Technology, advantages and applications of vacuum plasma treatment

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Vacuum plasma surface treatment of flexible polymer materials is a vital tool in the production of high quality metallized products. This process allows the re-engineering of the polymer surface prior to metallizing by changing the chemical and physical properties, such as the surface energy, in a controlled manner. Plasma treatment is conducted inside a vacuum chamber, thus the atmosphere and process conditions are precisely controlled and reproduced. This is different from the offline corona discharge where treatment is conducted in normal atmospheric conditions. Vacuum plasma allows the functional treatment of various types of polymer materials to enhance adhesion and durability of the deposited coating onto the substrate.

This article will outline the technology of plasma treatment sources, their advantages and final applications for various products.

Introduction

Currently there are many applications for metallized flexible films in various fields e.g. food packaging, electronics and information storage, flexible printed circuit boards and solar window films. Thin coatings of various materials are deposited on flexible films by physical and chemical methods such as physical vapour deposition (PVD) and electrolytic deposition.

In such applications, the surface of the polymeric films has to be modified before metallizing to improve surface energy and the adhesion required for the particular application. Polymers have different physical and chemical properties. In order to alter these properties of the polymer surface to achieve good adhesion many different processes have been employed. In particular, plasma treatment has been the most used process to achieve this by changing the surface energy and other properties of the substrate allowing the re-engineering of the polymer surface prior to metallizing. Plasma treatment is now considered as an efficient, economic, environmentally friendly, and versatile technique for improving the desired surface properties of polymer materials.

Different types of inline plasma treatment sources are available in the market and selection depends on the plasma source designed to handle specific gases that are required for the treatment of the polymeric film. New types of plasma sources can treat moving film at a line speed of >10 m/s (32.8 ft/s). The most important issue in the selection of the appropriate source is the production of an intense, uniform plasma flux at high power density levels and the ability to use various gas mixtures without interrupting the plasma source performance. Fully closed loop control of the plasma treater pressure regime would enable consistent and reproducible plasma treatment of the film.

> *"Polymers have different physical and chemical properties."*

What is plasma?

Plasma is the fourth state of matters because it is neither gas nor liquid and its properties are similar to those of both gases and liquids. It consists of a complex collection of ionized gas with positively and negatively charged particles, energetic neutrals, free electrons, photons and free radicals species. Each of these components have the potential of interacting with surfaces with which they come into contact. For this reason, plasmas can be employed to modify surface properties of a material without affecting the general characteristics of the base material.

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Plasma can be generated in air or in a vacuum. A good example is corona discharge, an offline process using air to generate plasma regularly used for treating flexible films to increase surface energy. On the other hand, vacuum plasma is basically a glow discharge generated inside a vacuum chamber at a low pressure of <0.1 torr (1 torr = 133,322 Pa) to ionize the gas. The gas can be ionized by applying various powers such as radio frequency (RF), medium frequencies, microwaves, and alternating or direct current. Free electrons gain energy from the imposed electric field, colliding with neutral gas molecules and transferring energy to dissociate the molecules and to form numerous reactive species. The primary source of ionization of the gas discharge is the electron-atom collision, where collision be-

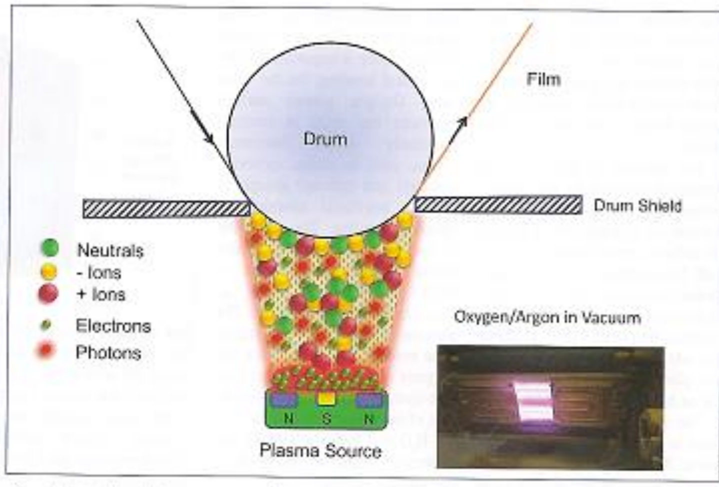


Figure 1: Plasma generated inside a vacuum chamber

tween electrons and gas atoms results in the ionization of gas atoms and the emission of more electrons:

$$e^- + G^0 \rightarrow G^+ + 2e^-$$

Go is the ground state gas atom and G+ is a singly charge gas ion. The interaction of these excited species including ions with solid surfaces placed in the plasma result in the chemical and physical modification of the material surface (figure 1).

Design of plasma treater

There are different designs of plasma treaters available in the market. Most manufacturers use a dual magnetron approach to generate plasma, others a dual magnetron hollow cathod approach to generate dense plasma. The basic design of the magnetron plasma treater (figure 2) consists of a water-cooled cathode with a magnetic assembly to capture secondary electrons to create a dense plasma near the cathode surface (target). The film passes between the cathode and opposite water-cooled grounded plate to receive the plasma treatment. There are different variations to this design to include an unbalanced magnetic arrangement.

