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Barrier properties enhanced

Pulsed DC magnetron plasma pre-treatment for packaging films in R2R metallisers enhances barrier properties

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Implementing surface treatment of a flexible web material into the vacuum metalliser is an optional way to enhance the adhesion of a subsequent depositing material. Tailored properties such as barrier, mechanical or electrical, could be enhanced to give an additional value to the final products. We report on an investigation into pre-treated flexible web with pulsed DC magnetron glow discharge plasma with respect to barrier properties demanded for the packaging industry. A correlation between adhesion of the metal on the polymer and other physical film properties are presented to highlight the importance of pre-treatment at high coating speeds, wider widths for homogeneous metallised Aluminium films. We further determine the surface energy prior to metallisation, scratch force and adhesion tests subsequent to metallisation, in order to substantiate the correlation of pre-treatment with pulsed DC pre-treatment power. These investigations were carried out recently on the latest high-productivity packaging machines designed and manufactured at Leybold Optics. We acknowledge the support of Uwe Rietzler and Dr Rüdiger Berger of Max-Planck Institute for Polymer Research, Mainz/D, for the technical analysis of the deposited films.

1. Introduction

The importance of barrier properties for thin films packaging has been increasing over the past 10 years. This can be concluded from the demand data of the different base materials, e.g. PET, BOPP, and CPP[1]. The purposes of plasma pre-treatment of webs are namely for cleaning, sealing, etching, and surface functionalisation[2–4]. The pre-treatment in the vacuum web coating technology has become an indispensable tool for diverse applications, e.g. to enhance the adhesion of metal on the polymer films for capacitors and packaging applications.

The desire to move from rigid to light weight flexible packaging continues to increase for economic and processing reasons. The latter reason can be exploited by further optimisation of the base film properties during production and the metallisation steps. One of the aims of these optimisation processes is to achieve the barrier properties required for the shelf-life of the final products.

The optimum barrier of a packaging material should provide total protection of the contents against gases, moisture, odours and micro-organisms. The demands of the consumer can be shortlisted with properties such as transparency, microwavable, hygienic and temperature-resistance, which can be fulfilled with other materials and process optimisation[5, 7]. Although the base film would not satisfy all these demands, the effect of enhancing the adhesion property of the web for packaging films by applying different pulsed DC input power would be a step in the right direction to attain some of these properties.

It is well understood, that barrier properties can be improved by depositing a thin layer of Aluminium on the polymer film. Oxygen or water vapour transmission rates would be reduced dramatically. The bottom line remains the efficiency of each process to achieve the desired barrier property[2, 8, 9].

This paper presents recent results on the efficient plasma treatment of wide webs, with the main target to reduce the permeability of gases for the standard specification for conditioning and testing flexible barrier materials.

2. Investigations
2.1 Plasma pre-treatment units

Commonly, the application of a direct current (DC) or radio frequency (RF) electric field to a glow discharge can be assisted with magnetic field to induce a higher discharge density. This well-established type of discharge is available for different geometrical configurations, cylindrical, circular and planar magnetrons[10]. Magnetically assisted pre-treatment processes have proven to enhance adhesion and barrier performance of the web, depending on an optimum input power dose.

When a constant potential difference is applied between the cathode and anode, a continuous current will flow through the discharge; giving rise to a DC glow discharge[8,11,12]. First, to sustain a DC glow discharge, the electrodes have to be conducting. When one or both of the electrodes are non-conductive, the electrodes become gradually covered with insulating material during the plasma processes. The electrodes will be charged up due to the accumulation of positive and negative charges, and the glow discharge will neutralise each other. This problem has been tackled by applying a time-varying potential difference[2]

● by applying an alternating volt-

Figure 1 (left):
Schematic (left) set-up of magnetron pre-treatment station in Pro-M:
1 = reactor chamber;
2 = electrode holder;
3, 4 = water cooling jackets.

