreover, the process possesses the capability of inducing a biaxial orientation, allowing uniformity of mechanical properties in the film.

Blown Film Extrusion can be used for the manufacture of co-extruded, multilayer films for high barrier applications such as food packaging. Plastic melt is extruded through an annular slit die, usually vertical, to form a thin walled tube. Air is introduced via a hole in the center of the die to blow up the tube like a balloon. Mounted on top of the die, a high-speed air ring blows onto the hot film to cool it. The tube of film then continues upwards, continually cooled, until it passes through nip rolls where the tube is flattened to create what is known as a 'lay-flat' tube of film. This lay-flat or collapsed tube is then taken back down the extrusion tower via more rollers (Fig.3.1).

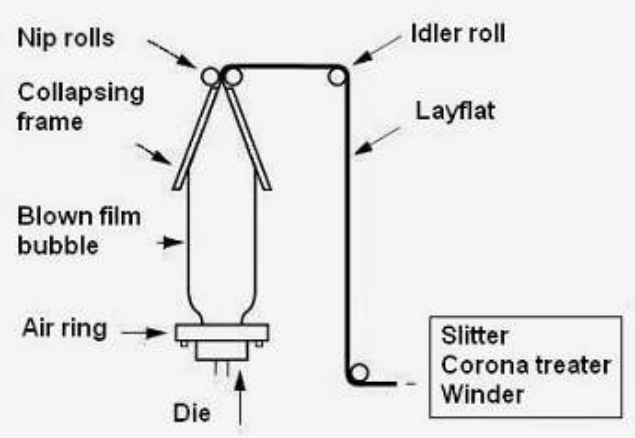

Figure 3.1 A common method of film manufacture is the Blown Film Extrusion also referred to as the Tubular Film Extrusion. Plastic is extruded through a circular die, forming a bubble before being collected by a frame.

The film is then either kept as such or the edges of the lay-flat are slit off to produce two flat film sheets and wound up onto reels. Polyethylenes (HDPE, LDPE and LLDPE) are the most common resins in use, but a wide variety of other materials can be used as blends with these resins or as single layers in a multilayer film structure. These include polypropylene, polyamide, and EVOH. In some cases these materials do not gel together, so a multilayer film would delaminate. To overcome this, small layers of special adhesive resins are used in between. These are known as 'tie layers'.
Polyolefin films possess relatively inert, low surface energy surfaces that show poor wetting and adhesion to printing inks. To allow printing, converters must apply surface treatment. The most commonly used is the corona treatment (in Figure 3.2, a bare-roll corona treater). As film moves between a high voltage electrode and an insulated roll, a uniform corona discharge, consisting of plasma of ionized gas and other reactive species, produces a level of oxidation of the film surface. The level of treatment is characterized by the surface tension measurement of the film.

The surface tension of a non-treated polyethylene film is about 30 dynes/cm. Adhesion of ink requires a surface tension >36 dynes/cm. An excessive level of treatment (>50 dynes/cm) will cause some degradation of the polyethylene film. With today's race to produce film faster, thinner and with lower tension it makes sense to optimize the treater set-up for the worst case scenarios.

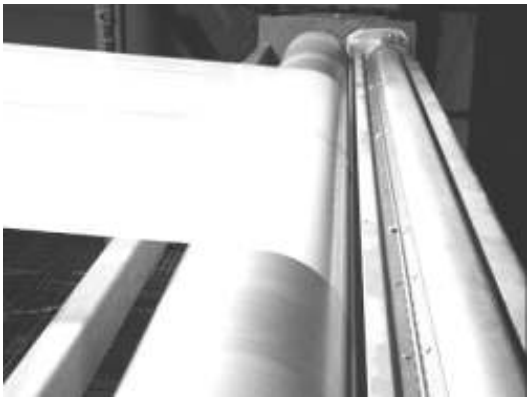

Figure 3.2 A bare-roll corona treater for pretreatment and refreshment of the surface tension.

3.3 TYPICAL PRETREATMENT ISSUES

Differences can occur in the surface pretreatment level, differences based upon the position of the corona treater station and the temperature of film at the time it enters the station. A lower watt density of treatment can adequately raise the film surface tension to the required level when the treater station is located at the top of the tower. This position of the treater is better than other positions where the treater station is located halfway down the tower or at the bottom of it just prior to the winder. This is because the film temperature at the top of the tower is higher, allowing the corona discharge to make the polymer surface more polar at a low state of crystallinity.

There are a number of other factors which impact treatment response and the ability of a blown or cast film to maintain a treatment level. One critical factor is the additive loading. The

additive loading is the amount of additives in parts per million (ppm) contained in the film. Erucamide, as well as other fatty acid-based slip additives are used in polyolefine resins to aid process ability. The initial impact of higher additive loading is to require increasing watt densities to raise the film's surface tension by a given amount.
Furthermore, higher additive loading will reduce the film's ability to maintain the effects of corona treatment. This is due to the tendency of additives to bloom or migrate to the surface and mask the effect of corona treatment. The subsequent disadvantage is that ink adhesion is sub-optimized with a decay of the primary pre-treatment occurring as early as the winding stage following extrusion, requiring a secondary pre-treatment on secondary converting equipment, such as printing presses (see Fig.3.3).

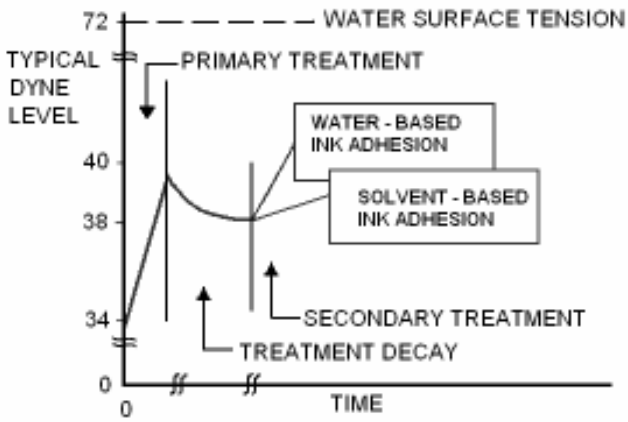

Figure 3.3 The surface tension level obtained with the primary treatment is then subjected to decay during the winding and the storage of films. A secondary treatment is necessary for refreshment of the dyne level.

3.4 OPTIMIZING THE USE OF TREATERS.

Upstream applications that require treatment of the outside of the film are fairly straightforward: the biggest challenge here is to avoid that air remains trapped inside the tube. A two-sided

covered roll system with stainless steel electrodes works well for this type of application.
Treating slit film is a much more delicate process than treating film in a tube format. Slit film requires careful handling as it has a tendency to wrinkle: this will cause backside and uneven treatment levels.

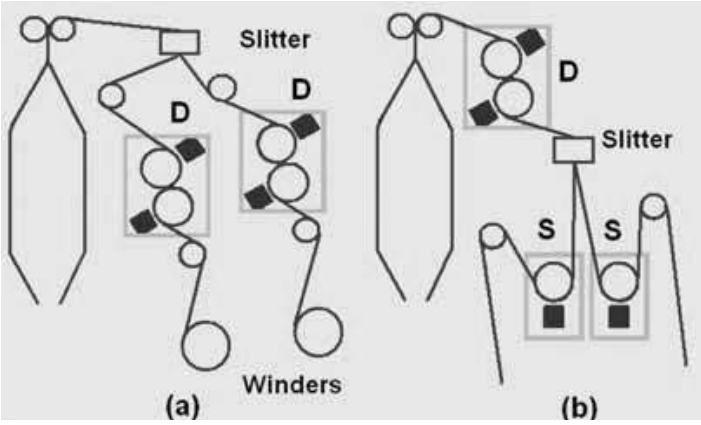

Figure 3.4 Different web paths for surface treatment (D for two-sided treaters and S for single-sided treaters).

A layout where treatment occurs after slitting (see Fig.3.4a) is not the best treatment configuration. Some companies create complex web paths for the substrate after slitting to utilize just single-sided surface treaters (Fig.3.4.b). These web paths require multiple idler rolls and nip rolls which add significantly to the cost and size of the station: a concept not desirable because of both cost and the potential for web handling issues that will cause backside treatment.
A cleaner and simpler solution is to use a two-sided treater before the slitter and then two single-sided corona treaters. This allows an easy web path for operators to thread. And more importantly, it allows the film to follow a relaxed natural path to ensure reliable treatment results.

3.5 PERFORMANCE UPGRADES

Traditionally film extrusion lines utilize a metal electrode and covered roll configuration. However there are exceptions. Some companies choose a bare-roll system to eliminate any roll covering concerns. While others have selected new atmospheric plasma systems for their extruded film applications. For simple applications that do not require lane treating, a fixed width metal tube electrode provides adequate treatment levels. For demanding fixed width applications a powerful metal fin electrode is ideal. Another option for applications that require higher power and large ground rolls is a universal treating system. This system features a comparably smaller base roll than a metal electrode system and features ceramic electrode technology.

Lane treatment requires a segmented electrode. There are two styles of segmented electrodes: flip segments and push/pull segments. Flip segments provide an economical solution for low power and less demanding applications. Operator friendly push/pull segments can handle greater amounts of power and are therefore better suited to lines that operate at moderate and higher line speeds.

Whether it is necessary select flip segments or push segments, it is also important to understand the benefits of stainless steel over aluminum. Aluminum material is low in cost and an easy material to fabricate, so it could be argued that aluminum is an excellent choice for electrode construction. That is until one looks at what happens to an aluminum electrode during use. The corona process creates a harsh environment for the electrode. Aluminum will oxidize over time causing the segments to stick together. This problem causes areas of treatment or non-treatment along the width of the electrode. Also, aluminum is a good conductor of heat. Corona electrodes operate in temperatures of 150 to 180 °C. It is very difficult for the aluminum electrode to remain parallel to the ground roll at these temperatures. Once the aluminum electrode warps, the air gap between the face of the electrode and the roll surface changes and so do the corona and ultimately the dyne level.

It is for these reasons that stainless steel electrodes are recommended because they offer superior performance, durability and lower cost over the life of the treater. An estimation of the budget according to short or long term and an

estimation of the role of reliability and consistent performance in the film processing is giving the best choice for the surface treating system.

4

EXTRUSION COATING AND LAMINATION

4.1 INTRODUCTION

Extrusion coating and lamination and the film lamination give rise to complex manufacturing techniques, which allow a converter to make high-performance packaging films. The physical properties and the related performance characteristics of composites obtained by extrusion coating and lamination can be comparable to that produced by film lamination. This is not surprising since many of the major components involved by these techniques in the production of the final composites are also the same.

In extrusion coating and lamination, the resin, melted and formed into a thin hot film, is coated onto a moving substrate such as paper, paperboard, metal foil, or a plastic film. The coated substrate then passes between a set of counter-rotating rolls, pressing the coating onto the substrate for a complete contact and adhesion. A coating extrusion system is shown in Fig.4.1.

The extrusion lamination, or sandwich lamination, is a process related to extrusion coating. In this case, the extrusion-coated layer is used as an adhesive layer between two or more substrates. A second layer is applied to the extrusion coating while it is still hot and then the sandwich is pressed together by pressure rolls. In film lamination, a fabricated film is adhered to a moving substrate by application of heat and pressure.

Film lamination includes several methods with different combination of heat and pressure to ensure foil adhesion. Examples of common composite films are the materials for beverage pouchstocks and the composites for the medical packaging industry.

The typical beverage pouchstock is a combination paper/PE/foil/PE and the material used for medical packaging usually consists of PET/PE/foil/PE. These materials have then four substrates and three interfaces among substrates, sometimes with adhesives or primers used at the interfaces.

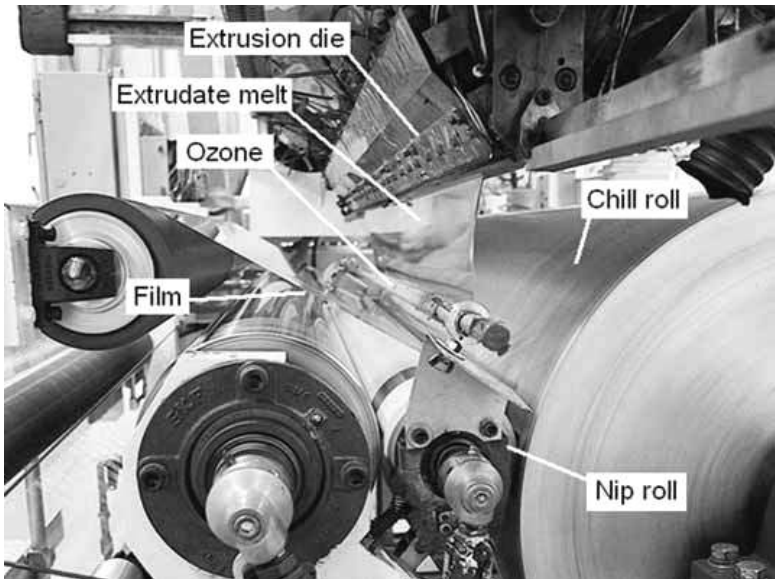

Figure 4.1 A coating extrusion system

Converters can laminate the four substrates by means of three separate operations or the layers are combined together in extrusion laminations.
In fact, the polyethylene layer can be inserted in the combination by means of a coating extrusion from PE pellets or with a laminate process of a PE film.

4.2 MODIFYING INTERFACES

A major factor influencing the extrusion bonds is the specific adhesion, that is the capability of the molten polymer to conform to or match the chemical composition of the substrate. In the composite polyester/PE/foil/PE for instance, the actual construction to consider is more likely polyester /interface/PE/foil/PE, where the interface between the polyester and PET film must be considered as a true layer.
At the polyester-polyethylene interface, a primer and adhesives, after surface modifications, are necessary so that the polyester will adhere properly to the PE (a detailed discussion on the role

of primers in extrusion/ lamination can be found in a paper of D. Bentley, PFFC magazine).

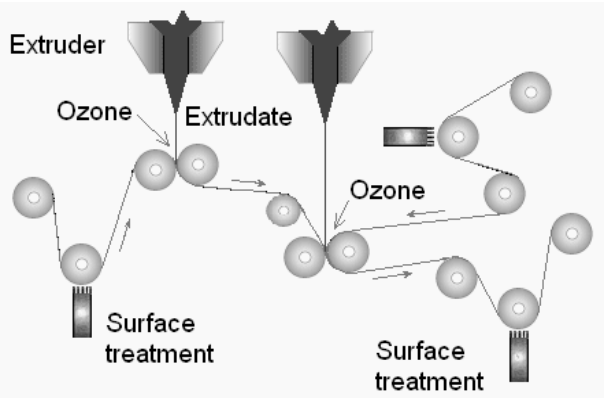

Figure 4.2 Typical co-extrusion line and the location of ozone and surface treatment stations.