In the hollow cathode design, the treater has magnets located on the opposite (untreated) side of the substrate which directs the plasma field toward the film surface. This produces a higher performing plasma treater, with a more compact design and efficient treatment. Plasma is generated from the hollow cathodes and the magnetic field, to remove adsorbed moisture, low molecular weight polymer (and additives) and to functionalise the film surface. Medium frequency power is used to strike the plasma and the electrode system is designed to reduce film charge build up (figure 3).

Plasma treaters differ in their designs and the type of power. Many designs and operating parameters aim at determining the most convenient gas mixture and power to achieve optimum plasma treatment. The design takes into account gas mixture rate, flow rate, power settings and voltage, etc. For example, the use of poor ceramic insulators would lead to a breakdown inside the plasma treater when a certain level of power is applied. Consequently, this would affect the final treatment of the polymeric film surface.

In operation, a variety of parameters can greatly affect the physical characteristics of a plasma and subsequently affect the surface chemistry obtained by plasma modification. The user can vary processing parameters, such as gas types and mixture rate, treatment power, treatment time and operat-

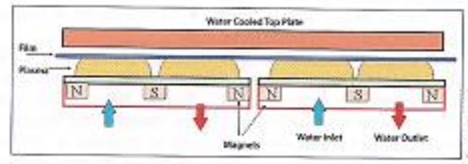


Figure 2: The basic design of dual magnetron plasma treater

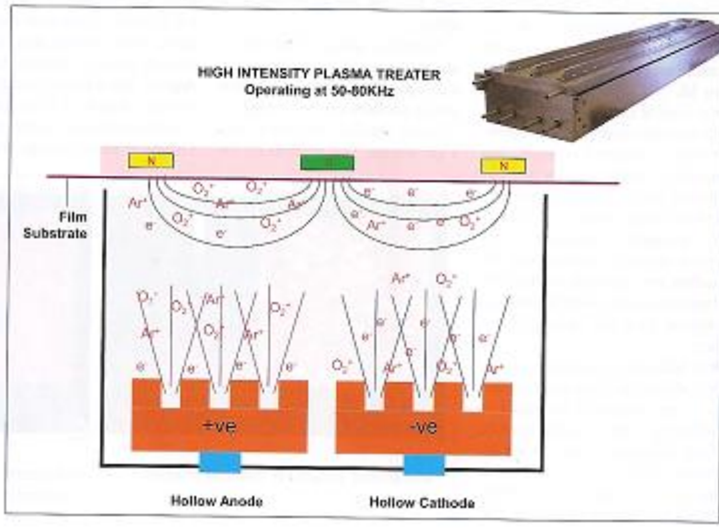


Figure 3: How a cathode plasma treater works

ing pressure. However, system parameters, such as electrode location, selection of insulators, magnetic field design, gas inlets and arrangement of water cooling are set by the design of the plasma equipment.

The selection of the excitation frequency supplied by the plasma power supply is an important factor that can influence the efficiency of surface activation and end result. This correlation has been confirmed by research. Most manufacturers of plasma equipment employ medium frequencies (MF) of about 30–100 KHz to excite and trigger the plasma. Others use DC, pulse DC or high frequency (13.56 MHz).

The standard mixture of gases used in plasma treatment of polymeric films is Oxygen:Argon, the ratio of which differs according to the plasma treater design. Some manufacturers recommend 20:80, while others recommend 70:30. It should be noted that with continuous operation the electrode target plate above the magnetic assembly becomes eroded and oxidised. This requires regular maintenance and cleaning to achieve uniform plasma density.

Advantages

Plasma processes have been developed to achieve specific surface properties including surface cleaning (a), adhesion promotion (b), enhancement of surface energy (c) and improving surface cross linking (d).

■ a) Surface cleaning

Plasma treatment enhances the removal of adsorbed moisture, low molecular weight polymer (and additives) and functionalizes the film surface before metallizing. The active species of the oxygen ions creates a chemical reaction with the surface contaminants of the film, resulting in their volatilization and removal from the vacuum chamber.

■ b) Adhesion promotion

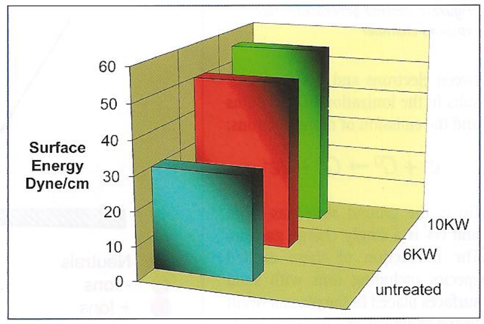
In vacuum metallization, adhesion is a very important parameter to achieving a high quality product. Good adhesion requires strong interfacial forces via chemical bonding and mild mechanical surface ablation. Energetic ions in the Oxygen: Argon (or other) gas mixture bombard the surface thus creating ablation which is important for the mechanical bonding. On the other hand, Oxygen plasma surface treatment can assist in creating chemically active functional groups, such as amine, carbonyl, hydroxyl and carboxyl groups, to improve interfacial adhesion by chemical bonding. The activation of C=O functional groups creates strong covalent bonds such as Al-O-C in aluminium metallization, thus improving adhesion. The photons in the UV plasma region have enough energy to break the polymer's carbon-carbon and carbon-hydrogen bonds. The by-products of these reactions include CO_2, CO, H_2O and hydrocarbons of low molecular weight are removed by the vacuum system.