Figure 2 (right):
Cross-section of the Pro-M machine showing the pre-treatment station.
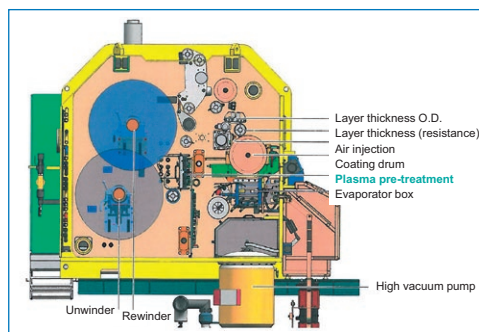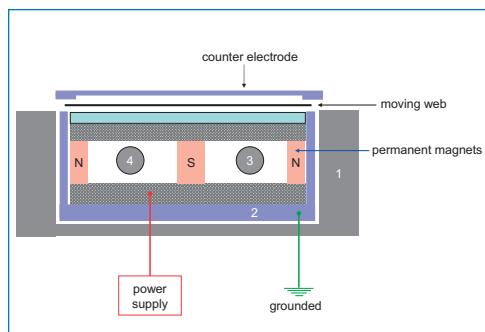
age (RF, 13.56 MHz) between the two electrodes, so that each electrode will act as the cathode and anode, and the charge accumulated during one half-cycle will be partially neutralised by the opposite charge accumulated during the next half-cycle, or

● a DC voltage can be applied in the form of discrete pulses, typically with lengths of milli- to microseconds. This can be regarded as a short DC glow discharge, followed by a generally longer afterglow, in which the discharge burns out before the next pulse starts.

With respect to both options, pulsed DC discharges operate at higher peak voltages and peak currents than in the RF glow discharge, thus higher instantaneous ionisation and excitation can be expected using DC discharges. This is absolutely the basic plasma phenomenon, whereby excitation and ionisation are highly non-linearly dependent on the field strength, thus reduced charge induced damage on a substrate can be achieved by using a very short cycle, i.e. the ratio of pulse-on-period compared to pulse-off period is very small[4, 12]. Precisely, the average electrical power is low, so that the chamber will not be excessively bombarded.

We have been able to apply both options to pre-treat thin polymer films for capacitor applications[5]. The efficiency of both operating modes has been investigated with respect to the surface modification effect induced. This paper will concentrate on the pulsed DC option which shows promising results.

2.2 Experiments

Experiments were carried out using a planar magnetron source, which has been designed to treat the moving web, housed in a *PRO-M 2500* (*Leybold Optics GmbH*) as shown in *figure 1*. The plasma discharge enhanced by a closed loop tunnel shaped magnetic field is generated in the 10^{-3} mbar pressure range. The two planar magnetron cathodes are cooled by water, are able to treat web widths up to 2500 mm (98.4"), and attain web speeds up to 15 m/s. They are operated in a typical input power dosage range up to 90 W s/m². Operating gases were admit-

ted through leak valves for Ar, N_2 and O_2 gas flow rates for all experiments. The maximum pressure attained in the winding chamber was 10^{-3} mbar range.

The DC discharges were maintained between the outer planar electrode earthed and an inner electrode powered by pulsed DC power supply (Advanced Energy DC pinnacle plus, 40 kHz at 1 micro-second). The strength of the magnetic field was constant for all experiments at 113 A/cm. The distance between the magnet assembly and
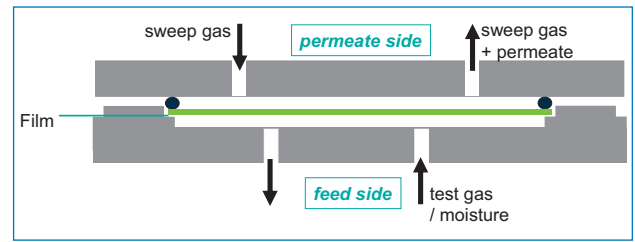
the target was fixed. *Figure 2* shows a schematic representation of the magnetron pre-treatment station used for the web processing in this comparative study.

