Plasma pretreatment of polymer web to increase the quality of commodity grade packaging films: an adhesion perspective.

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Abstract:

Pretreatment of polymer films using plasma exposure has the potential to increase metal adhesion, barrier and dyne level (wettability) prior to aluminium deposition. Economical methods to increase end quality to coating manufacturers are increasingly more essential for producers as the food packaging market steadily becomes more competitive, less in pricing and more in terms of quality; barrier, adhesion and convertibility/coating resistance to mechanical damage. Methods of plasma pretreatment were investigated on polyethylene terephthalate (PET) film, focussing primarily on adhesion improvements. Many variables in the process can inhibit the efficiency of the plasma pretreatment and need to be closely monitored and controlled to guarantee higher quality end products. These will be discussed as well as the mechanisms associated with adhesion.

Introduction

Aluminium has been vacuum coated, using resistance heated boats, on a roll to roll production scale metallizer for many decades. Over the years the market demand for certain characteristics in their metallized film has changed based on the preference from their customers, the change in packaging types and an advance in technology. To begin with little was performed in terms of characterising the film, as long as it had a coating of aluminium and there was an improvement in the "freshness" of the product at the end user. As technology has advanced metallized film producers have encountered obstacles to overcome to produce a film of higher quality to keep their customer satisfied, by providing improved barrier properties and greater resistance against mechanical damage during processes post metallizing. Barrier is mostly affected by defects, pinholes and "starry night" effect, due to the way the machine is being operated, maintained or the quality of materials used in the metallizing process. Adhesion, which will be discussed in more detail, is defined as the strength of which the coating (aluminium) is attached to the substrate, in this case Polyethylene Terephthalate PET film. The Aluminium adheres to the polymer surface using a range of different methods. Discussed below are a selection of the common theories.

Mechanical Binding

This is the simplest attempt to explain adhesion. This is where the aluminium and the polymer surfaces interlock in a "lock and key" fashion where irregularities occur in the topography. This theory is commonly used to explain the adhesion of electroless plating of polymers, using an initial treatment to roughen/key the surface prior to metallizing. The only issue with this theory is that it does not explain high adhesion on smooth surfaces, this is where other theories come into play [1].

Electrostatic theory

The difference in chemical potential between two materials causes a charge carrier diffusion of electrons and formation of an electrical double layer at the interface. It is the electrical attraction that provides the adhesive properties in this instance [1].

Diffusion Theory

This theory involves Brownian motion to explain adhesion. When two materials are put in close contact with each other, interdiffusion occurs in the case of molecules or polymer chains. This interlocks the two constituents. This theory however only occurs when the two materials are similar in chemical makeup or solubility, for example two polymers, so would not be of great significance in metallised films [1].

Covalent Bonds

Covalent bonds are said to be an essential makeup of the adhesion strength between aluminium and polymer web. Authors have found that oxygen needs to be present in the surface of the polymer to be able to create C-O-Al bonds [1]. This creates one of the highest bond strengths of around 1076 kJ/mol. As well as covalent bonds hydrogen bonds are also responsible for higher adhesion in films, but are of less significance than covalent bonds [1].

Ways to Improve Adhesion in Production

There are multiple ways to improve the adhesion of aluminium to a polymer substrate. The type of polymer film, whether it be PET, PE, CPP, BOPP, to name a few, is very dependant on the recipe of the bulk polymer, giving differences in characteristics of the surface and what chemical structures are present on the surface. Some polymers and polymer recipes have been chosen for the fact that they have oxygen containing groups on the surface to promote adhesion. Other films are modified on the surface by adding a low SIT (seal initiation temperature) layer to the surface. In this case the heat from the thermal evaporation will be enough to initiate melting of the top layer, which the aluminium then condenses onto, whereupon the cooling of the polymer afterwards causes a strong bond between the aluminium. The pitfalls of this method are that it adds further cost to the film and can potentially sacrifice some of the barrier qualities in exchange for the high adhesion.

Chemical treatment of the film is another method to increase the adhesion properties between the polymer and aluminium. Also known as chemical primers, chemical treatments commonly involve co-polyester or acrylic coatings added to the surface prior to metallizing. These are specially formulated to increase surface energy and enhance adhesion of the film surface. Treating/coating the film in this way again increases the cost of the film roll in the range of 10-100%. It has also been found that plasma pretreating chemically treated films can reduce the barrier functionality of the film. This needs to be noted when running chemically treated film in a machine typically set up to plasma treat "plain" film. This means that film producers need to be aware of the film properties their customers want, which may be high adhesion, high barrier, or both, meaning there needs to be compromise between one or the other when using certain techniques.