■ c) Enhancement of surface energy

Most polymers have a surface energy of <38 dyne/cm (1 dyne = 10^{-5} Newton). However, following plasma treatment the surface energy can be increased to >55 dyne/cm depending on the type and the condition of the polymer (figure 4). A dyne is the amount of force required to produce an acceleration of 1 cm/sec^2 on a mass of 1g. The dyne level of a material is called surface energy. The unit of measurement of surface energy is $dyne/cm^2$. This can also be expressed in mN/m.

Therefore, plasma treatment is used to tailor the surface energy of a polymer. Hydrophilic and hydrophobic surfaces can be created on polymers through interaction with a gas plasma. This depends on the type of gases used in the plasma. For example, oxygen is used to increase the wettability of a surface by increasing surface energy. This is the most common method in standard vacuum metallization. Other researchers have used different gas combination to reduce wettability and make the surface more hydrophobic. Wettability describes the tendency of a liquid to spread over and penetrate a surface. It can be measured by the contact angle between the liquid and the surface. The relationship between contact angle and surface energy is direct; contact angle decreases with increasing surface energy.

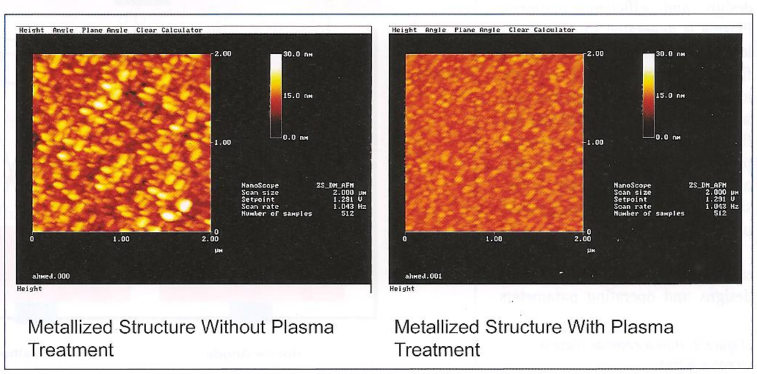
Contact angle measurements are sometimes used as a general indication of the presence of contaminants. The cleaner the surface, the lower the contact angle a drop of water will make with the surface. For example, a substrate contaminated with silicones may form a contact angle of greater than 90 degrees. On the other hand, most plasma treated surfaces yield a contact angle of 20 degrees or less. Change of surface energy and wet-



Source: Idvac Ltd.

Figure 4: Effect of plasma treatment on surface energy of 20 micron OPP film at line speeds up to 500 m/min (1640 fpm) using Ar/O_2 gas mixture

Figure 5: Metallized surface structure with and without plasma treatment



Source: Idvac Ltd.

	OTR cc/m²/day
Poor quality BOPP film	
Metallization with no plasma	330
Plasma treated film	30
Higher quality BOPP film	
Metallization with no plasma	30
Plasma treated film	11

Data source: Sigma Technologies International, USA

Table 1: Example of gas barrier improvement of metallized aluminium by plasma treatment

tability contribute to the densification of the coating structure (figure 5) depending on the quality of film.

■ d) Enhancing barrier properties of metallized films

Permeation of oxygen and water vapour into the layers of flexible films can lead to a serious deterioration of their performance particularly in food packaging. Flexible plastic substrates usually have poor barrier properties. Metallizing flexible films with materials such as aluminium increases the barrier performance of the film. Plasma treatment of the film prior to metallizing can enhance the barrier properties due to many factors.

It is important to mention that its effect on barrier is mainly a function of the quality of the film surface, adhesion and surface energy. Poor quality films may benefit more from plasma than high quality films with functional surface layers because high quality films have better Oxygen Transmission Rate (OTR) and the effect of plasma is less dramatic (table 1).

Conclusion

Plasma surface treatment of polymer materials greatly improves the durability of metallized films. It can enhance adhesion, surface energy, wettability, structure and barrier properties of the film. By introducing functional chemical groups in a controlled manner it allows the user to re-engineer the polymer surface The process is conducted inside a vacuum chamber where the atmosphere and process conditions are precisely controlled. This results in a reproducible treatment. The selection of the most convenient plasma treater depends on many factors including the final application, the gas mixture, maximum applied power level and the design of the plasma source. Depending on the film type and quality to be treated the process parameters have to be tuned for the required type of films to achieve the best results. Plasma surface treatment of polymers in a vacuum is now a vital tool in the vacuum metallizing industry.

Further Readings

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