Figure 3:
Schematic representation of the permeation test cell.
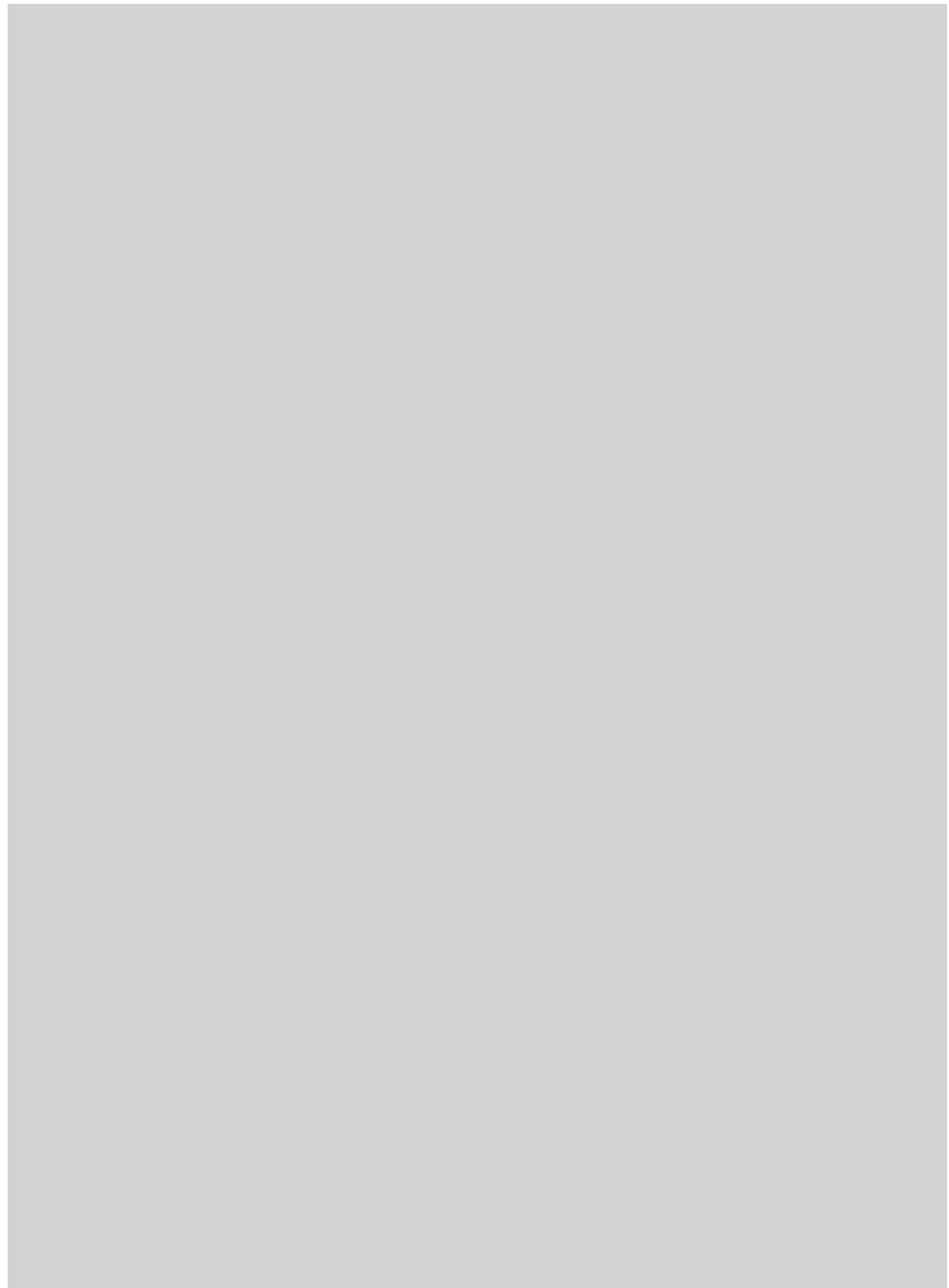
2.3 Web processing

BOPP (20 micron), PET (12 micron) and CPP (20 micron) films delivered by different suppliers were used for all the pre-treatment tests for web width 2500 mm (98.4"). A maximum of 20 kW DC pulsed 1/40 Hz input power was used in comparative to 5 kW RF input power. The packaging machines are designed up to 20 m/s (66 fps), for these test purposes 12 m/s (39.4 fps) was used. The process gases used were argon, nitrogen and oxygen, flow rates will be stated where applicable.

2.4 Film analysis – techniques
2.4.1 Homogeneity distribution

Offline measurements were carried out using a *Gretag Macbeth D200-11* with a red filter (624 nm), and the online measurements were recorded automatically using the *Nagy* layer measurement system. The on-line layer thickness is measured at fixed positions across the web using *Nagy* measurement devices. The measuring probes are installed in the pivot arm and scans across the whole substrate width.

2.4.2 Offline adhesion analysis

The offline adhesion analysis is based on total light transmission before and after the tape test. For reproducibility, results are based on the measurement of ten samples.

