Distinguishing Roll-to-roll or reel to reel Surface Treatment Techniques: Corona and Atmospheric plasma

Two technologies are relevant for Industrial plasma systems: Vacuum or low pressure plasma treatment, and Atmospheric plasma treatment.

As opposed to vacuum plasma systems, atmospheric plasma systems do not require airtight vacuum chambers. Materials can be moved through a treatment zone via a conveyor belt. (Niemira, 2012)

For this comparison to Corona only atmospheric plasma is relevant to consider.

Corona is a specific type of atmospheric plasma. At first glance atmospheric plasma and corona treatment seem to be very similar.

Despite their shared objective of enhancing material properties, and similar operational principles, the impact control of Corona and atmospheric plasma treatments, is different yielding distinct outcomes in various applications.

Both in Corona and plasma the gas is decomposed into a mixture of neutral and charged particles that interact with exposed surfaces of the material. When the object is an open cell structure, the plasma particles will interact with the inner surface as well.

By understanding the underlying mechanisms and effects of both Corona Discharge and technologies that rely on precise surface modifications, we can better appreciate their contributions to industries.

In this article, we will delve into the disparities between Corona and Atmospheric Pressure plasma, unraveling their distinct characteristics and effects.

Corona treatment: Illuminating Material Transformation

Corona treatment is a technique frequently employed in industries such as printing and packaging. It is commonly used to activate (or functionalize) the surface of many plastics. It increases their surface energy and therefore improves properties as printability, adhesion etc.

Corona discharge involves the creation of a controlled electrical discharge in the air surrounding a material's surface. This discharge generates a highly energetic plasma, composed of ions, electrons, and excited molecules.

- **Process**

A corona is actually a particular type of atmospheric plasma: It’s an atmospheric plasma using ambient air (approx. 78% Nitrogen, 21 % Oxygen, 1% Argon) as plasma gas. It, therefore, does not require gas injection systems and has no running cost associated with gas consumption.

The main difference between corona and atmospheric plasma treatments lies in the fact that chemistry is not a parameter when working with corona. The operator has no control over the gas mixture used for the treatment, it will always be approx. 78% Nitrogen, 21% Oxygen 1% Ar with various amounts of water vapor, depending on the humidity level at the moment of the treatment.

High humidity levels are an issue for plasma treatment as it destabilizes the discharge and can lead to arcing.

An arc is when small sparks of hot plasma are created in the discharge. Those arcs can damage the treated material, even puncture holes in it.

- **Benefits**

When the plasma interacts with the material's surface, it leads to several beneficial application effects:

1. **Surface Modification:** Corona treatment can induce micro-level changes in the material's surface topography, resulting in enhanced print quality, reduced ink spreading, and improved overall appearance. The energetic plasma breaks molecular bonds on the material's surface, creating functional groups that enhance its wettability. This is particularly valuable in improving the adhesion of inks, coatings, and adhesives.

2. **Cleaning:** The reactive species present in the plasma can effectively clean contaminants and activate the surface, making it more receptive to subsequent treatments.

- **Challenges**

The chemistry of the corona treatment is dominated by oxygen, even though there is almost 4 times less oxygen than nitrogen present. This is explained by the extremely high reactivity of oxygen in the plasma state. It completely masks the other possible chemistries and leads to strong oxidation of the polymeric substrate material.

Actually, Corona treatment can be seen as a controlled destruction of the surface (Figure 2). It's this oxidation that leads to the surface modifications and the increased surface energy.

The strong oxidation of the polymeric material has some unwanted effect:

- It decreases the average molecular weight of the polymeric chain leading to ageing of the treatment over time.
- In extreme cases the oxidation can lead to the formation of a layer of low molecular weight oxidized fragments (LMWOF) on the surface or even destruction of the material.

The creation of LMWOF on the surface of the film will lead to a very unstable surface as those fragments can easily be removed/washed away from the surface and are certainly not a good base for any adhesion layer.

- Corona treatment depends on the external humidity conditions of the environment and therefore quality consistency is a challenge.

- Corona only activates the surface. There is no direct coating process.