Likewise, a pretreatment between the foil and PE is necessary to form a sufficient bond between those two substrates. Application of a surface modification to a substrate before an extrusion coating or extrusion laminating operation requires combinations of corona, flame, ozone and atmospheric plasma equipment to optimize adhesion (in Figure 4.2, a combination of ozone and surface treatments).

4.3 COMBINED SURFACE TREATMENT

The corona discharge, particularly bare roll and universal roll designs, and flame treatment at atmospheric pressure have both been effective for improving adhesion of various substrates on extrusion coating lines. The more recent variable chemistry atmospheric plasma treatment (APT) proved to be able to significantly promote covalent bonding of coatings to substrate surfaces. Corona or atmospheric plasma treatments are often combined with ozone application in the coating extrusion and lamination. Let us consider for instance the coating with LPDE.
To have adhesion, it is necessary to provide oxidation of the non-polar plastic material. For molten plastic to oxidize, high

temperature and contact with air are required. And in fact, LDPE oxidizes at high temperatures (300-330ºC) in the extrusion coating process. But excessive oxidation caused by running at low speed and high temperatures can promote odor and taste problems for the product contained in the packaging.
For this reason, extrusion coaters and laminators seek to use lower process temperatures and blow ozone (O_3) directly onto the molten plastic, thereby oxidizing it. Moreover, for further avoiding odor and taste modifications, surface treatments are used, instead of employing special resins or chemical priming of the substrate.
In spite of a common use of ozone application together with various surface modification techniques such as corona and atmospheric plasma, the influence of the combined action on the most popular plastics has not been quantified by exhaustive experimental data. In the next section we will discuss the role on the heat seal strength.

4.4 EXTRUSION COATING EXPERIMENTS

The analysis of a process such as extrusion coating and laminating is rather complex. We just discuss the role of the surface treatments in this coating process, reporting some results obtained comparing ozone/corona with ozone/APT treatments. In particular, two experimental runs were performed by coating low-density polyethylene onto oriented polypropylene and polyester films. Ordinary heat seal strength techniques were used to quantify the affects of the variables on heat seal strength vs. seal temperature. Including atmospheric plasma treatment, five variables are thought to affect adhesion and heat seal strength, namely: substrate surface modification, melt temperature, line speed, air gap, and coating weight. Besides these factors, several ozone-related parameters were identified that could affect adhesion and heat seal strength.
These parameters were ozone flow rate, ozone concentration (power setting on ozone unit), and geometry of the applicator set-up such as horizontal distance and angle from horizontal. The levels used in this design are found in Table 1, accomplished by a combination of oxidation of the extrudate and treatment of the substrate. The level of oxidation is a function of the melt temperature, the line speed, the air gap and the coating weight.

Variable	Condition 1	Condition 2
Substrate Treatment	Ozone/APT	Ozone/Corona
Melt Temperature	315° C	315° C
Line Speed	90 m/min	90 m/min
Ozone Air Gap	15.24 cm	15.24 cm
Coating weight	10 g/m²	10 g/m²
Ozone	Yes	Yes
Ozone Rate	2.08 m³/min	2.08 m³/min
Ozone Concentration	0.25 kW	0.25 kW
Horizontal applicator Position	2.54 cm	2.54 cm
Applicator Angle (from Horizontal)	0°	0°
APT Gas Chemistry	95%He + 5%C_2H_2	None
Watt Density	40 W/m²/min	40 W/m²/min

TABLE 1 - Variable levels utilized in experimental design for testing ozone/APT and ozone/corona treatments.

Some combinations of these variables will yield acceptable adhesion but also produce undesirable effects such as increased taste and odor or poor heat seal strength.
The Atmospheric Plasma trial runs were performed on the Enercon APT pilot line. The extrusion coating trial runs were performed on the Equistar Millennium Petrochemical extrusion coating pilot line. For all extrudate runs, a LDPE film was coated onto OPP and PET film. The samples were prepared and tested according to ASTM test method F88. The heat seal tests were made on a heat seal machine using a pressure P= 206.8 kPa and a dwell time T= 1 sec.
As a result, the measurements display that the use of APT surface modification to the OPP and PET substrates increased heat seal strength by a similar amount as the corona treatment of the substrate.
The ozone treatment of the extrudate is the same. Figure 4.3 graphs the effects of substrate treatment and heat seal strength.

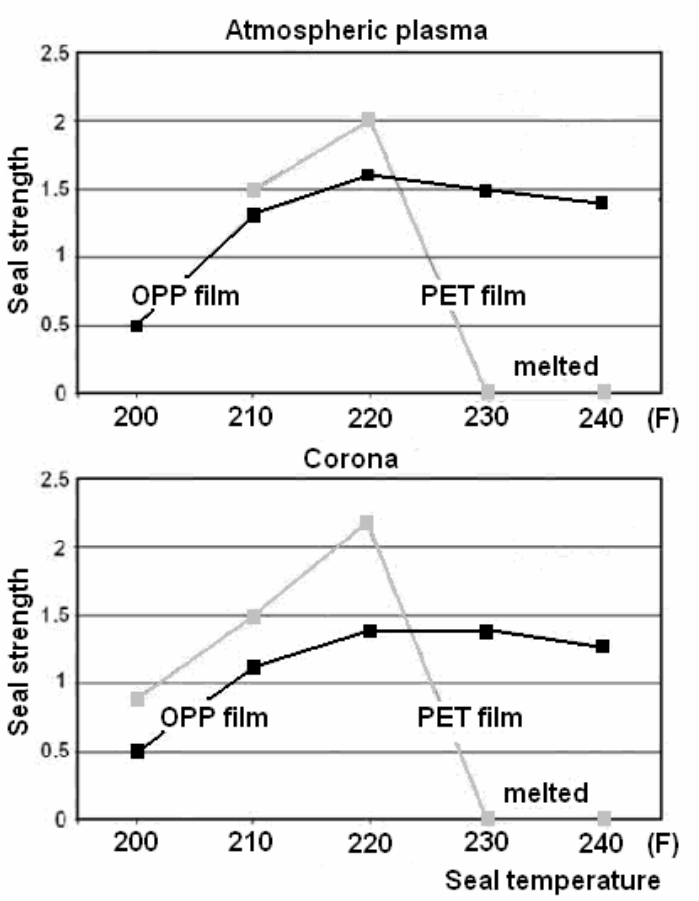

Figure 4.3 The seal strength (Lb./In.) as a function of the temperature seal (F) for atmospheric plasma treated films and corona treated films.

Let us remember that the atmospheric plasma glow discharge provides a treatment with high uniformity and homogeneity, along with the ability to micro-etch and confer functional properties to the surface of films (in this case with carbon-based functionality). In the case of OPP film, the level of heat seal strength is 20% higher than the level obtained with the corona pretreatment. Surely, the performances of the extruded film can

be increased adjusting the melt temperature and the line speed. As a conclusion we can tell that a further enhancement of the heat seal strength of extrusion coated films can be obtained optimizing the atmospheric plasma treatment combined with ozone.

5

SURFACE TREATMENTS FOR ROTO- AND FLEXO-PRINTING

5.1 INTRODUCTION

Solvent-based printing and coating can have common elements. There are the applications of a relatively high solvent-content material to a moving web or film, the rapid solvent evaporation by movement of heated air across the wet surface, and the removal of the solvent-laden air exhausted from the system. But printing involves the application of an image on the substrate, not just of a homogeneous coating.

There are two basic processes utilized for printing flexible packaging – rotogravure and flexography. In the gravure printing, the image area is engraved on the surface of the image carrier, which is a copper-plated steel cylinder or also chrome-plated to enhance wear resistance. The gravure cylinder rotates in an ink fountain.

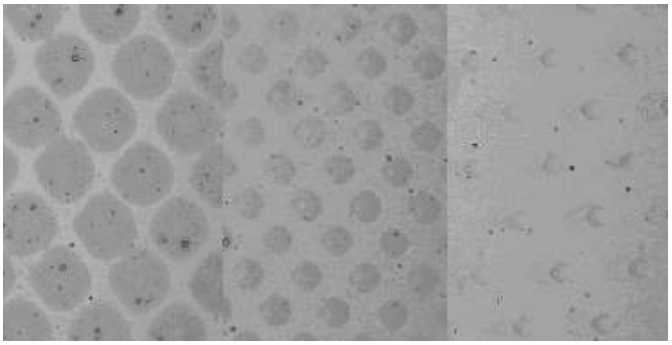

Figure 5.1 Rotogravure printing of a polymeric film observed by means of a microscope with different ink percentages (70, 40 and 10%). The image side is 0.5 mm.

The ink is then picked up in the engraved area and scraped off with steel "doctor blade". The image is transferred directly to the web when it is pressed against the cylinder by a rubber covered

impression roll, and the product is then dried. The inks used in rotogravure printing contain from 55 to 95 volume percent low boiling solvent.
Magnifying the printed image, it is possible to see the dots of different colors, placed by the printing rolls on the substrate. The dots as a whole create the continuous image. Figure 5.1 shows a trial of rotogravure printing, observed by means of a microscope: the polymeric film is printed with different ink percentages.
In flexographic printing, the image area is above the surface of the plate. The distinction is that flexography uses a rubber image carrier and alcohol-based inks. The process is usually web-fed and is employed for medium or long multi-color runs on a variety of substrates, but the major product categories within the flexography market are flexible packaging and laminates. In Figure 5.2, a schematic view of the rotogravure and flexo printing.

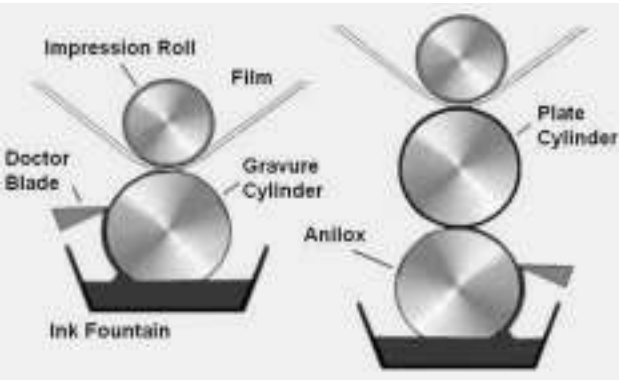

Figure. 5.2 A schematic view of the rotogravure and flexo printing

To optimize the flexographic printing, it is necessary to choose anilox rolls, printing plates, and inks according to the printing substrate surfaces and related surface treatments. For example, a fine anilox roll is typically appropriate for a smooth printing substrate using a low volume of ink; if a rougher surface is to be printed upon, a higher volume of ink is required with, therefore, a lower line anilox.

Moreover, other factors must be considered to increase the quality of printing: for instance, the proper impression height must be chosen according the substrate compressibility in printing process. By all the process parameters, it is possible to create effective standards for the precise type of anilox rolls and plate cylinder required for each substrate to be printed.

5.2 PRINTING ON PLASTICS

Generally, plastics have chemically inert and non-porous surfaces with low surface tensions causing them to be non-receptive to bonding with printing inks, coatings, and adhesives. Polyethylene and polypropylene are the lowest in surface energy of the various plastics and are the two materials most often subjected to surface treatment to improve their bonding characteristic. Surface treatment, however, is not limited to these two materials and can be used to improve the bonding ability of virtually all-plastic materials as well as some non-plastic materials (Fig.5.3).

The two non-plastic materials most often subjected to surface treatment are foil and paper. All substrates, plastics, films, paper and foils, when treated at the time they are produced, provide a better bonding surface for the following converting processes, such as printing, coating, lamination and so on.

Let us consider the printing of a polymeric film. In the surface treatment before printing, the major role is played by the difference in the surface energy between ink and substrate. If the surface energy of the ink is higher than that of the substrate, it will not "wet out" and the resulting adhesion and print quality will be poor.

The surface treatment increases the surface energy and then the wetting and ink adhesion. This secondary treatment is usually corona refreshment of the substrate just before printing to ensure proper ink adhesion.

Conventional thinking indicates that pre-treated material does not require additional in-line treatment, when solvent- based inks are used for printing. However, many advantages can be gained from adding in-line surface treatment to printing and converting processes. The benefits from in-line surface treating are a better ink adhesion and wetting, elimination of pin-holing in solid colors and gradients, and overall improved print quality.

Figure 5.3 Inspection of a universal treater, the most common surface treater used to increase the surface properties of substrates before printing or converting.

5.3 METHODS OF SURFACE TREATMENT

The four methods by which surface treatment is accomplished are as follows: 1) the corona discharge, 2) the etching with acid or atmospheric plasma, 3) the flame treatment and 4) priming (used alone or in combination with corona discharge).

A corona treating system is the most prevalent technology used to treat flexible packaging substrates and it is also very easy to insert the treater in the converting line. Corona is designed to increase the surface energy to allow improved wettability and adhesion of inks, coatings and adhesives. As a result, the materials treated will demonstrate improved printing and coating quality, and stronger lamination strength.

The system consists of two major components: the power supply, and the treater station. The treater station applies power to the surface of the material through an air gap via a pair of electrodes, one at high potential and the other, usually a roll, which supports the material, at ground potential. Between the

electrodes, the corona discharge is established, as shown in Fig.5.4. Only the side of the material facing the high potential electrode should show an increase in surface tension.

Figure 5.4 In the airgap between electrodes, the corona discharge is established.

The most common types of electrode for solvent based printing applications are ceramic tube electrodes. The ceramic electrodes with tightly controlled watt density and frequency can now be operated over a treater roll coated with a special ceramic. The result is an improved level of treatment on difficult to treat substrates such as cast film, polypropylene with high levels of slip additives, etc.

5.4 PROPERLY SIZING A SURFACE TREATING STATION

There are six major factors to determine a suitable size and type of surface treater for a given application: 1) the basic material type, 2) the additive load, 3) the web width, 4) the line speed, 5) the number of sides to be treated and 6) the dyne level required.

From this information, the watt density ($W/m^2/min$) requirement can be calculated. Although watt density applied is directly related to the increase in dyne level (surface tension), the relationship is not linear and different for each type of treated material.

Generally, the greater the applied watt density, the greater the increase in surface tension. This determines the output power required, as well as the type of treater station. These calculations can vary by manufacturers and are based upon their own application experience. It is then possible that very different recommendations for the same application are suggested from different treater manufacturers.

5.5 SURFACE ENERGY LEVEL

Different flexible packaging substrates have different initial surface tensions. This can range from 29-31 dynes/cm for polypropylene to 41-44 dynes/cm for polyester. It can be measured in laboratory by using dyne solutions or dyne pens.

But laboratory measurements of surface tension may not yield an accurate reading of what the surface tension is. In fact most films, treated at the point of extrusion, have a treatment level subjected to decay with time.

The decay can also be influenced by a number of factors including additives, ambient temperature during storage, and the effects of rewinding, among others. Due to the decay, it is quite common for secondary treatment to take place just before printing to "bump" the substrates back to their original surface energy levels.