A modified image scanner was used to scan the metalised sample in bright light, which transformed it into a digital image. Home-made software processed the digital image of the film to determine all defects (pin spots, scratches). The digital image of the film was then stored as a reference. Thereafter, a tape test was carried out by using a *tesa 4129* adhesive tape size 100 x 2 mm [3.94" x 0.08"] (l x w). This was pressed firmly on the test area of a metallised film. A 2.4 kg (5.3 lbs) metal cylinder was rolled over the taped sample thrice. Finally, the tape was pulled at a rapid pull force applied approximately perpendicular to the test area.

After the tape test, the sample was scanned. The reference digital image was compared with the latter image. The difference in light
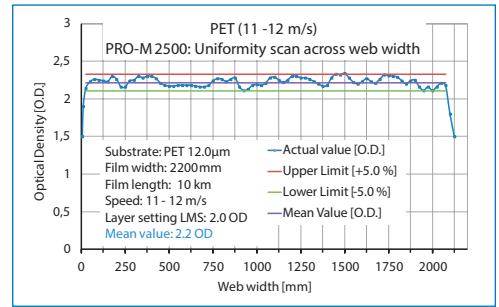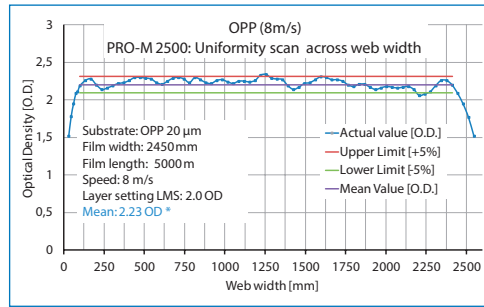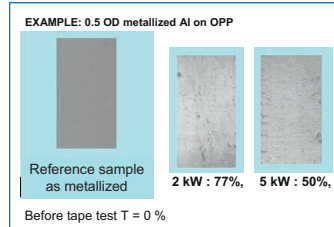

transmission was used as an adhesion factor.

2.4.3 Atomic force microscopy (AFM)

A *Dimension 3100 CL* microscope was used to examine the topography and the scratch force of the metalised samples. The contact and non-contact modus were applied

EXAMPLE: 0.5 OD metallized Al on OPP

Reference sample as metallized | 2 kW : 77%, | 5 kW : 50%,

Before tape test T = 0 %

using the cantilever type *Olympus W2*, K = 42N/m, at a range of 33.5–94.1 N/m and frequency = 300 kHz at a range between 278–389 kHz.

Each sample was prepared by placing a drop of clean water on a glass slide and dehydrated overnight. The root mean square roughness (RMS) on three different positions and three different scales (1 micron, 5 micron and 10 micron) on each sample was analysed.

2.4.4 Scanning electron microscopy (SEM)

The cross sections of the samples were analysed using the focused ion beam *Nova 600 NanoLab* (*FEI* company) and *SEM Gemini* (*Zeiss*). The accelerating voltage was held constant at 1 kV. All images were recorded at 2500- and 5000-fold magnification.

The electron beam was focused to hit the sample at a perpendicular position to the cross-section of the sample. Higher magnifications and acceleration voltages could not be implemented due to charging effects at the boundary interface between Aluminium and polymer film.

2.4.5 X-ray photoelectron spectroscopy (XPS)

XPS is an ideal technique used for surface analysis and it has the following attributes: quantitative atomic identification, chemical sensitivity, sampling depth variability from about 0.2 to 10 nm depending on the material, and it is insensitive to surface roughness.
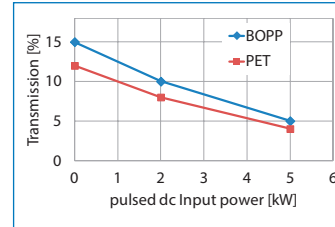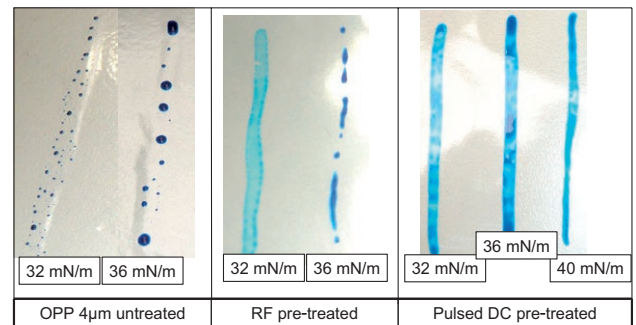