On a specific system the only parameter to control during a corona treatment is called the dosage (Equation 1).

$$d = \frac{Plasma\ power}{Web\ width\ \times\ Web\ speed} = \frac{[W]}{[m]\ \times\ \left[\frac{m}{min}\right]} = \frac{[W \cdot min]}{[m^2]}$$

aw*otion 1: Corona dosage calculation*

Increasing the dosage usually leads to an increase of the surface energy up to the point when the materials gets damaged by the treatment.

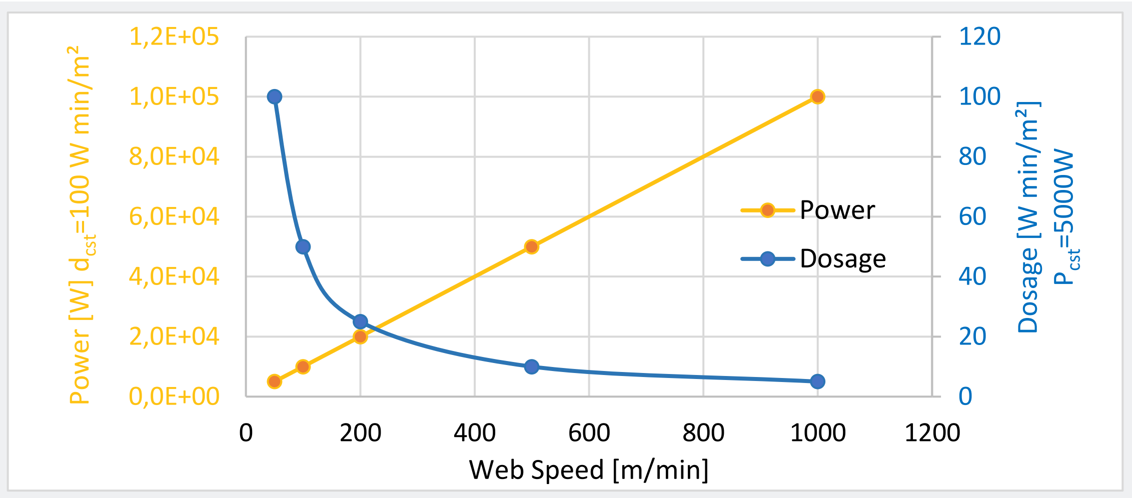

Figure 1: Yellow: Increase of power to keep a constant dosage (100 W·min/m²) while increasing treatment speed. Blue, decrease of dosage when increasing the treatment speed while keeping the plasma power constant (5 kW).

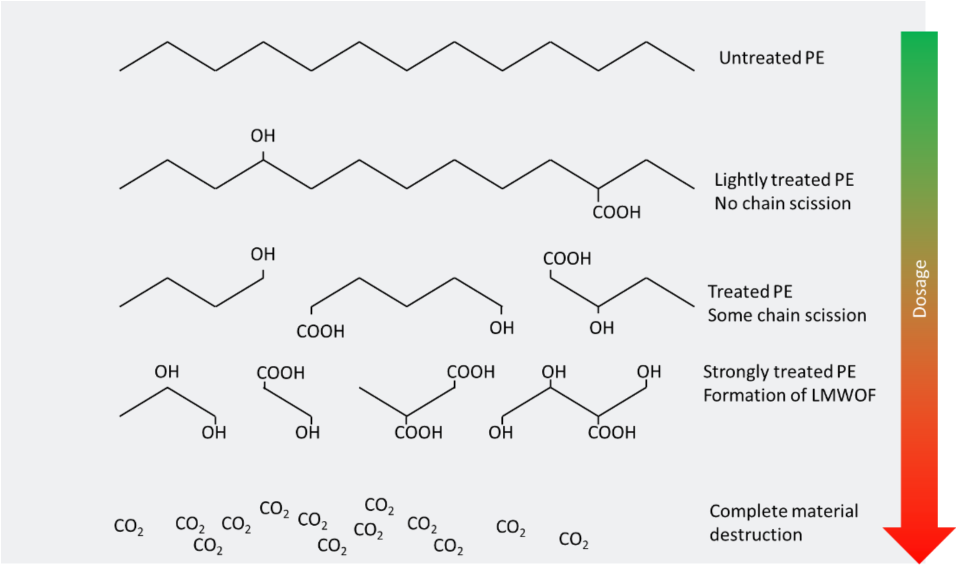

Figure 2: Schematic description of corona (activation) treatment on Polyethylene (PE) with surface degradation by oxidation. The more functions you add, the more you damage the PE.