In the corona treatment there is an in-line process parameter directly proportional to surface tension, able to evaluate the treatment level. That process parameter is the watt density per linear unit squared. As a result, in-process statistical quality control can be implemented by a control system that instantaneously controls watt density and outputs deviations throughout the printing production run. If the material has not been pretreated, however, it impossible to have a proper treatment level just by post-treatment. Recommended treatment levels are found in Table 1 (at the end of the chapter). Film suppliers have traditionally provided treatment levels in the 36-42 dynes/cm range. These treatment levels are adequate for flexographic printing using solvent-based inks but are just barely acceptable for bonding with solvent-based adhesives.

As far as the treatment level is concerned, it is necessary to pinpoint that it has upper limits. Very high treatment levels create polar groupings, which are hydrophilic and may absorb excessive water, causing a reduced bonding layer at the

substrate surface. In addition, overtreatment may produce low molecular weight products at the surface, which do not maintain adequate bonds to the bulk substrate.

Figure 5.6 Beneficial effect of having sufficient substrate tension is shown in the figure. In the upper part the adhesion is perfect. In the lower part without treatment is instead highly ink defective.

New water-based inks and solvent-free adhesives have necessitated the placement of corona treating equipment on many converting machines. This is partly because the new inks and adhesives have a higher surface tension and don't wet the film as well as solvents, and partly because of fatty-acid slip additives present on the surface of the film. Initial treatment on the extruder is accomplished before much of the slip additive has migrated to the surface.

The slip additive has relatively poor wetting characteristics and can cause problems in bonding unless subjected to a second in-line corona treatment. Even before the advent of new types of adhesives and printing inks, a high percentage of converting machines were equipped with corona treaters simply as an assurance tool for avoiding problems caused by inadequately treated film from a supplier. Figure 5.6 depicted a flexo-printed image for which the corona treater was not in operating mode, then turned on to raise the polypropylene substrate surface

tension to a minimum of ten dynes higher than the surface tension of the water-base ink.
The current state of the art in surface treatment is able to provide good practical solutions; nevertheless, the technology of surface treatment must advance to meet the needs of constantly changing materials and production parameters. Not only does the technology of surface treatment need to continue to advance, but also the surface science must increase too, to have a better understanding of the mechanisms by which surface treatment affect surface characteristic changes at the molecular level.

Process	Flexo/Gravure			Litho			Offset/Letterpress			Screen & Pad		
Substrate/ Native Dyne	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV
PE / 30-31	38-44	36-40	38-50	40-46	37-42	40-50	40-46	37-42	42-54	42-48	38-44	44-60
PP / 29-31	38-44	38-40	40-50	40-46	38-42	40-50	40-46	37-42	40-54	42-48	38-44	44-60
PVC/ 33-38	38-44	36-40	36-50	40-45	37-42	36-52	40-45	38-42	40-52	42-48	38-44	42-60
PET/41-44	44-52	40-46	42-54	46-58	42-46	44-56	46-56	42-46	46-60	48-60	42-48	44-62
PS/38	38-44	35-40	42-48	40-45	37-42	42-50	40-46	38-44	42-58	42-48	38-44	42-58
PU/ 43	40-46	30-42	38-50	40-46	38-42	38-52	40-45	38-44	42-56	42-50	38-44	42-58
ABS/35-42	42-46	40-44	40-52	42-45	40-45	42-52	42-48	38-46	45-52	42-48	40-45	48-56
PA/ 40	44-52	40-46	42-54	46-58	42-46	44-56	46-56	42-46	46-60	48-60	42-48	44-62

TABLE 1

Recommended surface tension level for substrate, printing process and ink type.

6

CLEAR BARRIER FILMS

6.1 INTRODUCTION

The consumer's preference to visually inspect packaged products through packaging prior to purchase acts in such a way that transparent barrier flexible substrates are of interest to many in the packaging industry. Numerous methods have been used to manufacture transparent barrier coatings with varying degrees of success. This chapter will present new evidence for clear barrier deposition through the use of plasma processing. To protect a product from oxygen or moisture penetration and therefore the product shelf life, standard packaging films of polyethylene, polypropylene and polyester are not enough.

To have packaging films with barrier properties the substrates must be laminated, co-extruded or coated. Barrier films have structures rather complex because barring oxygen or water vapor transmission is rarely the only feature the package must provide. Converters frequently need barrier combined with printing, sealing and/or peeling. Foil is a widely used barrier material. But foil lamination is not the right solution if a clear barrier is needed in packaging.

Although innovations continue in lamination and co-extrusion, the barrier material developments generating the most excitement today involve coatings. Extrusion coating can create structures with a combination of barrier, sealing and peeling features and makes it possible to join materials that would be hard to laminate. Since coating typically is a lower cost operation than lamination, coated structures often represent a cost advantage as well.

Certain films combine a passive aluminum oxide barrier coating with an active barrier layer. The result is a clear material that allows consumers to see products, with barrier properties equal to or better than thin-gauge foil, that can maintain an oxygen level of less than 1% for more than a year. Other products incorporate a barrier layer of ethylene vinyl alcohol (EVOH) to protect pharmaceutical products requiring protection from both

moisture and oxygen. To protect UV-sensitive products, where it is desirable to have a clear package, an ultraviolet (UV) inhibitor can be added to the packaging film.

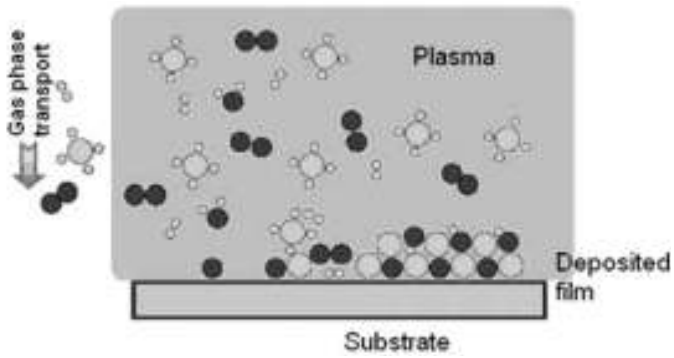

Figure 6.1 PECVD is a technique commonly used to deposit layers of insulating materials and amorphous or polycrystalline silicon. Plasma stimulates a reaction on the substrate surface of two or more vapor phases, breaking down the parent molecules and allowing the reaction to occur at a lower temperature than conventional CVD

We have discussed in the previous chapters the role of surface treatments in enhancing the surface film properties, in particular the role of corona and plasma treatments. We want to discuss here the use of atmospheric plasma treatments as a step process for deposition and polymerization of clear barrier coatings.

The use of plasma in coating is known as PECVD, plasma enhanced chemical vapor deposition. PECVD is a process to deposit very thin films from a vapor state to a solid state on substrates (Fig. 6.1). In this process, species to be deposited are generated in the plasma discharge. As a result, deposition using the same source gases is taking place at lower temperatures than in conventional CVD, which requires high temperature to break bonds and to release desired species from input gases. The chemical reactions involved in the process are occurring after creation of plasma from the reacting gases,

essentially at room temperatures. Plasma is any gas in which a significant percentage of the atoms or molecules are ionized.
Plasma can be created by an AC discharge between two electrodes where the in-between place can be filled with gases. Plasmas with low fractional ionization are of great interest for material processing because the energy exchange between the electrons and neutral gas is very inefficient. In this plasma, therefore, the electrons can be maintained at very high equivalent temperatures - tens of thousands of K, equivalent to several eV of average energy - while the neutral atoms remain at the ambient temperature. These energetic electrons can induce many processes that would otherwise be very improbable at low temperatures, such as dissociation of precursor molecules and the creation of large quantities of free radicals. Because electrons are more mobile than ions, plasma is normally more positive than any object it is in contact with. Ionized atoms or molecules feel then an electrostatic force and are accelerated towards the neighboring surface.
Thus all surfaces exposed to plasma receive energetic ion bombardment. This bombardment removes contaminants and changes the film surface properties. When the ion density is high enough, a significant sputtering of a deposited film occurs. By inserting in the plasma the desired precursor, a coating of the surface is obtained.

6.2 CLEAR BARRIER COATINGS

The continuing and growing interest in clear barrier for flexible packaging inevitably led us to investigate the opportunities of the use of plasma processes in producing barrier coatings. Clear barrier typically means inorganic oxides or nitrides of metals deposited on substrates. While deposition of inorganic oxides at reduced pressure is fairly routine, such processes and equipments are expensive. The prospect of being able to add value by depositing an inorganic oxide barrier layer using an inline, inexpensive, atmospheric pressure process is extremely attractive.
Much of the current development effort is directed toward plasma polymerization and oxidation of organo-silicon compounds to yield a thin functional layer of SiO_x on a substrate such as a plastic film or sheet. Organo-silicon compounds are a logical choice. These materials are easily selectable as liquids

at room temperature and are considered good candidates for thermal evaporation into the plasma gas stream. Producers of atmospheric plasma treaters are now working to develop the equipment and process methodology for deposition of a thin functional coating of SiO_x on plastic sheet that will display barrier functionality.

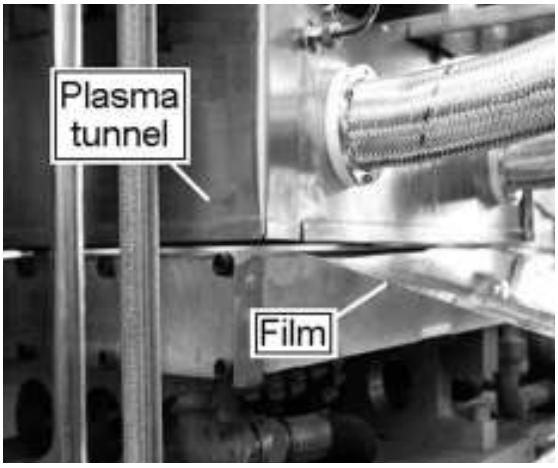

Figure 6.2 Plasma device for atmospheric clear coating deposition.

In the following section we will discuss Enercon plasma equipment (see Fig.6.2) currently in place at one of the customer's pilot facilities that is able to deposit a very thin SiO_x on plastic sheet as a successful anti-fog coating. It is not thick enough to be a barrier coating but it is a significant step on the path to clear barrier. The reduction in moisture transmission rate observed in experiments tells that the research is moving in the right direction and we can tell that to get good barrier we will need the procedural capability to perform multistage plasma polymerization.

6.3 THE PLASMA TUNNEL

Figure 6.3 shows the schematic diagram of the atmospheric PECVD reactor of Enercon, used in experiments for the deposition of SiO_x at a low temperature. The plasma source has

side-by-side electrodes, enabling a plasma treatment without a dielectric coating over a ground plane. Gases were supplied to the treatment line using mass flow gas control, mixed in a turbulence chamber and subsequently dispensed to the assembly. The gas mixture, inclusive of tetramethyldisiloxane (TMDSO) and compressed air, was used to deposit SiO_x.

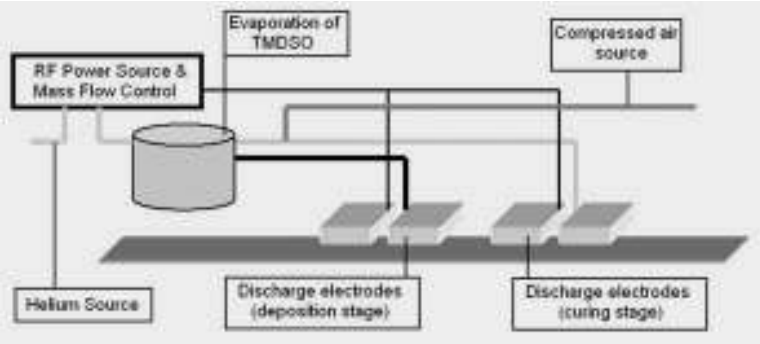

Figure 6.3 In the plasma tunnel, the process of deposition of a precursor mixed with helium and compressed air is followed by the plasma curing.

The flow rates of TMDSO, Helium and compressed air are varied for the optimization of the SiO_x film. SiO_x was deposited on PET film and immediately exposed to a “curing” helium plasma at the same power and frequency settings as the deposition plasma.
Among the interesting characteristics of the deposited film, a very important one for the shelf-life of the products is the water vapor permeation of the film. The water vapor transmission rate (WVTR) can be measured using commercial equipments (for instance the device produce by MOCON Inc., PERMATRAN-W-700). A coating thickness of 35 nm on a PET film - 0.5 μm thickness is able to reduce the WVTR from the value of 46 g/(m^2-day) to the value of 33 g/(m^2-day).
The treater assembly can be coupled to an evaporator in order to provide the capability of evaporating liquid and solid precursors. If a solid precursor is being used, it is liquefied prior to feeding it to the evaporator.

A temperature range from 70 °C to 100°C has been found to be sufficient for most materials of interest. The evaporated precursor was delivered to the treatment assembly by sweeping it from the evaporation chamber with Helium.
Plasma gas is then mixed with the gas or vaporized material prior to being fed to the electrode. The plasma methodology allows for the deposition of a liquid precursor, atomized and sprayed onto the substrate as it passes through the plasma field. So long as the particle size of the atomized liquid permits the formation of a liquid film over the substrate, the effect of the plasma field and the subsequent curing give a final product comparable with vapor deposition results.
Several treatment units can be combined in line in a single tunnel system to afford the versatility required to tailor each deposition process to the requirements of the finished product (see Fig.6.4).

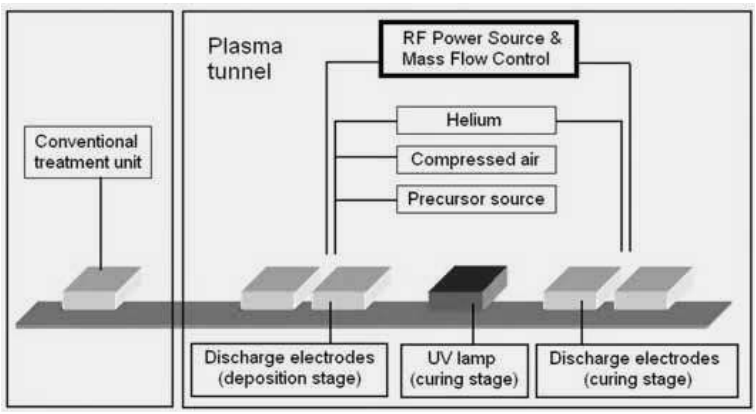

Figure 6.4 In the plasma tunnel it is easy to insert other devices for the curing of the coating.

The system comprises a first conventional plasma-treatment unit used to clean the surface of the substrate to improve adhesion by removing moisture and other small molecules. A combined vapor-deposition / plasma unit is then used to deposit a vaporized precursor. A curing station is used after the vapor

deposition to polymerize the precursor and form a solid film over the substrate. The station may consist of an infrared lamp, an electron-beam unit, an ultraviolet lamp, or a visible light source. In the last two cases, an appropriate photoinitiator is added to the precursor prior to vaporization. Finally, another plasma-treatment unit is used to enhance the curing and to smooth the surface of the coating film. The plasma treatment further improves the surface properties.