Adhesion measurement techniques

Testing for adhesion following metallizing can be performed in many ways ranging from the most simple industry standard, the "tape test", going up to replicating laminated layers representative of what would be utilised in packaging applications.

Tape Test

The tape test is an extremely simple technique that benefits from having the ability to be used at the machine or in a laboratory by any operator or technician. The test recommends Scotch 610 tape that has a standard typical bond strength [to steel] of 47N/100mm, calculating as 7N/15mm. Peeling the tape off at a 180° angle reveals either a fail (delamination of the aluminium layer) or a pass (the aluminium retains integrity) when viewed on a light box or through a light source. This qualitative test allows a quick quality control of rolls, however it has been observed that some samples with poor adhesion using other techniques can pass the tape test. The data sheet of the tape also states that 3M is aware of this tape being used for this application and does not recommend it due to the variation in adhesion with it being a pressure sensitive film and differences in adhesion levels throughout the tape from the manufacturing process. However, it is not a test to be overlooked. The reason why this particular tape is used is due to the technical data sheets being available to give guidance on what the adhesion may be to an extent, which is extremely invaluable information at the short timescale it takes to perform the test.

EMA, Heat sealed EAA Peel test

The heat sealed peel test was designed by the European Metallizers Association (EMA) and has since been adapted for the tests in this article to follow the ASTM F88 and F904 standards and the ISO 11339-2005 standard as well as tailoring the method towards the equipment available in the laboratory. This method involves heat sealing EAA (Ethylene Acrylic Acid) film to the metal surface and peeling the EAA at a 180°

angle. The way in which the interface peels can tell a lot about the adhesion characteristics.

1) An adhesive peel is where the adhesive (EAA) peels from the aluminium interface leaving the coating intact, demonstrating good adhesion between the aluminium and substrate.
2) Cohesive peel where the aluminium is partially removed by the EAA film leaving parts of the coating behind on the substrate.
3) Delamination is defined when the entire aluminium coating is removed from the substrate by the EAA film. When the adhesion of the aluminium to the substrate is high other failure modes of the EAA can be observed.
4) Material breakage is when the EAA has been pulled to an extent where it breaks at the seal interface.
5) Remote material break is the same phenomenon, but the EAA fails away from the seal interface.
6) Material elongation is when the EAA film is pulled to an extent where it is stretched and elongated starting from the intact seal interface.
7) Peel with elongation is when the EAA film is peeling away from the Al surface and stretching at the same time, displaying a failure between the EAA and the Al and not the Al and the substrate (Figure 1).

The limitations of the method are that in the standard it is recommended to use 1 mil EAA. Following extensive trials it was found that the tensile strength of 1 mil EAA is around 2-3 N/15mm and many adhesion promoting techniques exceed this range. Using 2 mil film the tensile limitation is around 5-6 N/15mm.

Solvent Based Adhesive Lamination

Another method of peel test is also used to recreate realistic environments that would be seen in packaging at the seal interface. The solvent based adhesive lamination test utilises the same peel technique as the EMA peel test but using different seal constituents to create the peel interface. First a layer of solvent adhesive is applied to the aluminium surface and a PET or sealant web (PE, CPP, OPP) laminated to the top. Non stick paper is added in between part of the lamination to create a seal interface where the peel test can be made [2]. This method is advantageous due to the lamination replicating a layer stack, or part of a layer stack, that may be found in a typical food package. Not exposing the film to high heat, like the EMA/EAA method may have an effect on the peel characteristics and the bond strength observed.

When measuring the peel strength of the aluminium to PET film there are many different failure modes that can occur depending upon the adhesion strength. Failure modes according to the ASTM F88 standard are: adhesive peel, cohesive peel, delamination, material break, remote material break, material elongation and peel with elongation (Figure 1). When adhesion testing it was difficult to characterise what the adhesion values were and the characteristics of the overall peel length using the ASTM standard alone. It was devised that the failure modes/ peel characteristics were also categorised into four main categories (Figure 2):

- Low initial peel force followed by low peel force for the full peel area
- High initial peel force followed by low peel force for the full peel area
- High initial peel force followed by high peel force for the full peel area
- Extremely high adhesion at the interface from EAA to metal resulting in elongation and failure of the EAA with no metal removal.