Atmospheric Plasma: Energizing Surface Enhancement

Plasma treatment solutions enable the modification of surface characteristics at a microscopic (nanoscale) level, to clean, activate, etch and coat materials. Therefore Plasma treatment is used in a variety of industries; such as medical and life sciences, electronics and filtration…

- **Process**

The process is performed at ambient pressure. The film is processed continuously.

Depending on the chemistry, different types of processes are performed.
CPI offers two kinds of treatment: grafting or coating.

For grafting the substrate is exposed to the highly reactive species of the plasma gas. The interactions between the substrate and those species will modify the surface chemistry. New chemical functions will be grafted on the material surface. The nature of the grafted functionalities can be adjusted by carefully controlling the gas composition.

For coating, vapors of a specific molecule are added to the plasma gas. Those vapors are activated by the energetic species in the plasma and will react on the surface to create a coating. This process is called AP-PECVD (Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition). Depending on the nature of the precursor, coating with very specific properties can be deposited.

Atmospheric plasma systems are reliable and have a good operational equipment efficiency.

- **Benefits**

Plasma technology's advantages make it a versatile and efficient choice for various surface treatment applications.

The biggest general benefit of plasma technology for surface treatment solutions is the controlled atmosphere in which the process is executed. This independence from environmental conditions, offers several benefits :

1. The technology enables high precision surface cleaning, activation and etching.
2. It consistently delivers high-quality nano coatings.
3. Plasma technology requires minimal chemistry consumption.
4. It operates at a low process temperature (<50°C), making it suitable for sensitive substrates.
5. The process has low environmental impact, contributing to sustainable production.
6. Coatings with specific characteristics are created in a one-step coating process

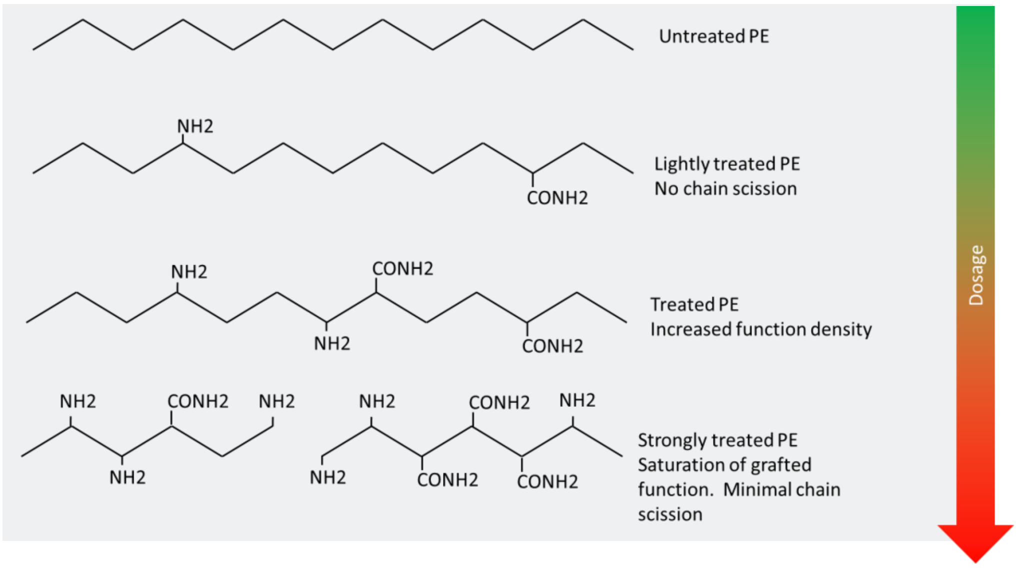

Figure 3: Schematic description of atmospheric plasma (grafting) treatment on Polyethylene (PE); no surface degradation by oxidation as oxygen is not present in the gas mixture.