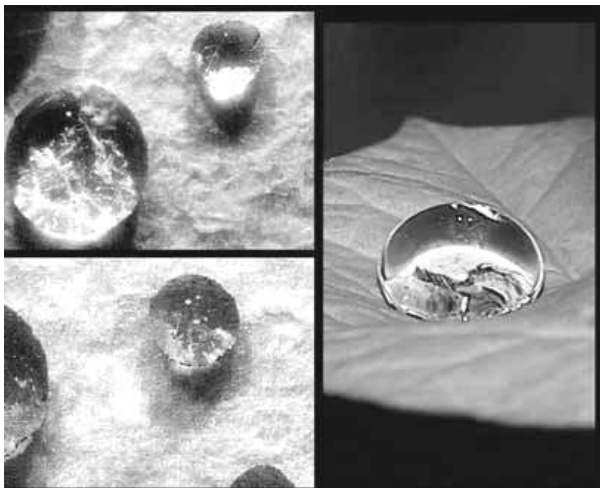

Figure 6.5 Examples of hydrophobic and oleophobic surfaces.

6.4 IMPROVING THE SURFACES

Organic substrates such as polypropylene, polyethylene and polyester of various thickness can be coated with the plasma tunnel using various materials with desirable properties for specific objectives.

For instance, polyester substrates can be coated by vapor deposition in a helium plasma at atmospheric pressure using vaporized silicon-based materials (siloxanes, alkyl-silanes, silsesquioxanes) mixed with the plasma-gas stream and diffused into the treatment area. The resulting products exhibited improved surface properties with regard to moisture- and oxygen-barrier characteristics, scratch and abrasion

resistance, chemical resistance, and low friction. Positive results are obtained with fluorine-based precursors (fluorocarbons, fluorosilicones) to provide hydrophobic and/or oleophobic properties (Fig.6.5).
Chlorine-based precursors (chloro-carbons, chloro-silicones) produce barriers with biocide properties; and organo-metallic complex precursors (silver, copper or aluminum complex) produce barriers with electrostatic, dissipative, conductive, biocidal properties. Three examples illustrate the combination of process steps that can be produced in the plasma tunnel (see the Table). The tests in the Table have the same substrate material (PET film), the plasma gas is helium and the precursor is fed in with a varying proportion.
The data collected from experiment show that the production of plasma-enhanced coated substrates at atmospheric-pressure conditions is possible with properties comparable to than previously obtained under vacuum plasma conditions.
The plasma tunnel design can be used for treating and modifying the surface properties of organic as well as inorganic substrates without vacuum equipment or material-thickness limitations. Based on the collected experimental data, it is possible to tell that a large variety of other compounds can be used as precursors with related new methodologies. The multi-stage atmospheric plasma system that we have discussed is flexible enough to allow the investigation of several processes. Due to its high modularity, it is also possible to move this system toward a true industrial equipment.

Example 1	**HYDROPHOBIC/OLEOPHOBIC**
Pre-treatment	Plasma gas: helium
Deposition	Precursor liquid fluoroacrylate monomer (with 5% Irgacure-184 photoinitiator)
Mixing step	Mixed with plasma gas prior to injection (plasma gas: helium)
Curing	Low Pressure Mercury UV Lamp
Post-treatment	Plasma gas: helium with 5% acetylene
Results	The resulting coated product exhibited hydrophobic and oleophobic properties with excellent adhesion to the substrate.

Example 2	**HYDROPHILIC/ANTI-FOG**
Pre-treatment	Plasma gas: helium
Deposition	Precursor liquid polyethyleneglycol monoacrylate (with 5% Irgacure-184 photoinitiator)
Mixing step	Mixed with plasma gas prior to injection (plasma gas: helium)
Curing	Low Pressure Mercury UV Lamp
Post-Treatment	Plasma gas: helium with 5% acetylene
Results	The resulting coated product exhibited hydrophilic and anti-fog properties with excellent adhesion to the substrate.

Example 3	**BIOCIDE/ANTI-BACTERIAL**
Pre-treatment	Plasma gas: helium
Deposition	Precursor liquid acrolin and/or chlorinated acrylate with 5% Irgacure-184 photoinitiator)
Mixing step	Mixed with plasma gas prior to injection (plasma gas: helium)
Curing	Low Pressure Mercury UV Lamp
Post-Treatment	Plasma gas: helium with 5% acetylene
Results	The resulting coated product exhibited biocide, anti-bacterial properties with excellent adhesion to the substrate.

Table - Three procedures to obtain hydrophobicity/oleophobicity, hydrophilic/anti-fog, biocide/anti-bacterial results. The same procedures were applied to polyester, polypropylene, polyethylene, polycarbonate, polyamide, polyimide and cellulose derivative films, paper and fabrics (woven and nonwoven) with similar results.

7

MODIFYING THE SURFACE FEATURES WITH PHOTOGRAFTING

7.1 INTRODUCTION

Flexible packaging comprised of polypropylene has poor wettability and adhesion properties, making it difficult to apply other layers such as inks, adhesives and coatings. Atmospheric plasma and a photografting technique can be combined for permanent surface tension and coating adhesion. Polyolefins such as polypropylene have low levels of polar functional groups on the surface and have poor wettability and adhesion properties, making it difficult to apply other functional layers such as dyes, inks, adhesives and coatings. To improve wettability and therefore adhesion, flame or corona treatments are usually applied on the surface of film. These treatments introduce polar groups and enhance surface energy. However, the corona or flame surface treatment is not stable and the resulting surface modification is uneven, showing variations during printing or coating processes.

Atmospheric plasma glow discharge technology is an effective discharge treatment process which homogeneously modifies the surface chemistry, highly increasing the bonding of dyes, inks, adhesives and coatings to surface substrates for films or three-dimensional objects. Moreover, plasma treatment has significantly greater longevity than corona discharges. For certain substrates, plasma treatments is not able to provide enough surface tension longevity and therefore the polymeric surface must be further treated, for instance with the photografting of a suitable primer.

The combined treatment - photografting that delivers a proper molecule to a surface prepared by atmospheric plasma treatment - offers a potentially dynamic method of improving adhesion of inks, coatings and adhesives on plastic parts. Photografting is a photochemical process of nanotechnology. With photografting, a chemical bond is formed between the

polymeric substrate and a monomer or oligomer, grafted on the surface to modify its features.

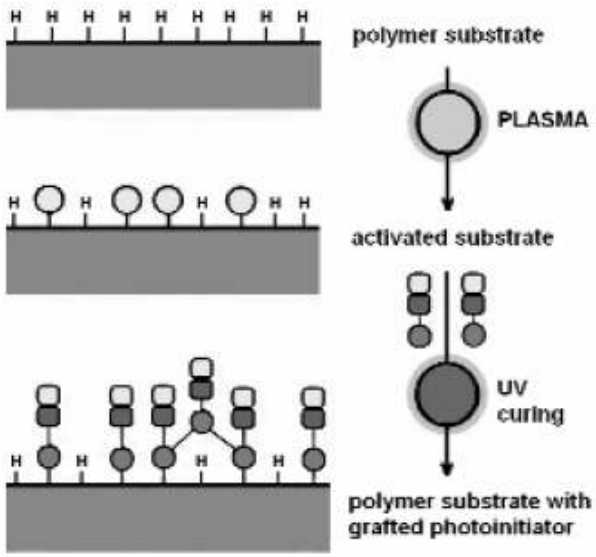

Figure 7.1 Plasma treatment activates the substrate surface, upon which a monomer is grafted via UV curing.

If the monomer or oligomer is photoreactive, and/or photoinitiators or photosensitive materials are added, it is possible to not only have photografted species on the substrate but also a polymeric surface that can be further photo-polymerized. With this polymerization, it is possible to build a copolymeric membrane on the substrate surface, where specific reactive species are trapped. A self-cleaning polymer can be realized, for example. Or, it is simply possible to polymerize inks or coatings with UV treatment. For materials such as polyolefins, the surface has such poor wettability and adhesion that it is difficult to apply not only inks or coatings but also the primer for photografting. The primer itself needs to be anchored at the film surface: the plasma treatment activates and functionalizes the surface creating bonding sites on which monomers can be grafted with UV curing (Fig.7.1).

7.2 ATMOSPHERIC PLASMA AND PHOTOGRAFTING

Plasmas have unparalleled capability for production of chemically reactive species at a low gas temperature while maintaining high uniform reaction rates over relatively large areas. In the past, the majority of plasma processing has been done at low pressure in a vacuum chamber. However, atmospheric pressure plasmas are now available and provide in certain circumstances a critical advantage over low-pressure plasmas because they do not require expensive vacuum systems. During the past few years, roll-to-roll atmospheric pressure plasma discharge systems have been developed for operation at commercial speeds.

These systems produce glow discharges with a low gas temperature, typically below 300 °C, and provide efficient reaction rates for deposition over increasingly large surface areas. When compared to corona discharges, atmospheric plasma 1) produces significantly more homogeneous and uniform surface activation across material surfaces, 2) increases the micro-roughness and clean the surface, and 3) introduces active species.

Atmospheric plasma power densities are not high enough to damage polymeric materials. The principle for using a photografting technique on surfaces initially requires the surface to be activated through physical pre-treatment, for instance a corona or atmospheric plasma.

The photoreactive material to be innested on the surface is prepared in a proper solution. The liquid solution (solvent or water based) is applied after surface activation in very small amounts of approximately 1 g/m^2. It is applied to surfaces using a printing device. The carrier liquid is then removed by evaporation. The reactive photoinitiator is then grafted onto the surface by UV light exposure. Anchoring of the photoinitiator to the surface ensures practically unlimited storage stability, as the surface tension and wettability assume permanence, provided exposure to UV light is avoided. In the subsequent polymerization, the photoinitiator grafted on the surface reacts forming a chemical bond between, for instance, ink or coating and the surface (Fig.7.2).

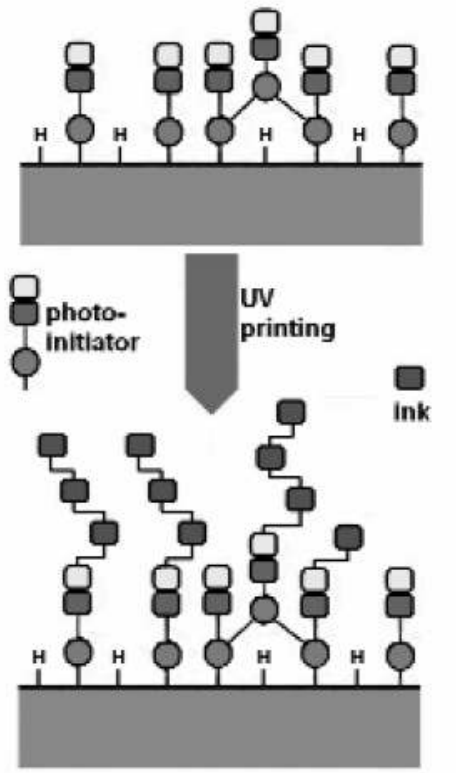

Figure 7.2 After photo-grafting, it is possible to apply and graft UV inks on the surface.

The unique advantage of the plasma-photografting approach is that a previous atmospheric plasma glow discharge treatment creates a homogeneously functionalized polymeric surface, enabling the photografting solution to perfectly adhere to the substrate surface. Moreover, the cleaning of the surface and the micro-etching obtained with the plasma treatment are positive factors which suggest that plasmas treatment will enable stronger surface bonds than corona.

7.3 AN EXAMPLE

A polypropylene substrate was used for trials in the Enercon laboratory. An atmospheric plasma glow discharge treatment station was set at 2.2 kW of output power which reacted a

mixture of 6.4 l/min of helium and 1.6 l/min of oxygen for pretreating the polypropylene material.
A water-borne photografting solution (Ciba Prime IT) was applied to the surface with a printing device, infrared/air dried and UV cured. Approximately twenty percent of the photografted surface was printed with a small solid color block shape using a UV flexo ink. All treatment devices were integrated into a continuous processing line. Following treatments, the surface energy and the ink adhesion were tested. A 15% increase in ink adhesion between the printed control sample and the printed plasma/photografted sample is observed (see Table). The most important results are the observed extended longevity of the plasma/photografting treatment relative to polypropylene substrates. The surface energies are maintained in excess of one year from application.
The studies on treatment longevity have been conducted in the Enercon Laboratory and confirm, after an initial small change, a non-degrading surface tension of 48 dynes/cm over a minimum of a one-year period. In addition, ink adhesion tests have confirmed ink retention following tape peel adhesion methods over the same one-year period. The use of atmospheric plasma glow discharge technology in advance of uniform surface deposition and fixation of a photografting molecule appears to offer excellent surface adhesion properties for UV flexo inks. Surface energy levels of 52-54 dynes/cm were achieved after the combined plasma treating and photografting processes, and the final photografted polypropylene surface is expected to remain permanently at this surface energy level as indicated by the longevity studied. Also noteworthy is that there was no observed change in substrate color or organoleptic measures such as odor following this treatment protocol.

Condition	Ink Adhesion	Dynes/cm
Untreated (control)	-	35
Untreated printed	85%	-
Plasma + Photografting	99%	52

Table: Ink adhesion and surface energy for the untreated sample and for the plasma-photografted sample.

8

HIDDEN PROBLEMS IN SURFACE TREATMENTS: PINHOLING

8.1 INTRODUCTION

Excessive corona discharge can damage films with microscopic pinholes, which make them useless as barrier film. The surface modification of polymeric films is often necessary to improve surface printability. Improvements in metallization, lamination and adhesive bonding strength are also critical in ensuring the performance of packaging structures, particularly those which offer high oxygen and moisture vapor transmission barriers. Corona discharge and flame treatments are capable of producing the required level of surface energy, however, the surface properties provided by these techniques are not always optimal or an excessive treatment can damage the film.

8.2 THE CORONA DISCHARGE

A corona discharge is a process by which a current develops from an electrode with a high potential in air, by ionizing it as to create plasma around the electrode. Corona discharge usually involves two asymmetric electrodes: one highly curved and one of low curvature, the grounded electrode. High curvature ensures a high electric field. The starting mechanism is the following: a neutral atom or molecule, in the region near the curved electrode, is ionized by an exogenous environmental event to create a positive cation and a free electron.

The electric field then operates on these charged particles, separating them and preventing their recombination. The electric field increases the kinetic energy of charged particles. As a result, energized electrons create further electron/positive-ion pairs by collision with neutral atoms. The same separating process continues creating an electron avalanche. Ion species created in this avalanche are attracted to the ground electrode, completing circuit and sustaining the current flow. Therefore, corona discharge is basically plasma in a transient, formative phase. In a simple atmospheric pressure gap between

electrodes, as the voltage between electrodes is increased and the breakdown field strength exceeded, a corona discharge is established. Near electrodes, where the concentration of travelling electrons is highest, a faint glow of light is visible, caused by the recombination of ions and electrons. This glowing light removes energy from the ionized gas at a high enough rate to prevent the formation of atmospheric plasma.

