Clearing the Air on Atmospheric Plasma Surface Treating Systems

Enercon Industries Corporation

The term "atmospheric plasma" is creating a buzz throughout the main stream converting industry. The promise of higher dyne levels, longer lasting dyne levels, superior adhesion performance, grafted surface chemistry and an ability to apply variable chemistry to adapt to ever changing application requirements are benefits worthy of converters' attention.

As atmospheric plasma surface modification technologies become more mainstream, potential users of these technologies in the printing, coating and laminating industries are becoming confused by what is "mixed-messaging" that some surface treatment equipment suppliers are using to ride the wave of atmospheric plasma technology's popularity. Today the terms atmospheric plasma, chemical corona and air plasma are being recklessly interchanged.

It is true that the '4th state of matter' can be achieved at both high and low temperature and pressure. It can also be asserted these plasmas consist of free electrons, ions, radicals, photons and other species. However, it is non-thermal plasmas, and particularly non-thermal – atmospheric pressure plasmas which are best suited for continuous surface pretreatment of substrates within the converting industry.

To further clarify, corona discharges are not absolute plasmas. Although a corona discharge can be regarded as an atmospheric pressure plasma discharge, the surface modification provided by conventional corona discharges are exceedingly one-dimensional compared to gas phase atmospheric pressure plasmas which can offer an expanded range of surface modifications, both physically and chemically. Understanding the origins of atmospheric plasma will help to successfully clarify the performance potential of true atmospheric plasmas compared to common corona discharges.

Atmospheric plasma systems are not enhanced corona discharge treating systems. The treatment attributes of atmospheric plasma systems were originally developed with low pressure vacuum plasma systems as the guide. Most will recognize that the capabilities of a vacuum plasma system far exceed those of a corona system. This article will review the vast technical differences between corona based systems and true atmospheric plasma systems.

Corona

Corona treating systems are designed to increase the surface tension of polymers in order to improve wettability and adhesion of inks, coatings and adhesives. Treated materials demonstrate improved printing and coating quality, and stronger lamination strength.

The system consists of two major components; the power supply and the treatment device. The power supply accepts standard utility electrical power and converts it into single phase, higher frequency power that is supplied to the treating device. The treating device applies this power to the surface of the material, through an air gap, via an electrode design. Only the side of the material facing the high potential electrode should show an increase in surface tension.

When air is exposed to different voltages, an electrical discharge develops. A high voltage is required to ionize air. Normally corona treating systems operate within an electrical voltage range of 10-20 kV. In its simplest form corona can be portrayed as a capacitor. Voltage is applied to the electrode and ionizes the air in the air gap, creating a corona which will increase the surface tension of the substrate passing over the electrically grounded roll.

When this occurs, neutral molecules and electrically charged molecules collide. These collisions cause neutral molecules to become electrically charged, resulting in filamentary discharges or "streamers". Such filamentary discharges create a non-homogenous cloud of ionized air.

When a substrate is placed under a corona discharge, electrons bombard the treatment surface with energies two to three times that necessary to break the molecular bonds on the surface of most substrates. The resulting free radicals react rapidly with other free radicals on the same or different molecular chain, resulting in cross-linking. Oxidative affects on treated surfaces increase surface energy as a result of polar groups being created on the surface, primarily in the form of hydroxyl groups, carbonyl groups, amide groups and carboxylic acid.

As previously mentioned high voltage is required to ionize air. A by-product of this high voltage is the aforementioned filamentary discharges. These discharges prevent uniform treatment on a molecular level and in fact damage surfaces on a nano-scale. It is important to note, that while this results in inconsistent treatment across the substrate surface, it is usually adequate for basic converting applications.

Exposure of corona treated surfaces to high levels of ambient humidity and temperature accelerates polymer side chain mobility and treatment degradation. Migration of slip additives can be accelerated and therefore also need to be taken into consideration when optimizing a process solution for converting corona treated substrates.

Converters looking for improved corona treatment should consider high definition corona systems where optimized dielectrics are used to minimize filaments, pin-holing and backside treatment potential.

Gas (Chemical) Corona

Gas or chemical corona treatment is electrically similar to corona processes. A process gas other than air, such as nitrogen, is ionized in order to increase the surface tension of primarily non-porous substrates. Because of the potentially lower breakdown voltage of process gases, gas corona treating systems can operate at an electrical voltage much less than 10 kV.

While these systems provide an improvement over air corona, they fall considerably short of the results achievable with atmospheric plasma. As we will see, atmospheric plasma creates a 4^{th} state of matter which differentiates its surface modification potential beyond what either a corona or chemical corona system can achieve. In turn, the treatment results of an atmospheric plasma system not only outperform corona systems, but they also offer limitless possibilities.

Bridging Vacuum Plasma to Atmospheric Plasma

The low density non thermal plasmas characterized by vacuum plasma systems provide effective yet gentle surface treatment evenly across entire surfaces. In vacuum plasmas, the inter-bombardment of electrons, ions, VUV and UV rays combine to create profound surface modification effects. The technology is also highly effective at etching and cleaning surfaces by removing organic material and creating chemical bonding sites on the surface. The controlled environment of a vacuum plasma system enables advanced treatment techniques such as chemical vapor deposition. Vacuum plasma systems are limited to use where batch processing is an acceptable means of production.