2.4.6 Contact angle/dyne tests

Contact angles of non-metallised films before and after pre-treatment were measured by the static and dynamic sessile drop technique using a *DSA 10* goniometer (*Kruss GmbH*, Germany). MilliQ-H_2O, n-Hexadecane and 1,5 Pentandiol were used as test liquids with a drop volume of 10 microlitres. All values are the average of five measurements per sample. The OWENS-WENDT approach was used to calculate the surface free energy (mN/m, kJ/cm²) from the contact angle values measured[12]. The dyne test (ASTM-D2578) was used to confirm the calculated values.

Figure 4 (left):
Uniformity scan of metallised BOPP film across the web of PRO-M 2500 machine.

Figure 5 (right):
Uniformity scan of metallised PET film across the web of PRO-M 2500 machine.

Figure 6 (left):
Transmission analysis of 2 kW and 5 kW plasma-treated films. The higher transmission values indicate higher removal of metal from the surface.

Figure 7 (right):
Transmission analysis for PET and BOPP upon surface treatment before metallisation 1.0 OD.

Figure 8:
Surface energy depicted from standard calibrated liquids.

32 mN/m	36 mN/m	32 mN/m	36 mN/m	32 mN/m	36 mN/m	40 mN/m
OPP 4µm untreated		RF pre-treated		Pulsed DC pre-treated		

2.4.7 Permeability tests (barrier properties)

Three different permeability instruments (*Mocon, Systech, Permlab*) were used according to ISO 15105-2, annex A, to determine the oxygen transmission rates (OTR) of films at 23 °C (73 °F), 30 °C (86 °F) and 40 °C (104 °F) at 50% relative humidity (rh) as a relationship to the input pre-treatment power. Likewise, ISO 15105-3, the water vapour transmission rate (WVTR) of the films were tested at 23 °C (85% rh) and 37.8 °C (90% rh). Double measurements were carried out for all the instruments. The average values are reported here.

The permeation cell as illustrated in *Figure 3* is evacuated and then a single gas feed was applied at a given pressure on the feed side of the membrane while the permeate side was closed. Pressure increment was expected due to permeation of the gas via the sample film on the permeate side. The difference in pressure rate was used to evaluate the permeation property of the metalised film.

3. Film analysis – results
3.1 Homogeneity distribution

For these investigations, samples were collected randomly from all over the web. Otherwise, an uneven distribution in machine and transverse directions (MD, TD) could present a false interpretation of the subsequent results.

For PET and BOPP samples, the uniformity scans showed dispersion within 5% of the upper and lower specification limit. The process conditions are stated in *figure 4* and *figure 5*. The loop control of the Aluminium wire feed rate with the coating speed was implemented to obtain the desired optical density. This property was recorded for all the samples before the other analyses presented here were carried out. Additionally, it can be confirmed that the optical density is not directly related to the metal coating thickness.

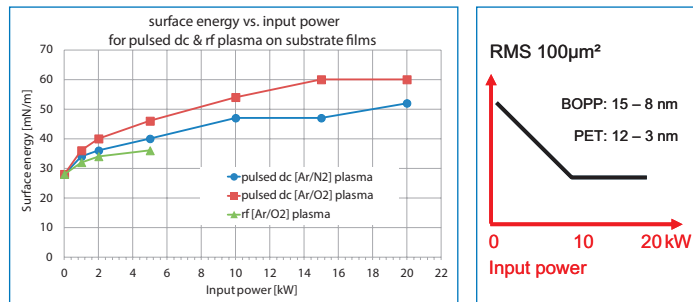### 3.2 Pre-treatment effects on adhesion

The significant effect of the pre-

treatment on metallised BOPP films can be illustrated by executing the tape test on a 0.5 OD film as shown in *figure 6*. It indicates the higher plasma treatment yield to less material being removed upon the tape test. The issue to reinforce the interface due to chemical adhesion by inducing chemical bonds that increase the level of chelation with Aaluminium. The plasma activation step thus produces hydroxyl and carboxyl groups to enhance the adhesion.