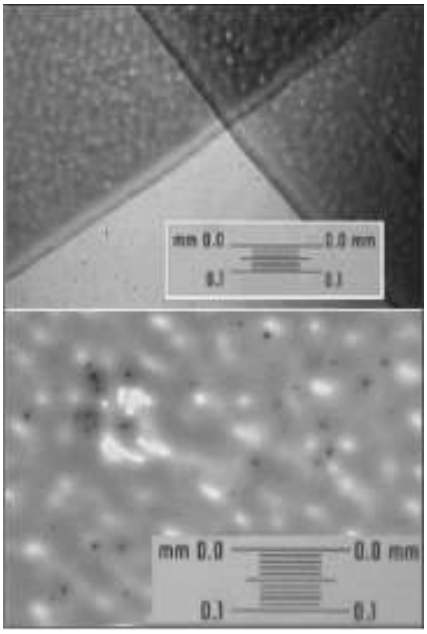

Figure 8.1 A flexo-printed PET film observed with microscope. In the lower image the damage (pinholing) produced by sparks.

At higher voltages or smaller gaps, the energy put into the molecules by electron collision exceeds the ability of the corona discharge to dissipate the energy and plasma is formed. In corona devices, the flow of cations and electrons tends to be confined to fairly narrow channels and the discharge has a filamentary profile. Sparks can occur if defects are present on the surface of the ground roll or on its covering. At the point on cathode where the spark connects, a large amount of heat is

generated by the impacting cations, damaging the electrode surface. Electrons impacting the anode surface do not cause much damage, since they are lighter than cations.

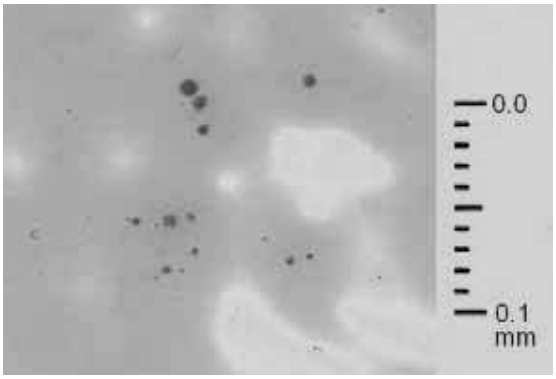

Figure 8.2 The core of pinholes has a size ranging to 10 microns.

8.3 PINHOLES

One particular film property, becoming increasingly important for food safety, is the following: the film must impede the passage of oxygen and moisture from environment into the package. Usually, films are subjected to corona treatments to increase surface properties. In fact, when corona discharge possesses a highly filamentary profile, enhanced by dirty and defects on the ground roll, the resulting sparks can damage the substrates.

The polymeric film covering the ground roll can become populated by microscopic pinholes: we can easily see them when film is printed and observed by microscope. In the low part of Fig.8.1, pinholes appear as dark blue dots. In Fig.8.2, we see the same region of a flexo-printed PET film with higher magnification. The ink texture on the film surface is different from the array of dots, typical of rotogravure printing. The core of a blue dot has the size of 10 microns.

With these images obtained with microscopy, it is impossible to check the depth of damage produced by sparks. A different investigation can be performed with a confocal laser-scanning microscope (CLSM), an optical device able to give high-resolution images.

The key feature of confocal microscopy is its ability to produce in-focus images of thick specimens, in a process known as optical sectioning. Images are acquired point-by-point and reconstructed with a computer, allowing three-dimensional reconstruction of complex objects. The confocal microscope takes an optical cross-section in the bulk of the observed sample, but it does not image objects that are above or below the focal plane.

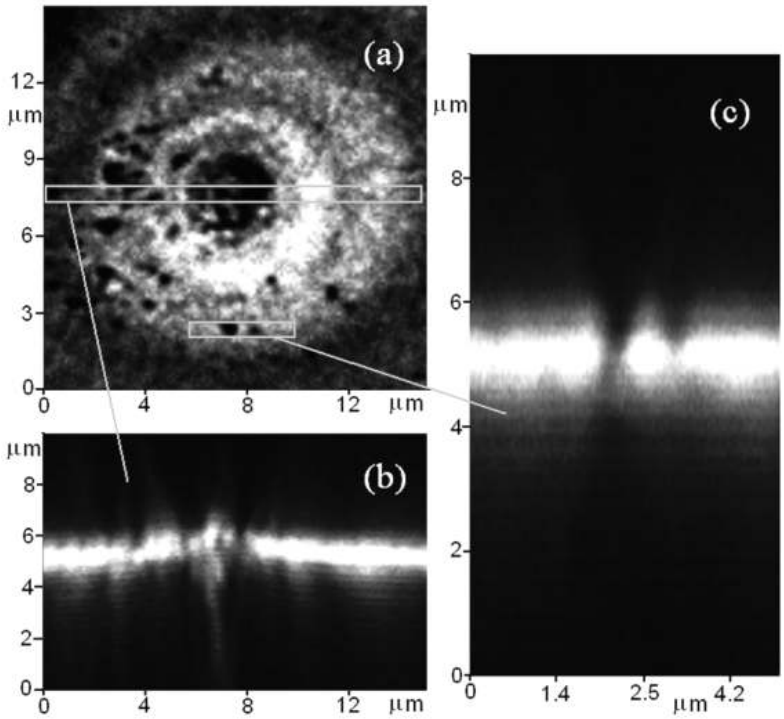

Figure 8.3 CLSM view of a pinhole in the PET film: (a) the surface and (b) and (c) cross-sections.

For this reason, confocal microscopes can offer not only a high-resolution view of the surface, but also cross sections of the film. In the Fig.8.3 we can see the region near a pinhole. From the high-resolution view (a), a complex structure with a central

hole (3 microns wide) and small satellites around it can be seen. The two cross-sections (b) and (c) exemplify the depth of the structure. Images show the ink film on PET substrate as a bright band of approximately 1 micron thickness. The homogeneous PET substrate (80 microns thick) has no details as evidenced by microscopy, except near pinholes. In (b), the damage is extended at least for 6 microns in depth.
Clearly, a corona spark discharge is able to perforate a thin film and turns the substrate in a highly defective one.

8.4 AVOIDING DEFECTS WITH PLASMA

The atmospheric pressure plasma is characterized by a highly uniform and homogenous glow discharge with almost no propensity for pinholing surfaces. An atmospheric plasma treatment (APT) is able to raise surface energy on a wide variety of materials while leaving physical, mechanical and barrier surface properties intact. The APT process works on material surfaces in a way which is similar to the vacuum plasma treatment process.
The excitation of gas molecules is accomplished by subjecting a gas at atmospheric pressure to an electric field at high frequency. Free electrons gain energy from the imposed electric field, colliding with neutral gas molecules and transferring energy, dissociating the molecules to form numerous reactive species. It is the interaction of excited species with solid surfaces placed in opposition to plasma that results in the chemical and physical modification of material surface. The effect on a given material is determined by the chemistry of reactions between the surface and reactive species living in plasma. At low energy treatments, the plasma only changes the surface, effects being confined to a region only several molecular layers deep.
Three surface processes simultaneously alter substrates: ablation, crosslinking, and functionalization. In ablation, the bombardment of the polymer surface by particles and radiation breaks covalent bonds of the polymer backbone. The long molecular components become shorter and as volatile oligomers or monomers are swept away with exhaust. Crosslinking is done with an inert process gas (argon or helium). The bond breaking occurs on the polymer surface: since there are no free-radical scavengers in plasma, bonds can form

between nearby free radicals on different chains (crosslink). Functionalization is a process where surface polymer functional groups are replaced with different atoms or chemical groups from the plasma.

Plasma produces a microetching of the surface with a depth around 4-6 Å, that is, it does not modify mechanical properties of the film but strongly increases surface adhesion of inks and co a tings. Therefore, plasma does not burn pinholes in the film structure as corona treaters sometimes do if spots of dirt or moisture or some other conductive material are present on the film. Since plasma is cleaning the surface, any further corona refreshment will not be affected by the presence of dirt.

9

HIDDEN PROBLEMS IN SURFACE TREATMENTS: GROUND ROLLS

9.1 INTRODUCTION

Is corona treating technology simple? This apparently seems to be a simple question. In fact, until a few years ago, the discussion of corona technology for surface treatment could have been limited to just two types of corona treating systems: covered roll systems and bare roll systems. But nowadays, new ceramic-coated ground rolls are enriching the technology and revolutionizing the corona systems.

The quality of corona treatment strongly depends on the ground roll surface. This surface has a certain level of resistivity, depending on the existence of a covering over the discharging electrode. The material, which is being conveyed over the ground roll, is also important. A different voltage will exist as different materials pass through the corona discharge and over the ground roll. These variations in load can drive voltages high enough to damage the material being treated.

The ceramic-coated ground roll systems are able to provide more power than their predecessors could and also eliminate common problems associated with covered rolls.

While the cost of a new silicone roll covering is not great, it is necessary to realize that there are more costs associated with replacing them, than just the cost of the new sleeve. A silicone covered roll becomes damaged from either overexposure to corona or because it was damaged by sharp devices. The damage can be severe enough to cause a high voltage trip (it may be possible to hear a "snap" or see an arc). In this case it is necessary to shut down the production line, because this event occurs during a treatment run, to replace the roll covering. Of course, the damage may not be enough to cause a high voltage trip. The producer does not realize the existence of the damage until the production run is completed.

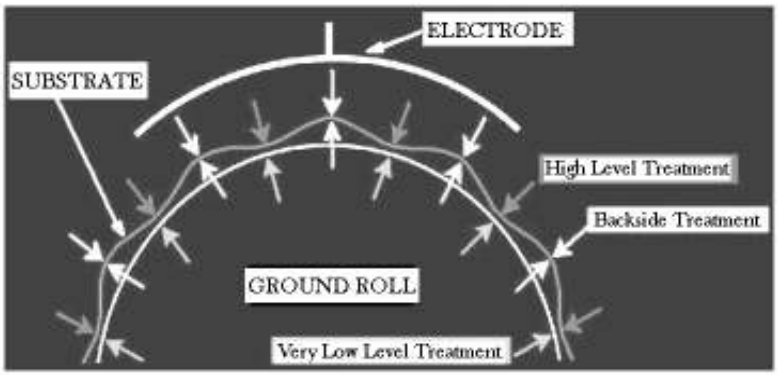

Figure 9.1 Backside treatment happens when the film is not in perfect contact with the roll. There are areas where the treatment is strongly reduced

The damage to substrates consists of pinholing or backside treatment (Fig. 9.1). These two problems are often difficult to detect and certainly compromise the final product quality. Costs of waste time and production can quickly add up to more than just the cost of the roll covering. Backside treatment occurs when air is trapped between the backside of the web and the ground roll. The air beneath the web becomes ionized and corona treatment occurs. When corona discharge occurs, the total energy in the air gap will be distributed between the top and bottom of the web. With a portion of the total energy applied to the undesired bottom surface, the power amount applied to the desired top side will be reduced. Generally, the treatment on the top surface of the material will decrease.
The primary cause of backside treatment can be attributed to a lack of station cleanliness, specifically a dirty ground roll. Imaging the web contacting the surface of the ground roll, it is clear that any high point or build-up on the roll surface potentially lifts the material off the ground roll face. The immediate area surrounding the point is no longer contacting the roll face, resulting in an air gap. The air gap beneath the material allows corona to be generated.

Reducing the accumulation of dirt or residues on the surface can substantially reduce the conditions for backside treatment to occur. Other causes of backside treatment are wrinkling and slippage of films. Slippage of materials on the ground roll results in a laminar airflow layer underneath the web. A possible corrective action is obtained applying a nip roll to ensure the material positively contacts the roll face. In applications where low tension or thin materials are involved, nipping may cause other material problems. In these cases, it may be necessary to choose other solutions.

9.2 THE ROLLS

With the ceramic-coated ground roll systems, the corona treatments enter in the era of atmospheric pressure plasma treatments. It is possible to choose among several treating systems. The most recent treaters are the Universal Roll systems. Let us conduct a short review of the definitions of all types of surface treatment roll coverings (silicone sleeves, epoxy-coated rolls, glassed steel rolls, ceramic covered rolls, conductive ceramic coated rolls, universal ceramic coated rolls and atmospheric plasma rolls).

Before starting the description, let us remember an important parameter, the dielectric strength of a barrier, which is the ability to withstand excessive voltages. The electrode's wall thickness covering material is determined by its strength. The lower the dielectric strength, the thicker the wall must be. A thicker wall requires more power to produce an efficient corona. The unit measure of dielectric strength is V/mil (1 cm = 393.70 mil).

9.2.1 Silicone Sleeves: the most common roll covering is a silicone sleeve. These sleeves have good dielectric strength (450 V/mil), which allows them to handle all basic corona treating applications. Silicone sleeves are very economical and replaceable. The downside is they can be damaged from over-exposure to corona discharge or accidentally by the slip of an operator’s device. While the cost of a new silicone roll covering is not great, costs from unexpected downtime and comprised product quickly add up. Life expectancy of a silicone sleeve is six months.

9.2.2 Epoxy coated rolls: epoxies coated rolls offered a more durable covering than silicone and are also a good choice for basic corona treating applications. The dielectric strength is comparable (450 V/mil). Epoxy coatings have harder surface than silicones or rubbers and many converters select them as added insurance against unexpected roll failure from exposure to corona or accidental damages. Life expectancy of an epoxy covered roll is one year.

9.2.3 Glassed-steel rolls: these rolls provide the highest dielectric strength (800 V/mil). According to these roll covering suppliers, these coverings provide an energy savings and has a high efficiency which results in improved treatment levels. In most cases the roll diameter for a glassed-steel roll will be smaller than comparable roll coverings.

9.2.4 Ceramic Covered Rolls: these rolls are covered with a thick ceramic covering (1.5 mm to 2.5 mm) that is applied via a plasma-spray technique. This roll covering replaces the rubber or epoxy coverings used with metal electrodes. The purpose of the roll covering is to provide a dielectric buffer between the metal electrode and the roll covering allowing the air to ionize and create the plasma corona in the air gap.
Ceramic roll covering is widely used because of its resistance to physical damage. This type of electrode / roll combination cannot be used to treat conductive films. These rolls are ideal for high speed treating applications and offer exceptional durability (two year limited manufacturer's warranty). Usually the initial cost of a ceramic covered roll is greater than a silicone covered roll, but a cost comparison over the life of the station can work out favorably for a ceramic roll covering.