- **Challenges**

Because atmospheric plasma requires a complex gas management system and a constant injection of gas, the associated costs (capex and running) are much higher than the cost associated with corona.

How to choose the treatment solution?

Being able to select the chemistry of the treatment allows to specifically tune the treatment for an application.

When working with atmospheric plasma the composition of the gaseous atmosphere in the plasma discharge is very well controlled. This allows to control the chemistry inside the discharge and fine tune the properties of the treatment. As the gas composition is controlled it's possible to prevent oxidation of the polymeric material by avoiding the presence of oxygen in the discharge. This allows for treatment at higher dosage without degrading the material and leads to stable surface after treatment with minimal ageing *(Figure 4)*.

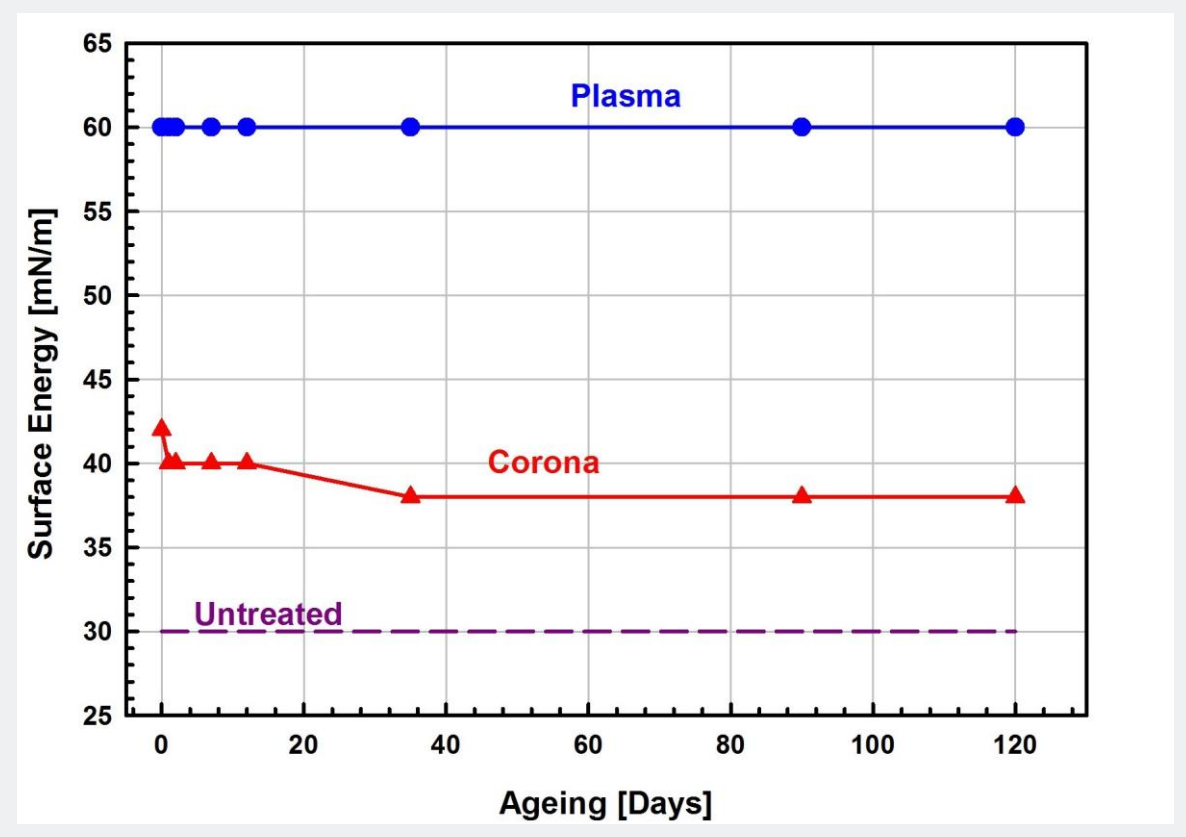

Figure 4: Comparison of the evolution of the surface energy (SE) over time of a BOPP film treated by plasma and corona. SE measured with calibrated inks

While in corona treatment the surface energy is usually used to control the quality of the treatment: higher surface energy is better. This is completely not true for atmospheric plasma treatment. Here the nature of the grafted groups is more relevant than the surface energy.