Theoretically, the adhesion could be influenced effectively at the interface. Thus, the tape test with thicker films (3.0 OD) would not show a clear result as indicated with thin films.

XPS studies have been carried out to examine the interfacial area between the deposited metal and the substrate with and without plasma pre-treatment. It might be indispensible to understand the chemical composition of the polymer film after plasma treatment without using this technique. The pre-treat-

ed film's condition indicated higher binding energies related to the oxygen species and a higher atomic ratio of O/C at the interface which is responsible for interlocking of the Al and polymer layer.

With respect to a higher optical density film, e.g. 1.0 OD of BOPP and PET films were subjected at pulsed DC power up to 5 kW.

Figure 7 indicates that the light transmission decreases with the higher input power. These results confirm the findings of H. Yasuda[2], that the functional groups create a higher surface energy, forming stable metal oxide formations and promote interlocking of metal-polymer at the interface.

The explanation of this difference is due to the morphological differences for both polymers. PET contains carbonyl, hydroxyl and vinyl groups, and mostly could be amorphous and semi-crystalline, which would yield additional O/C at the interface[18]. Thus less removal of the metal layer, i.e. low transmission was measured for PET as

Figure 9 (left):
Surface energy calculated from contact angle results with respect to the input power.

Figure 10 (right):
An overview of the surface roughness of BOPP and PET metalised film.

Figure 11 (left):
Topography of BOPP metallised film.

Figure 12 (right):
Topography of PET metallised film.
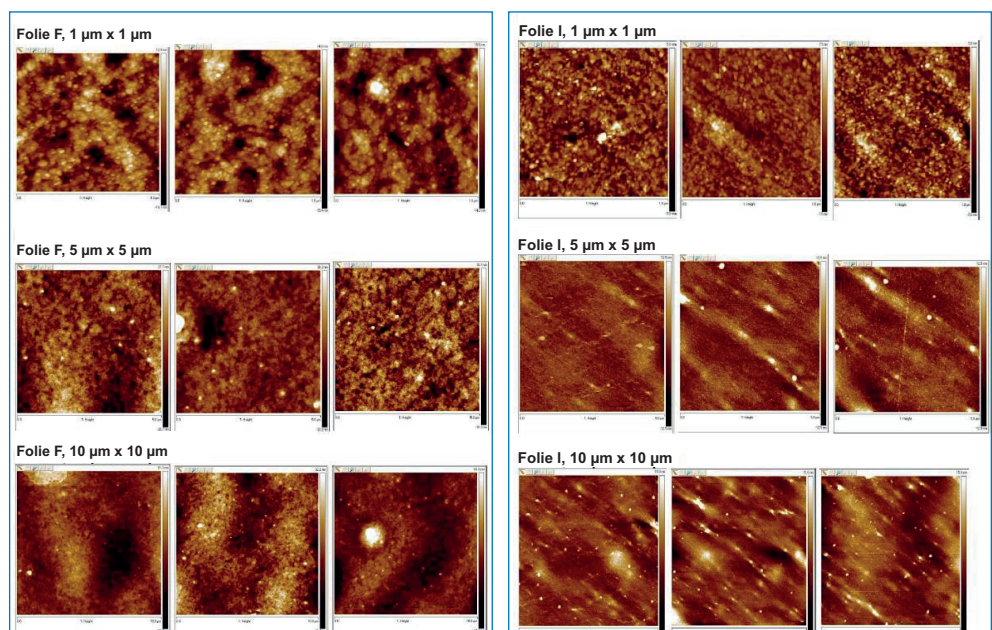
compared to BOPP metallised films.

From another point of view, the effect of surface treatment for thin base films would require lower input power to generate a change in surface energy. *Figure 8* presents the dyne test (ASTM Std. D2578) based on the wettability of calibrated liquids for an untreated 4 micron film as compared to RF and pulsed DC pre-treatment at 0.5 kW. It was evident, that the 4 micron thin base films would be overtreated at a higher input power. A saturation of surface species and degradation would more easily be expected for such thin capacitor films than for packaging films. From *figure 8*, 500W RF input power increased the surface energy from ca. 28 mN/M to 32 mN/m, whereas a DC pulsed treatment achieve values around 40 mN/m. The reason for this discrepancy is due to the physical fact that pulsed DC discharges operate at higher peak voltages and peak currents than in the RF glow discharge, thus higher triggered ionisation and dissociation can be expected which would yield to higher surface energy.