9.2.5 Conductive Ceramic Coated Rolls: conductive ceramic is a thick coating (0.05 mm to 0.13 mm), applied via a plasma-spray technique (Fig.9.2). The coating protects the ground roll from oxidation and corrosion. This covering replaces chrome or nickel plating which are porous and will allow oxidation between the roll core and the plating. From an application standpoint, a conductive ceramic-coated ground roll in a bare roll system is recommended when treating metal foils or the nonconductive side of conductive films. The conductive ceramic coating

ensures a conductive path to ground from the conductive web surface. The primary benefit of the conductive ceramic is to prevent oxidation to the metal roll surface.

Figure 9.2 A treatment station with a conductive ceramic roll

9.2.6 Universal Rolls: the universal ceramic-coated roll has a proprietary ceramic coating, applied to the roll core via a plasma- spray process. The universal ceramic coating is non-conductive and also serves as a dielectric covering on the ground roll. It is possible to use a universal roll system (Fig.9.3) to treat metallized films or foils.
Because the high voltage electrode and the ground roll are covered with a dielectric, the corona is established in the air gap between the electrode and metallized film or foil. It is important that the metallized surface of the film be in contact with a clean and grounded idler roll. This idler roll can be covered with conductive ceramic to provide a ground path from the conductive film surface. The universal ceramic-coated roll system provides superior treatment levels, with elimination of film wrinkling and backside treatment. It eliminates also the pin-holing on the metallized surface.

Moreover, the higher efficiency ceramic covered roll requires less power to meet the same treat requirements.

Figure 9.3 The universal system provides superior treatment levels, with elimination of film wrinkling and backside treatment

9.2.7 Atmospheric Plasma Ceramic Coated Rolls: atmospheric plasma ceramic is applied using a plasma-spray process similar to Universal rolls. Although many aspects of this technology are proprietary, its primary advantages against all other ceramic-based roll coverings are here described.

9.3 UPGRADE OF ROLL COVERINGS

Changing the type of roll covering could benefit several treatment operations. However, it is necessary that the surface treater manufacturer determine how a change in roll covering may affect the rest of the surface treating station.

For example, a change in the roll covering surely results in an alteration in sizing of the roll diameter. It is then necessary to determine the effect of new geometric relationships between electrode and roll. The new mechanical device must adequate to electric framework of the treater, to create a plasma

discharge between electrode and ground roll. On new installations, the choice is much simpler, because it can be managed according to the main production requests.

10

THE FLEXIBLE FUTURE

10.1. INTRODUCTION

Flexible displays and photovoltaic panels, RFID devices incorporated in packaging: these are examples of electronic devices on flexible substrates. Modifying the substrate surfaces will be the key for the success of manufacturing them by roll-to-roll processes. The flexible future of electronics needs then a surface treatment integrated in the production process.

During his lecture at Politecnico of Torino in November 2007, held for the Laurea ad Honorem in Engineering, Alan J. Heeger, professor at the University of California Santa Barbara and Nobel Laureate in 2000, proposed a new way for a sustainable further development of solar energy: the flexible polymeric solar cell panels.

In the late 1970s, Heeger and his colleagues Alan MacDiarmid and Hideki Shirakawa discovered that they could get a polymer, the polyacetylene, to conduct electricity doping it with iodine. From that discovery, a new generation of materials was developed exhibiting the electrical and optical properties of metals or semiconductors, at the same time retaining the attractive mechanical properties and processing advantages of polymers.

Further discoveries led to the development of polymer photovoltaic cells. Heeger, during his lecture in Torino, and showing a roll-up flexible solar panel, expressed interest in sustainable advancements of solar cell technology, obtained with printed solar cells using roll-to-roll printing technology.

Most conducting polymers can be achieved in the form of printable inks: they are soluble in common organic solvents and hence can be deposited by simple solution processing and printing technologies. Thus, solar cell production can be much easier and consequently much less costly than that for inorganic semiconductor devices. Thin polymeric films on flexible substrates are in fact achievable by well known and widespread printing methods like screen, ink-jet, offset, or flexo printing.

According to Heeger, printing promises to give lower-cost conversion of sunlight into energy solar cell research. The technology is capable of printing solar cells onto a very large area (Fig.10.1), which is needed to get the most sunlight converted into usable energy. Solar technology is still expensive: the goal of research with printing technology is to introduce a new and more cost-efficient alternative technology for producing solar cells.

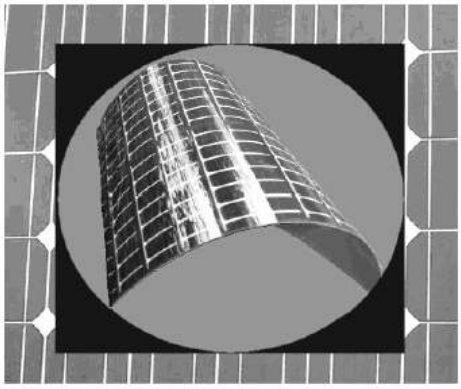

Figure 10.1 A flexible solar panel. Commercial panels are available for portable power stations.

The production of flexible displays has the same problems. The advantages in manufacturing these devices by roll-to-roll processes are evident. In addition to extremely low production costs, the flexible nature of these devices dramatically enables not only their application within a broader range of stationary and portable applications, but also their integration with other flexible materials.

10.2 FLEXIBLE DISPLAYS

Silicon-base display technology integrates all components of the electronic device on a single substrate, as opposed to the assembly or packaging from a number of discrete components. This technology offers benefits in terms of reliability, size and costs. On the other hand, organic semiconductor technology

offers completely new and attractive routes for integration, due to the use of fabrication processes that differ radically from the ones within silicon industry.
In this respect, a major strength of organic electronics, in particular of optoelectronics, is that it is based on solution processing. There is the possibility to deposit the materials by additive processes in only those areas where their specific functionality is required, as exemplified by ink-jet printed red, green, and blue emitting pixels in polymer OLED displays. An organic light-emitting diode (OLED) is any light emitting diode (LED) whose luminescent layer is comprised of a film of organic compounds.
The layer contains a substrate that allows suitable organic compounds to be deposited. Rows and columns of organic conducting polymers, deposited by a simple printing process, establish the addressing system of pixels. The resulting matrix of pixels can emit light of different colors. A great benefit of OLED displays over traditional liquid crystals displays is that OLEDs do not require a backlight to function and thus they draw far less power. The polymer light-emitting diodes (PLED) involve luminescent conductive polymers emitting light when subjected to an electric current.
No vacuum process is required in production, and the emissive materials can be applied on the substrate by a technique derived from commercial inkjet printing. The substrate used can be flexible, such as PET, allowing flexible PLED displays to be produced inexpensively. Printing PLEDs onto flexible substrates opens the door to new applications such as roll-up displays and displays embedded in clothing. In fact, commercial flexible displays are now available, ultra-lightweight and thin (Fig.10.2).
The intrusion of water into displays can damage or destroy the organic materials. Therefore, improved sealing processes are important for the device manufacture and may increase the longevity of displays.
The improvement of ink adhesion to substrates and of the sealing strength is one of the first steps to obtain a polymer display or a flexible solar panel with enough longevity. In the second paper of this series, we discussed how the combined action of ozone and plasma could be used to increase the sealing strength.

Figure 10.2 Flexible displays. The display can rolled-up in the control device.

10.3 ATMOSPHERIC PLASMA AS TECHNOLOGICAL BRIDGE-BUILDER

Another very promising development is linked to the printing industry and is the use of conductive inks, in producing antennae with rotogravure presses. Highly conductive inks are heavily filled with silver and proprietary additives to enhance the conductivity of transponders in radio-frequency systems. New conductive inks exhibit high flexibility, which creates a material ideally suited for portable wireless electronics such as RFID tags and smart cards.

Using conductive inks to produce printed antennas, at high speeds in roll-to-roll systems, is a significant milestone for RFID market development, to further reduce costs of production. Ensuring that the conductive silver inks adhere to base materials such as PET and PP suggests that surface treatment must be uniform and provide the necessary level of surface tension.

Strong evidence of increasing print adhesion performance using an atmospheric plasma treatment (APT) technology was recently obtained with the commercial system of Enercon. The application of atmospheric plasma technology is suitable for all the roll-to-roll printing activity for flexible substrates, and then

with very interesting opportunities in the development of flexible panels, displays and polymeric electronics.
Atmospheric plasma devices allow for completely homogenous surface treatments, because in these systems, a uniform and homogenous plasma at atmospheric pressure is produced, differing from the corona discharge (in Fig.10.3, a comparison between corona discharge and plasma is shown).

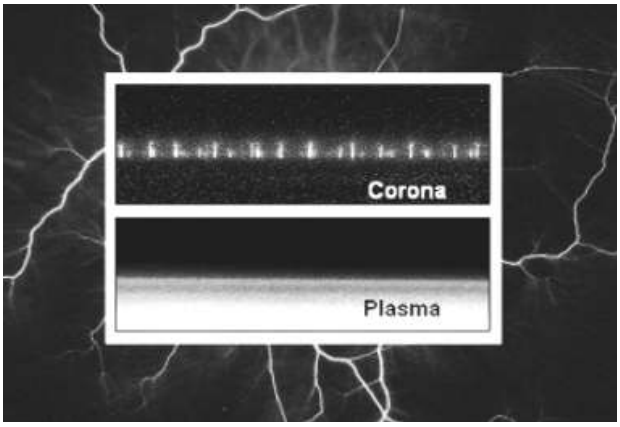

Figure 10.3 The corona discharge compared with the uniform plasma between planar electrodes. The corona discharge is not uniform on the substrate.

At the low exposure energies, the plasma effects are confined to a region only several molecular layers deep and do not change the bulk properties of the substrate. The surface is subjected to ablation and activation processes. The bombardment of the polymer surface with energetic particles and radiation of plasma produces the ablation. The plasma bombardment is able to create a nanoroughness on a polymeric film that does not modify the mechanical bulk properties of the film but strongly increases surface adhesion. As we discussed in the second chapter, testing the peel adhesion of printed polyester films with corona- and APT-treated samples, show that the APT-treated samples (at a power density of 10 $W/m^2/min$) has the adhesion surpassing that of corona- treated

polyester (see Fig.10.4). Trials were performed with a Bare Roll Corona Treatment Station and with Plasma3 APT System, both from Enercon.

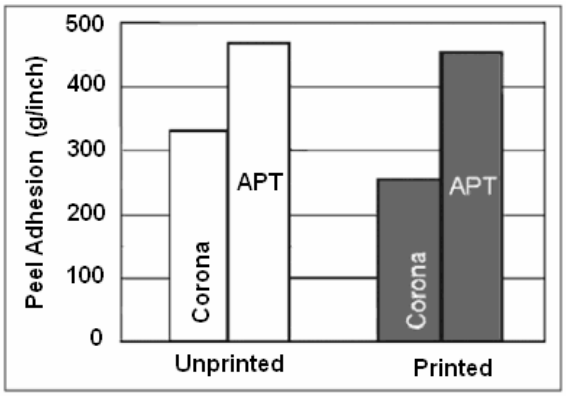

Figure 10.4 Average peel adhesion for unprinted and printed polyester film, after treatment with a power density of 10 W/m^2/min.

The APT system operated with a Helium/Oxygen plasma. The plasma combined actions of cleaning, etching and functionalizing surface processes enable manufacturers to optimize the ink adhesion.
The ability to manufacture organic electronics at commercial flexible packaging speeds is several years away, but researchers are working now to integrate their results with printing innovation in order to develop processes adaptable by packaging converters. A crucial step is to ensure a perfect adhesion of inks, conductive or polymeric, on the substrate, and this is obtained with APT systems.
APT cleaning and functionalizing surface treatment processes are able to increase adhesion and seal strength, and this is fundamental for the production of flexible displays and solar panels. A proper surface treatment has then a key role in the commercial future of flexible electronics.

11

PLASMA TREATMENT ADVANTAGES FOR TEXTILES

11.1 INTRODUCTION

The textile industry is searching for innovative production techniques to improve the product quality, as well as society requires new finishing techniques working in environmental respect. Plasma surface treatments show distinct advantages, because they are able to modify the surface properties of inert materials, sometimes with environment friendly devices.

For fabrics, cold plasma treatments require reliable and large systems, which in fact are existing and well known in converting industry. On textile surfaces, three main effects can be obtained depending on the treatment conditions: the cleaning effect, the increase of micro-roughness (in anti-pilling finishing of wool) and the production of radicals to obtain hydrophilic surfaces. Plasma polymerization, that is the deposition of solid polymeric materials with desired properties on textile substrates, is under development.

The advantage of such plasma treatments is that the modification turns out to be restricted in the uppermost layers of the substrate, thus not affecting the overall desirable bulk properties.

11.2 ISSUES OF TEXTILE INDUSTRY

The textile industry is concerned with the following interrelated issues: development and production of raw materials, converting them into finished products, meeting customer expectations with human health and environmental safety, and making a profit. Many of these issues parallel the general priorities of society, that is, sustainable production systems in environment safety, economies of rural and industrial communities, and consumer interests.

Finding new products, alternative raw materials, and processing technologies more "environmentally friendly", obtained with new natural processes and conditions, is central for further

developments of textile industry. Moreover, the production needs innovative recycling technologies for wastes, because the amount of post-consumer textiles annually generated turns out to be considerable for the increasing environmental concerns.

Since their introduction, synthetic fibers have a significant impact on the quality of life. Nevertheless the demand for natural fibers continues to increase, for their many outstanding properties including aesthetics, comfort, and biodegradability. Besides research efforts on traditional natural materials that is cotton, wool and silk, many researches are also focused today on exploring fibers from alternative crops and agricultural by-products, which are often under-utilized. The abundance of recyclable natural fibers and agricultural residues drive researchers to develop alternative structural composites for textile applications.

Using natural or synthetic fibers, with old or new agricultural materials, the textile industry must go towards sustainable technologies, developing environmentally safer methods of processing and finishing fabrics. One way, now under study, is the processing with biological systems, rather than conventional chemistries. This new frontier in biotechnology for textile processing includes cross-linking in polymers to impart easy-care properties, surface modification to enhance absorption/dyeing and aesthetic properties, and enzyme systems for scouring, antipilling and for imparting anti-felting properties to wool.

Optimization of bulk and surface properties of materials can represent a promising approach for meeting technical and economical requirements. Because of costs related to study and production of new fibers, polymer researchers now focus on modifying existing fibers to impart the desired aesthetic or functional properties.

Conventional fiber modification methods include various thermal, mechanical, and chemical treatments. An alternative important method to modify the fiber, to increase the uptake of dyes and finishes or to impart unique functionality, is performed through cold plasma. The reactive species of plasma, resulting from ionization, fragmentation, and excitation processes, are high enough to dissociate a wide variety of chemical bonds, resulting in a significant number of simultaneous recombination

mechanisms. Moreover, plasma opens up new possibilities for polymer industrial applications where the specific advantages of producing pore-free, uniform thin films of superior physical, chemical, electrical and mechanical properties have been required.