As shown in *Figure 5* various treatments led to similar surface energies (approx. 55 mN/m) while the adhesion strength increases from < 100 N/m for the corona treated sample to 900 N/m for the sample treated with "Plasma C". Plasma A, B and C are all using Nitrogen as plasma gas but are using different dopant gases. This clearly illustrates that a high surface energy is not the relevant parameter to control adhesion.

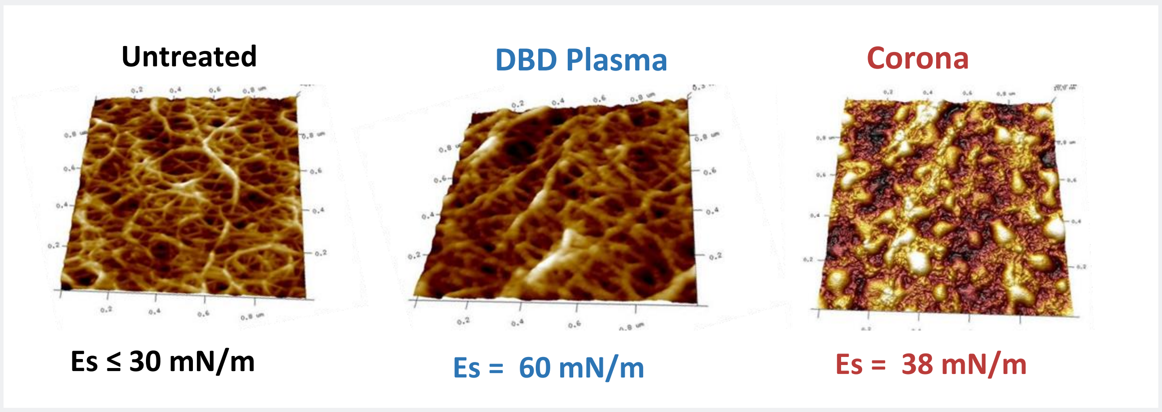

Figure 5: Evidence of surface damage on BOPP treated with corona discharge. Both plasma and corona samples were treated with the same dosage. Atomic Force Microscopy (AFM) image recorded in taping mode, scale 1x1 µm².