Another method which is widely used in surface engineering is the contact angle measurement of a test liquid. Understanding the instability and reproducibility required for such measurements, a static and dynamic sessile 10 microlitre drop of MilliQ H_2O, n-Hexadecane, and 1,5-Pentandiol were used to determine the relationship between surface energy and pre-treatment. *Figure 9* indicates the incorporation of additional oxygen radicals via pre-treatment to the polymer would create higher surface energy. Although the oxidation effect of aluminium metal to form hydroxides is susceptible upon treatment of polymer surfaces with oxygen for the packaging industry, the present investigation as shown in *figure 9*, confirms previous reports that the surface energy induced by Ar/O_2 is higher than Ar/N_2 plasma due to the higher bombardment energy of the oxygen radicals.

3.3 Topography, cross-sectional view and scratch force

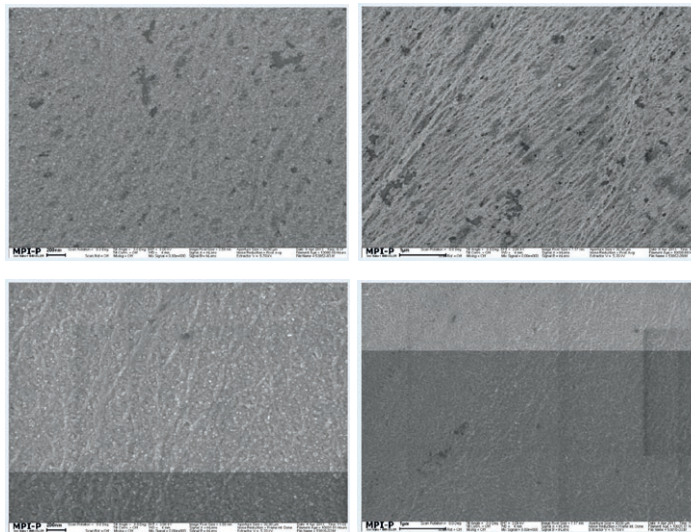The average roughness values of BOPP and PET attained were 8

nm and 3 nm respectively for input power below 10 kW and at 20 kW (*figure 10*). *Figure 11* shows the topography of the metallised BOPP film treated at 10 kW. The roughness values for the root mean square (rms) of the surface topography for 1 micron², 5 micron² and 10 micron² do not show a significant difference between non-treated and treated polymer surfaces for over 10 kW. Below 10kW, the roughness value decreases with ascending input power. Likewise for PET films (*figure 12*), which portray a lower roughness value than BOPP, the same trend was observed. Apparently, the polymer film is being treated to yield a smoother film, and then the deposited Aluminium replicates the surface structure of the polymer. This indicates the low roughness values obtained upon pre-treatment can be related to the roughness values of the deposited metal. High substrate surface roughness is a key factor that adversely affects barrier performance[17], thus in respect to surface treatment, this characteristic is important
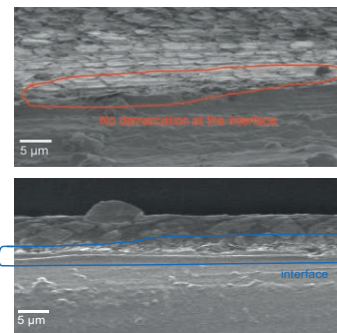

Furthermore, the scanning electron microscope (SEM) examine the surface (*figures 13* and *14*) and boundary (*figure 15*) interface of the metal and polymer, an additional homogeneous interface layer was observed for all plasma treated films. This interface layer as seen in figure 15 clearly indicates the growth of a smooth adhesion layer which might be responsible for interlocking the polymer and the metal.

The metal adhesion on polymer was examined at different input powers, by implementing the scratch force of the AFM cantilever. Considering the growth pattern of the metal film to be uniform,

Figure 13:
SEM micrographs – surface view of untreated (200 nm and 1 micron scales) OPP metalised film.

Figure 14:
SEM micrographs – surface view of plasma treated (200 nm and 1 micron scales) OPP metalised film.

Figure 15:
SEM micrographs – cross-section of non-treated (top) and pre-treated (bottom) BOPP metalised film, the latter indicates a nano-interface film formed.