Main advantages of a plasma polymerization methods are: 1) applicability to almost all organic, organo-metallic and hetero-atomic organic compounds, 2) modification of surface properties without altering the bulk characteristics, 3) low quantities needed of monomeric compounds making it non energy intensive, and 4) wide applicability to most organic and inorganic structures.

Plasma applications include: 1) cold plasma discharge synthesis of new polymeric structures, 2) plasma induced polymerization processes, 3) surface grafting of polymers, and 4) surface modification of polymers.

Characteristics that can be improved include wettability, flame resistance, adhesive bonding, printability, electromagnetic radiation reflection, surface hardness, hydrophilic/hydrophobic tendency, dirt-repellent and antistatic properties.

Plasma treatments can be used to develop textiles to protect from exposure to dangerous environments. Important requirements for protective apparel are barrier effectiveness and comfort for the wearer. The effectiveness of protective apparel worn for instance by patients and health care workers continues to be a major concern of textile industry, because of the risks of infection when the protective apparel fails. An effective protection in medical applications demands higher-quality and reliable adhesive bonds, and the plasma treatment is providing enhanced adhesive bond strength and permanency for medical devices and disposables.

Researches on modifying the surface characteristics of fibers using plasma technology are performed by many scientific groups. A special plasma application, in fact rather relevant for textile industries, is that developed by Sarmadi and his group, at the Plasma Research Institute of the University of Wisconsin. They are evaluating multifunctional reactive dyes and plasma treatments for imparting insect control.

Plasma surface treatment used to modifying the functional properties of fibers possesses advantages in comparison with traditional techniques. Plasma includes less water usage and

energy consumption, with very small fiber damage, thus making plasma process very attractive. It will be used to enhance the quality of textile products in fabric preparation and in dyeing and finishing methods.

11.3 TEXTILE APPLICATIONS.

Research in the field of plasma applications for textile treatments is very wide and it is impossible to discuss all possible developments. Let us summarize a few exemplary applications with related plasma gases, in the following list.

1) Enhance mechanical properties. Softening of cotton and other cellulose-based polymers, with a treatment by oxygen plasma. Reduced felting of wool with treatment by oxygen plasma. Top resistance in wool, cotton, silk fabrics with the following treatment: dipping in DMSO and subsequently N_2-plasma.

2) Electrical Properties. Antistatic finish of rayon, with chloromethyl dimethylsilane in plasma.

3) Wetting. Improvement of surface wetting in synthetic polymers (PA, PE, PP, PET PTFE) with treatment in O_2-, air-, NH_3-plasma. Hydrophilic treatment serves also as dirt-repellent and antistatic finish. Hydrophobic finishing of cotton, cotton/PET, with treatment with siloxan- or perfluorocarbon-plasma. Oleophobic finish for cotton/polyester, by means of grafting of perfluoroacrylat.

4) Dyeing and printing. Improvement of capillarity in wool and cotton, with treatment in oxygenplasma. Improved dyeing polyester with $SiCl_4$-plasma and for polyamide with Ar-plasma.

5) Other properties. Bleaching wool, treatment oxygen-plasma. UV-protection dyed cotton/ polyester, with treatment HMDSO in plasma. Flame-retardant feature for PAN, Rayon, cotton, treatment: e.g. phosphorus containing monomers.

6) Metal-Coated Organic Polymers. Metal-coated organic polymers are used for a variety of applications. If the metallized polymer is expected to fulfil its function, it is essential that metals strongly adhere to the polymer substrate. This can be obtained with a plasma pre-treatment of the polymer.

7) Composites and Laminates. Good adhesion between layers in laminates depends upon the surface characteristics of fibers in layers and the interactions taking place at the interface. A

prerequisite condition of good adhesion remains the surface energy of fibers, which can be modified with plasma treatments.
8) Applications in Biology and Medicine. Fabric favoring overgrowth with cells for cell culture tests, fermentation or implants. Fabric not favoring overgrowth with cells for catheters, membranes, enzyme immobilization, sterilization.
9) Applications in Membrane and Environmental Technology. Gas separation to obtain oxygen enrichment. Solution-Diffusion Membranes to obtain alcohol enrichment. Ultra filtration membranes to improve selectivity. Functionalized membranes such as affinity membranes, charged membranes, bipolar membranes.
In the following chapters we will discuss more specific problems on natural fiber treatment (wool and cotton). Then Nylon 6 is discussed and a brief review of plasma treatment on other synthetic polymeric fabrics is performed.

12

PLASMA TREATMENTS OF NATURAL FIBERS

12.1 INTRODUCTION

There is an enormous potential in the plasma treatment of natural fiber fabrics. Plasma treatment has proved to be successful in the shrink-resist treatment of wool with a simultaneously positive effect on the dyeing and printing.

Wool has a complex scale structure on the fiber surface that introduces a number of problems such as felting and the formation of a surface barrier to dyestuff**.** Chemical methods are the major treatment for those problems. However, the effluents generated from wool dyeing and finishing processes are seriously contaminated with different kinds of chemicals, e.g. chloro-organic compounds from the anti-felting process. Plasma is proved to be the environmentally favorable alternative method, both corona and APGD methods. As for cotton, if a corona discharge is made before the application of finishing agents, more favorable conditions for agent fixation are created and chemical compound content in effluents is lower.

For all natural and synthetic fibers, let us remember that the penetration of the activating species in APGD plasma into materials is so shallow that the interior of the material is only lightly affected. Plasma treatment can thus be used as an effective technique for modifying the surface properties of fabric without much alteration to the interior of the fiber.

12.2 WOOL

The morphology of wool is highly complex, not only in the fiber stem but also on the surface as well. It is in fact the surface morphology, which plays an important role in wool processing. Unwanted effects such as shrinkage, felting and barrier of diffusion are most probably due to the presence of wool scales on the fiber surface. In the past, the modification of wool surface morphology was conducted either by chemical degradation of scale (oxidative treatment using chlorination) or by deposition of polymers on the scale.

However, in both processes, a large amount of chemicals generated from incomplete reactions polluted the effluent. The oxidation is also required to reduce the hydro-repellence of wool to obtain good dyeability.
Wool is composed at 95% of a natural polymer, called keratin. In the outer part, the cuticle, the cells are in the form of scale (see Fig.12.1). Cuticle cells overlap to create a directional frictional coefficient: the scales are moved by water and they have the tendency to close and join together with the typical movement that is proper to have a good textile, but it is also producing felting and shrinkage. Plasma treatment of wool has a two-fold effect on the surface. First, the hydrophobic lipid layer on the surface is oxidized and partially removed. Since the exocuticle, that is the layer of the surface itself (epicuticle), is highly cross-linked via disulfide bridges, plasma treatment has a strong effect on oxidizing the disulfide bonds and reducing the cross-link density.

Figure 12.1 A wool fiber in covered by cuticle scales. Very long cells are building the inner structure of the fiber.

The former plasma treatments on wool were done with the corona discharge but it was not giving a uniform treatment on the fabric: the cuticle is modified, being formed on the fiber micro-roughness and holes. The corona discharge, consisting of a series of small lightning-type discharges, has the advantage to be easily formed at atmospheric pressure by applying a low frequency high voltage over an electrode pair. Corona

discharge is usually inhomogeneous and then problematic for textiles. W. Rakowsky compared corona and glow discharge plasma, concluding that the second is better: both treatments are involving only a surface thickness and therefore do not modify the wool structure.
As the surface is oxidized, the hydrophobic character is changed to become increasingly hydrophilic. The chemical and physical surface modification results in decreased shrinkage behavior of wool top; the felting density decreases from more than 0.2 grams per cubic centimeter to less than 0.1 grams per cubic centimeter. After plasma treatment the fiber is more hydrophilic, then a layer of water can be formed during washing procedures with a reduction of friction among fibers and a consequent felt reduction.
With respect to shrink-resistant treatment, this effect is too small compared with the state-of-the-art chlorine/Hercosett treatment. Therefore, additional resin coverage of the fiber surface is required. It should be mentioned that the plasma treatment brings additional advantages, in particular increasing dyeing kinetics, an enhanced depth of shade, and improved bath exhaustion.
Rakowsky discussed treatments with plasma gases of O_2, air, N_2 at low pressure: he observed a regular abrasion of the surface, the removal of the fat acid layer, the reduction of aliphatic carbon (C-C, C-H) of about 20-30% and the appearing of carboxylic COOH groups. With N_2 plasma a better effect on the dyeing of wool is obtained: in fact, it produces amine groups on the surface possessing dye affinity.
To obtain measurements of the role of plasma on the dyeing processes, the coloration of a dye bath is evaluated in order to obtain the so called "exhaustion curves", that give the kinetic behavior of the dyes during a dyeing process as function of the dyeing process parameters. In the paper by I. Holme, 2000, Challenge and Change in wool dyeing and finishing, it is possible to find exhaustion curves for different plasma treatments on wool.

12.3 HYDROPHOBIC FINISH ON COTTON

Cotton is a major crop in many countries and it is still the most important textile fiber in the world, despite market inroads made by synthetic fibers such as polyester. Fabrics from cotton are

comfortable to wear and can be dyed a wide range of attractive colors. Each cotton fiber is an elongated cell: properly it is a seed hair, which grows from the seed in a closed seedpod called a boll. When the boll opens, these tubular fibers are exposed to air, lose moisture, and collapse to a flattened, twisted structure. The mature cotton fiber is actually a dead, hollow cell wall composed almost entirely of cellulose. The lengths of single cotton fibers vary, generally about one inch. It is important to understand the relationship between the structure of this unique natural fiber and its properties.
Many of its features are too small to be seen with optical microscopes. Electron microscopy gives clear images of cotton structure (Fig.12.2).

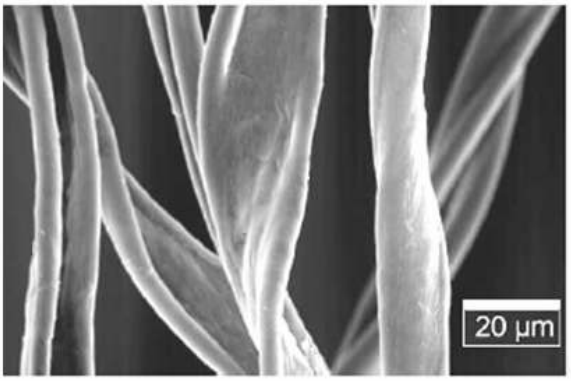

Figure 12.2 Cotton flat fibers.

The scanning electron micrograph can shows the extreme difference between the length and width of the fiber and the flattened, twisted shapes formed when the fiber dried.
A variation in the structures of fiber cross sections is present. Cotton fibers are natural products and then quite different from each other: when they grow, their hollow tubes fill with cellulose and when cotton is harvested, some fibers contain more cellulose than others. Fibers with nearly full tubes have somewhat bean-shaped cross-sections, but fibers with tubes that are not filled with cellulose are flatter.

The outer surface of the fiber, known as the cuticle, contains fats, waxes and pectins that confer some adhesive properties to the fibers, which together with a natural twist of the fiber means that cotton fibers are well suited to spin into yarns. When cotton yarns and fabrics are desized, scoured and bleached, the cuticle is removed and it is possible to obtain fibers with very high cellulose content. In fact, cotton fiber is mostly cellulose, which is a polymer of many individual glucose molecules. As we have previously told, a modification of the mechanical properties of the cotton fiber can be obtained by oxygen plasma. As in the case of wool, plasma modifies the surface of the cotton fiber, adding wettability.

With cotton, an objective is to increase hydrophilicity and reduce chemical waste of existing pre-treatment processes for cotton fabrics. Researchers in Portugal used a corona discharge in an air atmosphere and showed corona to be a very effective way of increasing hydrophilicity without affecting the integrity of the fiber or yarn (N. Carneiro et al.). The treatment leads to chemical and physical changes to the waxy cuticle layer of the cotton without damaging the cellulose backbone. Increased wetting of fibers was observed, together with a decrease in the pH of water in contact with the cotton.

With corona discharge, a similar effect over the waxy cuticle is expected as that obtained with softening finishing. If a corona discharge is made before the application of the softening agent, more favorable conditions for fixation are created, either increasing reaction with the fiber or increasing physical conditions for penetration. Softener content in effluents will be lower.

The increase of hydrophilicity of cotton is important from another point of view. Cotton warp yarns have to be sized prior to weaving to apply a protective coating to improve yarn strength and reduce yarn hairiness. Starch-based products are most frequently used for slashing cotton yarns. Carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA) are the next most frequently used sizing agents for cotton yarns. PVA is used primarily for slashing synthetic yarns, and is also often used as a secondary sizing agent to starch for cotton yarns. Size materials must be removed by desizing prior to dyeing and finishing woven fabrics. Sized fabrics must also be subjected to washing with water at temperatures around 90°C in order to

effectively remove size. A complete PVA size removal is difficult, with many disadvantages such as high energy and water consumption.
An atmospheric plasma reactor is used with air/O_2/He and air/He plasma (Cai et al.). A percent desizing ratio PDR of 99% was obtained with both air/He and air/O_2/He plasma treatments followed by cold and hot washing: as a conclusion, atmospheric plasma treatment may greatly increase the solubility of PVA on cotton in cold water. SEM observations revealed that, for both air/He and air/O2/He plasma treated fabrics, the fiber surfaces were nearly as clean as the unsized fabric, indicating that almost all PVA on cotton was removed. This agrees with the PDR results. In contrast, there was a substantial amount of PVA remaining on the fiber surfaces when fabrics were only cold and hot washed, while much less PVA was left on the fabric desized by H_2O_2.
Let us discuss how to induce a hydrophobic feature on the textile cotton surface. The textile surface has then the property to be less sensitive to spots. In this case, we need two processes: activation and polymerization. It is dependent on the power of source energy and pressure, on the time of exposure and on the plasma gas under use.
The research group of M. McCord at the North Caroline State University used CF_4 and C_3F_6 on cotton denim fabrics with a low-pressure low-temperature plasma system to increase hydrophobic properties of the surface. To determine the hydrophobicity, contact angle and wet-out time measurements were conducted and the effectiveness of CF_4 and C_3F_6 gases compared using atomic chemical composition as well as XPS analysis. Plasma treatments were performed on cotton denim fabrics in a RF (13.56 MHz) plasma chamber in a capacitively-coupled mode with the substrates placed on the lower electrode. During the treatments, pressure, RF input power, and exposure time were varied according to an experimental test matrix.
After the plasma treatment, the researchers evaluated the surface wettability by means of the sessile drop technique, where a distilled water droplet is placed on the fabric surface and observed through a telescope and the contact angle of the droplet on the surface of the fabric was measured. If we observed a greater contact angle, the greater is the surface

hydrophobicity. Contact angles of denim fabrics treated in C_3F_6 plasma increased with power and exposure time but decreased with increasing pressure. Overall, the hydrophobicity of treated desized denim fabrics was higher than that of treated sized denim fabrics. This indicates that sizes on the denim fabrics play a role in determining surface wettability even after fluorination in a CF_4, C_3F_6 plasma treatment. After CF_4 and C_3F_6 plasma treatment, $-CF_x$ hydrophobic chemical groups were obtained by the chemical reaction between surface molecules and fluorinated gases. The other carbon chain groups (hydrophilic groups) decreased, and their composition rates were changed according to plasma conditions.