Eight years ago Enercon embarked on a development project to determine if the results achievable with vacuum plasma systems could be replicated with atmospheric plasma systems for high speed converting applications. Extensive research and development led to the development of a system which optimizes dielectric, surface etching and surface modification characteristics of an atmospheric plasma surface treating system in a manner similar to vacuum plasma treatment systems.

Like corona and gas corona, plasma is the electrical ionization of a gas. However, the plasma (glow) discharge creates a smooth, undifferentiated cloud of ionized gas with no visible micro-discharges or macro- filaments. Also unlike corona or gas corona, plasma is created at much lower voltage levels.

As mentioned, corona converts the substrate surface from a non-polar state to a polar state. Oxygen molecules from the corona discharge area are then free to bond to the ends of the molecules at the surface of the substrate being treated, resulting in an increase in surface tension.

The same description holds true for plasma with major exceptions. The rate at which electron bombardment occurs within a gas-phase plasma is up to 100 times greater. In addition, a significantly higher amount of ion bombardment initiates chain scission of molecules (on organic substrates) across the entire substrate surface. This result is increased surface etching, and stronger bonding attributes across the web.

COMPARATIVE CONTACT ANGLE MEASUREMENTS FOR SURFACE TREATMENT TECHNOLOGIES

Polymer Type	Advancing Contact Angle before Treatment	After N2 Vacuum Plasma	After N2 Atmospheric Plasma	After N2 Chemical Corona	After Air Corona
Polypropylene	110°	48°	50°	66°	76°

Note: All post-treatment contact angle readings conducted at the same watt density.

As reactive gases are diffused toward the surface under the influence of electrical fields low molecular weight materials such as water, absorbed gases and polymer 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 surface, changing the chemistry of the surface and imparting the desired functionalities.

In addition to these surface reactions, plasma also facilitates the use of chemical gases which can produce controlled chemical reactions on the surface as well. Plasma technology also eliminates the possibility for backside treatment. These high-speed photos capture the optical differences between corona and plasma treatment. The corona image shows the expected "filaments", while the plasma treatment generates a homogenous discharge profile.

Typical corona with filamentary discharge

The homogenous glow of atmospheric plasma discharge

A major advantage of atmospheric plasma is its proven ability to produce long lasting treatment results on low polarity materials that would be unresponsive to corona treatment, such as silicone or fluoropolymer substrates. However the ability to clean, etch and functionalize surfaces has made atmospheric plasma a breakthrough solution for many industry leading firms. And, the ability to address many difficult to treat applications while employing plasma systems to eliminate the significant generation of ozone created by corona discharge systems offers environmental returns on investment.

The use of variable chemistry in these systems allows tremendous versatility by optimizing reactive gases for the specific application. Next generation atmospheric plasma systems are being engineered for other performance features of vacuum plasma technologies, such as plasma-enhanced chemical vapor deposition.

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Continue reading for an example of atmospheric plasma surface treating results.

One Defining Application

Five variables are thought to affect adhesion and heat seal strength; 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 (rate of flow of the ozone carrying stream), ozone concentration (power setting on ozone unit), horizontal distance of the applicator from the nip and angle of the ozone applicator. The levels used in this design are found in Table 2, 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.

Table 2 - Variable levels utilized in experimental design

Variable	Condition 1	Condition 2
Substrate Treatment	Atmospheric Plasma	Corona/Ozone
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%C2H2	None
Watt Density	40W/m²/min	40W/m²/min

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 60" atmospheric plasma pilot line. The extrusion coating trial runs were performed on the Equistar Millennium Petrochemical extrusion coating pilot line. For all extrudate runs, a LDPE (Melt Index 10, 10g/10min) was coated onto OPP and PET film. The material was processed in a 4.5" extruder through a 48" wide edge bead reduction die. The samples were prepared and tested according to ASTM test method F88. The heat seals were made on a heat seal machine using the following temperature T, pressure P and dwell time T conditions to make the seals: T= 127° C, P= 206.8 kPa, T= 1 s.

The measurements showed that the use of atmospheric plasma surface modification to the OPP and PET substrates increased heat seal strength by a similar amount as the combination of corona treatment of the substrate and ozone treatment of the extrudate. The analysis infers that the uniformity and homogeneity of an atmospheric plasma glow discharge treatment, along with its ability to micro-etch and functionalizing the surface of films (in this case with carbon-based functionality), seem to provide a similar level of heat seal strength for OPP and PET films extruded with LPDE resin.

Since it is common knowledge that the effectiveness of melt temperature on heat seal strength is much greater at higher air gaps and lower line speeds when using corona and ozone treatment combined, such adjustments may also improve the heat seal strength results of atmospheric plasma. The results indicate that it may be possible to further enhance heat seal strength of extrusion coatings to films by the use of atmospheric plasma combined with ozone.