Figure 16 (left):
OTR of pre-treated BOPP metalised film as a function of input power at various temperatures and 50% rel. humidity.

Figure 17 (right):
WVTR of pre-treated BOPP metalised film as a function of input power at various temperatures and rel. humidity.
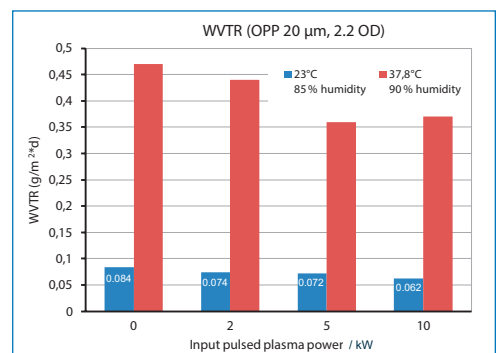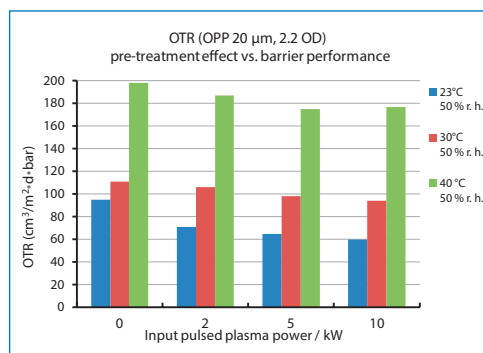
then at the interface the amount of contact force required to remove or induce a scratch is a reference for the adhesive strength of the metal on the film. For a general understanding, the pre-treated films required a unit force of 80–90 N/m as compared to 60–70 N/m for non-treated films.

3.4 Permeability of pre-treated polymer metallised films

Before presenting the effects of the pre-treatment on permeability, it is important to understand that the permeability coefficient has no relationship to the mechanism of transport, e.g. diffusive transport or the flux due to flow.

Applying the described measurement conditions as mentioned in 2.4.7, the OTR was measured in this study and the results are illustrated in *figure 16*. According to the results, the influence of the input power on OTR appears to be effective to create lower OTR values at higher input power. This further confirms the transfer of permeate through the film is retarded due to the interface created as seen on the SEM images.

From a similar perspective the effect of the temperature indicated higher OTR values, which reduce upon input power. The higher OTR values are measured due to increased mobility of molecules, increased pore sizes and hence the diffusion factor. The relative humidity defines the percentage of the mass that would be present in an equal volume of saturated air at the specific temperature; this effect could not be distinguished for the treated films.

The WVTR also indicated the reduction of transmission on higher treatment power for both temperatures and relative humidity as presented in *figure 17*. A similar trend was observed for the PET films. This is a clear indication that proper pre-treatment of the polymer are essential steps to reduce or block the macro- and micro-channels (voids) in the barrier film. Generally, the values of OTR and WVTR accepted in the packaging industry are 100 cm^3/m^2*d*bar and 1 g/m^2*d*bar respectively.

4. Conclusion

Surface functionalisation of polymer film has been presented to indicate the importance of adhesion with respect to the oxygen and water vapour barrier properties. This functionalisation was achieved by introducing polar groups using nitrogen or oxygen plasma at a specific plasma input power.

Based on our findings, the input power influences the amount of light transmitted through the metallised film after the tape peel tests. Furthermore, the surface modified films measured under AFM portray the relationship between input power and surface roughness, which is an evidence smoother surfaces have higher barrier properties.

The effect of improving the adhesion showed a decrease in permeation rates for both OTR and WVTR for the BOPP and is reduced. The degree of barrier performance can be related to micro- or nano-channels (voids) within the polymer film. These channels are in the bulk of the film, which can not be influenced by pre-treatment. As seen from the SEM micrographs, an indication of the formation of an interface layer, interlocking the metal and polymer. This layer seems to block or reduce the permeates from diffusion through the film. As presented by *Mocon Instruments*, permeants dissolve at the polymer interface[20], this implies the rate limiting step of diffusion would be at modified interfaces as presented here.

This is not a new technique, but an update of the ability to combine homogeneous, fast and wide web films, to reduce their permeation characteristics has been managed. This performance on simple base films in the market proves a major leap forward in performance over other proven techniques for pre-treatment of thin films. ∎

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