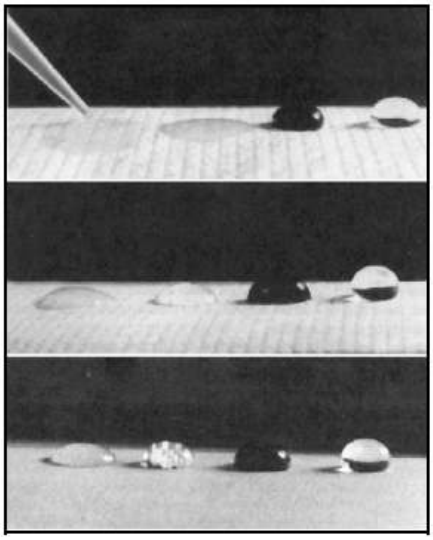

Figure 13.3 Four liquids (from left to right: isopropyl alcohol, mineral oil, synthetic blood and water) on surfaces of three materials (from top to bottom, woodpulp/polyester, polyester, polypropilene): according to the surface energies, liquid drops are showing different contact angles.

Measurements were made by B. Marcandalli et al. on the water contact angle for plasma treatment with CF_4 on cotton, PET and silk. For cotton, the angle changes from 30 degrees to angles ranging from 90 to 150 degrees for different

pressures and times of plasma treatment. On PET, the angle goes from 105 degrees to 120-155 degrees. CF_4 plasma imparts to the PET surface a structure similar to Teflon with a very high water repellence (Piccirilli); instead, a treatment with O_2 imparts to PET an hydrophilic surface. Examples of contact angles are shown in Fig.13.3: wettability is obtained for angles less than 90 degrees. Let us remember that a liquid is wetting a surface if the surface energy of the substrate is greater than that of liquid.

13

PLASMA TREATMENTS OF SYNTHETIC FIBERS

13.1 INTRODUCTION

As the textile industry seeks new ways for increasing the surface properties of natural, man-made and synthetic fibers, it will certainly find the new atmospheric plasma treatment (APT) technique interesting. With APT-based systems, adhesion, wettability, hydrophilicity or hydrophobicity, printability and other qualities can be improved on the textile product.

Let us take a closer look at polypropylene (PP) as an example. It is an excellent material because of its chemical resistance, high melt point, low cost and adaptability to a number of manufacturing methods. Despite these features, until now PP has proven very difficult to dye, a factor that has limited its application. A fiber with polar groups can be dyed much more easily than non-polar fibers because polar groups on the fiber surface bond with the dye. Because the PP polymer chain is non-polar and its surface is hydrophobic, the dye molecules do not bond chemically to the fiber. Furthermore, polypropylene has a different degree of crystallinity that further restricts its capacity to be dyed. Plasma treatments can add functional groups to the surface which improve its properties without damaging the volume of the fiber. This creates a polar surface that increases wettability and thereby also the fiber dyeability.

13.2 POLYAMIDES

Polyamides, also known as nylon, are the most widely used semicrystalline engineering thermoplastics and also yield excellent fiber. Nylons are characterized by their good thermal stability, flexibility and mechanical properties and are the most important synthetic textile fibers originally used for women's stockings. Nylon 6 (PA6) does not behave much differently from nylon 6,6: the only reason both are made is due to the fact that DuPont patented nylon 6,6. Other companies had then to invent nylon 6 in order enter the business. The research on the plasma

treatment on polyamide is mainly dyeability, wettability and surface properties. Oxygen and air plasmas are used to increase wettability and dyeability. An increase of bondability can be also observed, changing the bond from adhesive to cohesive.

Nitrogen-containing plasmas are in fact widely used to improve wettability, printability, bondability and biocompatibility of polymer surfaces and many applications of nitrogen containing plasmas for surface modification of different polymers have been investigated. For example, to improve the interfacial strength between polyethylene fibers and epoxy resins, which are cured by amino crosslinking, amino groups were introduced on the fiber surface to promote covalent bonding. Plasma treatments with NH_3 give rise to N-functionalities plus oxygen-containing groups due to post-plasma atmospheric oxidation (Tusek L. et al., Chan C.M. et al., Chappel P.J.C. et al.).

Although PA6 adsorbs more water than other frequently used synthetic polymers, it is still classified as hydrophobic in many applications. When water is used as a testing liquid, it can be observed that the introduction of polar groups on the surface due to NH_3 plasma treatment makes PA6 less hydrophobic. Nylon 6 fabrics were treated (Yip J. et al.) with low temperature plasma with three non-polymerizing gases (oxygen, argon and tetrafluoromethane) to investigate mechanical and thermal properties.

After plasma treatment, the properties of the fabric, including surface morphology, low-stress mechanical properties, air permeability and thermal properties, were measured by researchers, observing that nylon fabrics treated with different plasma gases exhibited different morphological changes.

Low-stress mechanical properties revealed that the surface friction, tensile, shearing, bending and compression properties altered after the treatments. The changes in these properties are possibly closely related to the inter-fiber inter-yarn frictional force, induced by the plasma treatment. It was also observed a slight decrease in the air permeability of the treated fabrics, probably due to plasma changing the fabric surface morphology. A change in the thermal properties is in agreement with the above findings and can be attributed to the amount of air trapped between the yarns.

For what concerns CF_4, it is a non-polymerizing gas that does not polymerize itself, but tends to form thin films on the fiber surface subjected to the glow discharge. Gazicki et al. examined CF_4 plasma treated fabrics and found that ablation was accompanied by the deposition of thin films on the fiber surface. Yip et al. suggested that a shorted exposure time will favor polymerization while a longer exposure time will favor ablation.

13.3 ACTIVATION OF PP, PE, PET AND PTFE.

Polypropylene (PP) is a very interesting material for plasma treatment: it is a very hydrophobic material with extreme low surface tension. On the other hand, PP is used in a large number of technical applications where an improved wettability or adhesion properties are advantageous. This is also the case of PP technical textile applications such as filters for medical applications. Since PP nonwoven filters can be wetted only with liquids with surface tension <35 mN/m, no water can pass through the PP-web without applying a high pressure: using oxidative plasma with a short treatment time can greatly improve wettability. Improvement of wetting in PP has been observed for air and NH_3-plasma.

As in PP and also in polyethylene PE, polyethylene terephthalate PET and polytetrafluoroethylene PTFE, treatments in air-, O_2- and NH_3-plasma are usually performed. These treatments are able to increase wettability but also adhesion for these materials (hydrophobic finishing on cotton/PET and PET already mentioned, are produced with siloxan- or perfluorocarbon-plasma, D'Agostino R. et al.).

Another very important problem is to increase adhesion of different polymer-metal systems, namely, PET-Al, Kapton-Al, and Teflon-Cu. To this purpose both reactive (O_2 and NH_3) and inert (He) gases have been used for plasma treatments. The results (D'Agostino R. et al.) obtained with PET are particularly interesting from both the fundamental and the industrial points of view. NH_3 plasma treatments were successful in obtaining higher PET-Al adhesion values at very short plasma duration: the shorter the NH_3 treatment time the higher is the adhesion increase. A treatment of 0.1 s is sufficient to promote a 15-20 fold increase of adhesion

13.4 PRINTING THE POLYPROPYLENE

The minimal dyeability of polypropylene nonwovens has limited the development and optimization of manufacturing systems for knitwear, fabrics and industrial fabrics. Therefore, polypropylene is a very interesting material to use to test APT systems. Polypropylene nonwovens have been treated with the plasma device of Enercon at atmospheric pressure on test frames. The key treatment parameters include the applied power, the type of gas, the gas flow and the ratio of components in the blend. Plasma treatments have been carried out applying both the plasma and the corona techniques. The surface tension of treated nonwovens was determined by special surface tension testing fluids.

The tension values notably increased in the APGD and corona treated samples. While the surface tension measured on the original substrate was 31 dynes/cm, with both the APGD (O_2/He plasma) and the corona treatment it grew to 52 dynes/cm. The samples were then printed with the American flag applying a four-color printing process to a photo-polymeric printing sheet using water-based ink. The ink was dried by ventilation.

The non-treated sample and the corona and APGD treated samples were then subjected to color adhesion tests using adhesive tapes. The tapes were applied on all the printed samples and left there for 60 seconds. When the tape was removed, the non-treated printed samples showed a total absence of color adhesion to the fiber; all color was removed by the tape. The corona treated samples retained about 90% of the image color. APGD treated samples showed 100% adhesion, thus losing no surface color. This shows how effective atmospheric plasma is in making surfaces functional to increase the adhesion of water-based dyes.

In order to evaluate color perception, on the other hand, non-treated samples were compared using a spectrophotometer, which measures the light reflecting on the surface along each wavelength. The resulting spectrum is shown in figure 13.1.

The APGD treatment on nonwovens significantly increases the reflection factor in the flag image of primary blue and red compared to the reflection factor of the non-treated and corona treated samples. PET tests on nonwovens using different blends of gas were carried out and showed a better dyeability

with water-based dye, with a treatment level in excess of 70 dynes.

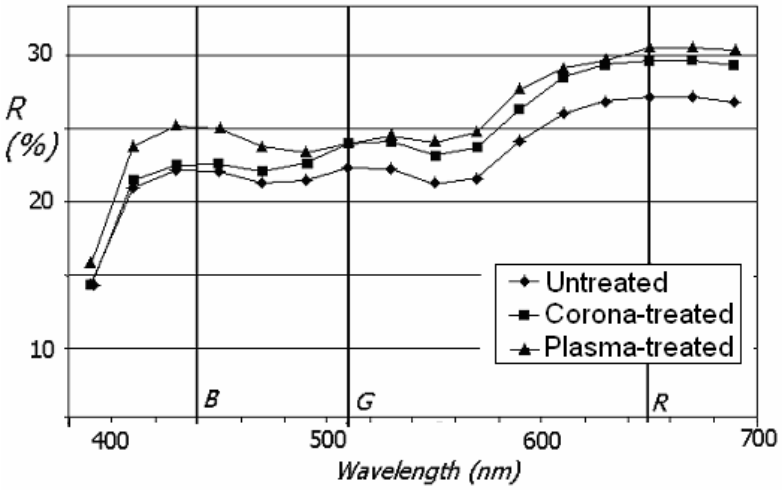

Figure 13.1 The spectrophotometer measurement of reflected light shows a considerable difference between the treated and non treated samples. Red and blue are the brightest colors with the APGD plasma treatment.

What happens on the surface of the polypropylene during an APT treatment? Analysis indicates that the plasma effects a bombardment of free radicals on the polypropylene surface, introducing oxidized functional groups on the surface, such as COH, C=O, COOH, C-O-C, ether groups, esters, hydroperoxides, and increasing the presence of oxygen.
Furthermore, nitrogen grafting phenomena have been observed with helium or He/O_2 blend plasma treatments, because of the presence of N_2 molecules agitated by the helium during discharge. The chemical groups formed by the glow discharge are responsible for the change in surface properties of the polymer. Also, by increasing deposit energy, the density of the cabonyl, acid and radical peroxide groups on the surface of the polypropylene can be increased.
In conclusion, we can say that the surface energy of fabrics treated with APT atmospheric plasma systems generally grows

notably and this results in a sizeable increase in wettability, printability and adhesion properties for treated fabrics.

REFERENCES

Carneiro N., Souto A.P., Silva E., Marimba A., Tena B., Ferreira H., Magalhães V. 2001, Coloration Technology, 117(5), 298.

Cai Z., Qui Y., Zhang C., Hwang Y-J. McCord M. 2003, Textile Research Journal, 73, 670.

Chan C.M., Ko T.M. Hiraoka H. 1996, Surf. Sci. Rep. 24, 1.

Chappel P.J.C., Brown J.R., George G.A., Willis H.A. 1991, Surf. Interf. Anal. 17, 143.

Coates D.M., Kaplan S.L. 1996, Plasma Processing of Advanced Materials, MRS Bulletin, August 1996.

D'Agostino R. et al., 2002, Plasma etching and plasma polymers, at http://www.cscp.ba.cnr.it/ attivric4.htm.

Dai X.J., Kviz L. 2001, Study of atmospheric and low pressure plasma modification on the surface properties of synthetic and natural fibres, Textile Institute 81st World Conference Melbourne, Australia.

Gazicki M., Yasuda H. 1983, Plasma Chem. Plasma Processing 3, 279.

Hesse A., Thomas H., Hocker H. 1995, Text. Res. J., 65, 355.

Holme I. 2000, Challenge and Change in wool dyein and finishing, 10th International Wool Textile Research Conference, Aachen.

Hansen G.P., Rushing R.A., Warren R.W., Kaplan S.L. Kolluri O.S. 1991, Int. J. Adhesion and Adhesives, 1(4), 247.

Hozbor M. 1993, Plasma Processes Boost Bondability of Rubber and Metal, Adhesives Age, 36, 32.

Kaplan S.L., Rose P.W. 1988, Plastics Engineering 44 (5), 77.

Lewis D.M., Shaw T. 1987, Review of Progress in Coloration, 17, 86.

McCord M. 2000, A Novel Non-Aqueous Fabric Finishing Process, Annual Report NCSU.

Marcandalli B., Riccardi C., Ardoino M. 2001, Trattamenti al Plasma per i Tessuti, Assotec (in Italian).

Piccirilli S. 2000, Trattamenti con plasma a bassa temperatura nel finissaggio tessile, Thesis, Politecnico di Torino (in Italian).

Rakowski W. 1992, Plasma Treatment of Wool, Biella Wool Textile Award.

Reece Roth J. 2001, Industrial Plasma Engineering, Institute of Physics Publishing, Bristol.

Sarmadi A., Ying T., Denes F. 1995, European Polymer Journal, 31(9), 847.

Sarmadi M., Denes F. 1996, Surface Modification of Polymers Under Cold Plasma Conditions, TAPPI, 79(8),189.

Sparavigna A. 2002. Plasma treatments for textiles: an innovative technology for traditional and technical fabrics. In Recent Res. Develop. Applied Physics, 5, 203.

Tusek L., Nitschke M., Werner C., Stana-Kleinschek K., Ribitsch V. 2001, Colloids and Surfaces A, 195, 81.

Yip J., Chang K., Sin K.M., Lau K.S. 2002, J. Mat. Processing Technology, 123, 5.

Wolf R.A. and Sparavigna A. 2005, Textile World, 155(10), 49.