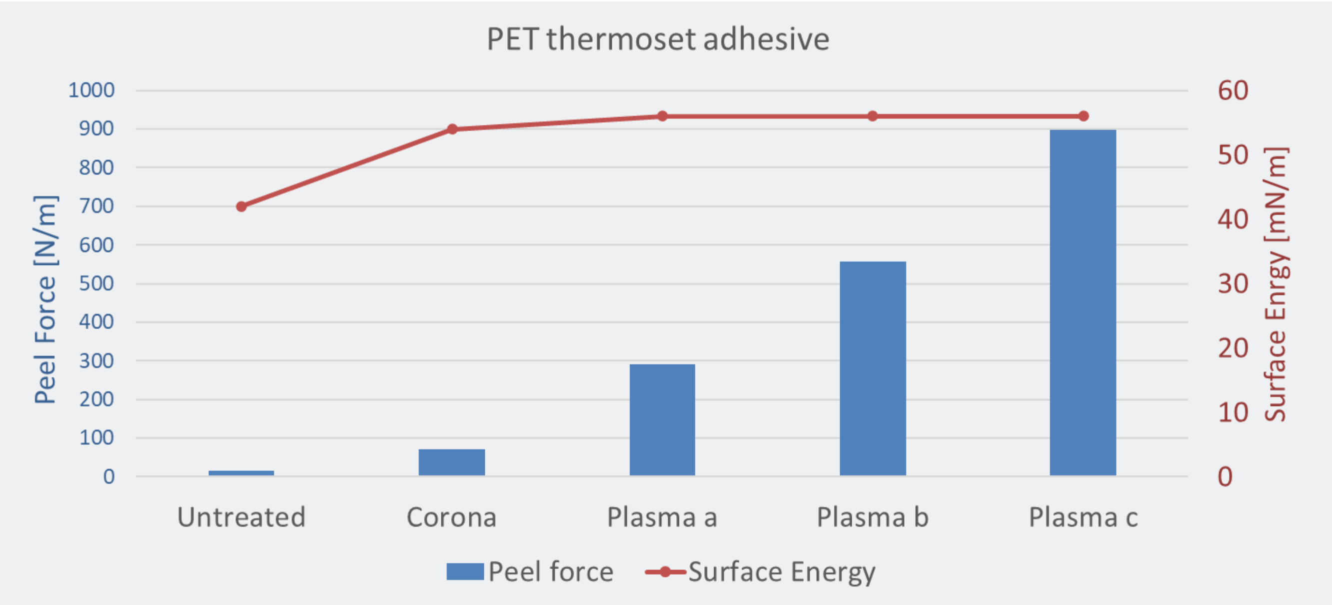

Figure 6: Pell force necessary to delaminate plasma treated PET glued with a thermoset adhesive and surface energy measured on the treated samples. Plasma A, B and C are plasma using different dopant gases.

Roll-to-roll (R2R) or reel-to-reel processing has emerged as a pivotal technique in modern manufacturing landscape to efficiently and continuously produce flexible materials and coatings.

Roll-to-roll (R2R) processing involves the continuous feeding of a flexible substrate from one roll to another, while various processes are applied in-between.

With plasma you can chose what functions and how many you want to a add without breaking the polymer chain. And you can coat.

- **Conclusion**

Even though the two technologies seem similar as they both use plasma (an ionized gas) to treat material surfaces, they should not be compared directly and are not really competing.

In today's industrial landscape, corona treatments are far more established and are used because of the simple and cost effective process. Yet corona treatment has clear limitations that can be overcome by using plasma.

CORONA	ATMOSPHERIC PLASMA
DOSAGE	**DOSAGE**
Power	Power
Film Speed	Film Speed
PROCESS PARAMETERS	**PROCESS PARAMETERS**
	Excitation frequency
	Gas flows
	Plasma gas N_2 Ar He
N.A.	Dopant gas O_2, CO_2, H_2,…
	Dopant gas concentration
	Liquid monomer
	Liquid monomer concentration
	Temperatures (lines, gas, manifolds…)

Atmospheric plasma allows for much more types of treatments from grafting up to nanoscale coatings and is therefore expected to grow strongly over the next years.

In the next article we'll have a closer look at the possibilities offered by atmospheric plasma for surface functionalization as well as for coating deposition.

About Europlasma:

Belgium based Europlasma is a pioneer and world leader in low pressure plasma technology.

For 30 years Europlasma offers turnkey low pressure plasma solutions, delivering both chemistry and equipment for a wide range of applications such as electronics, medical, technical textiles and filtration.

Europlasma specializes in vacuum or low pressure plasma surface treatment via Plasma Enhanced Chemical Vapor Deposition (PECVD). The PECVD process is executed in a controlled atmosphere. It assures a deep and very consistent treatment with no variation in coating quality. PECVD is the best solution for fine coating of 3D complex shapes and porous material.

Europlasma has an extensive active patent family protecting machine design, processes, methods for plasma deposition and offers different surface treatment solutions and a wide coating portfolio.

Compared to traditional wet chemical methods, depending on the application, one can realize with Europlasma coating technology:

- 80% reduction in use of coating chemicals,
- 100% reduction in water waste,
- 50% reduction in energy consumption and emission of CO_2.

Since 1993 Europlasma's vision is to help its customers achieve the highest performance and protection for their products, with the lowest environmental footprint. Europlasma achieves this by supplying innovative surface treatment solutions based on in-house low pressure plasma technology delivering both chemistries and equipment for medical, filtration, technical textiles and electronics applications.

About CPI:

Created in 2001, CPI is a pioneering company in cold plasma surface treatment. CPI is located in the south of France.

CPI uses cold plasma web (roll-to-roll) in a controlled atmosphere, at atmospheric pressure or under vacuum, to solve surface treatment problems on flexible substrates.

Applications include bonding, digital printing, flexible packaging, lamination, etc.

CPI offers both roll-to-roll turnkey atmospheric plasma solutions, and contract production treatment (toll manufacturing) .

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