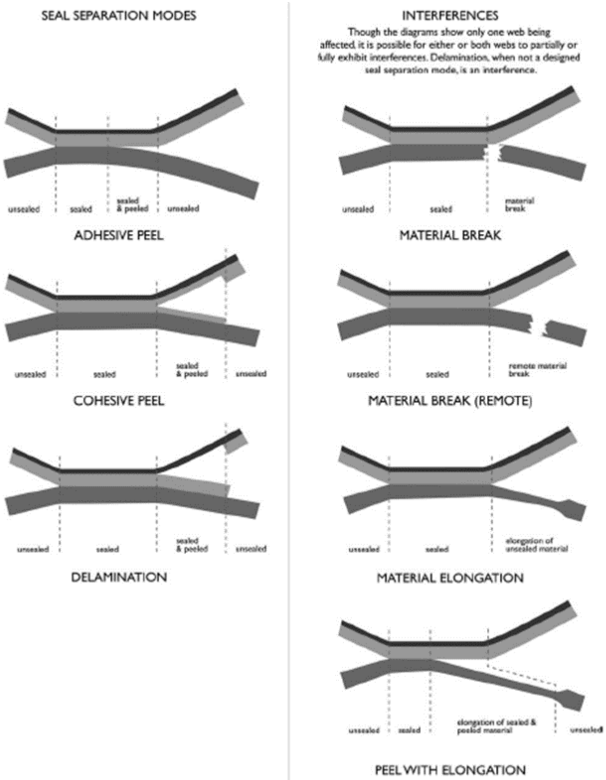

Figure 1: Peel test failures as explained by ASTM F88

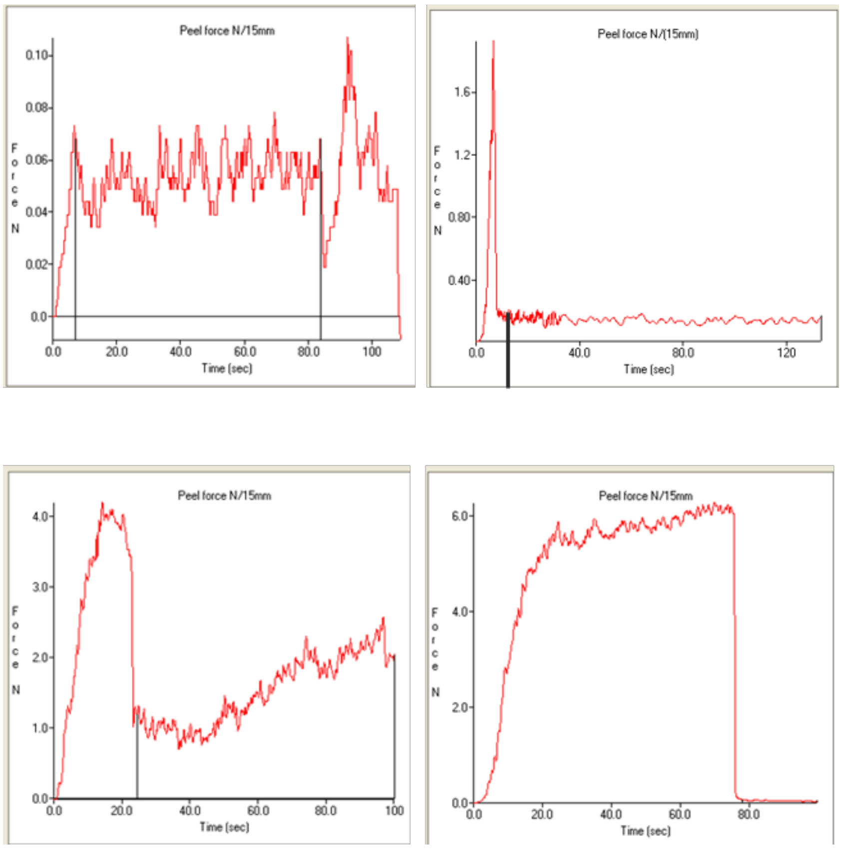

Figure 2: The four main peel force characteristics observed when performing peel tests.

Methodology

The machine platform used for the investigations was a modified 2015 Bobst K5000 roll to roll vacuum coater with a thermal resistive PVD source to deposit the Aluminium. The machine had a maximum effective coating width of 2450 mm and the maximum achievable line speed was 1000 m/min. The modified pretreatment device/unit that has been investigated in this study is in-vacuum plasma. Plasma pretreatment of the film occurs within the vacuum chamber immediately before where the aluminium deposition process is going to take place. The plasma treater used in these investigations was a Bobst design planar "magnetron" style treater. The assembly is a water cooled dual electrode construction using an AC 50kHz generator, therefore eliminating the need for a separate anode and increasing stability over using a DC generator.

The K5000 machine is divided into two seperate zones, namely the "winding zone" and the "evaporation zone". The evaporation zone is pumped with diffusion pumps and runs during typical production in a pressure regimen between $8x10^{-4}$ and $9x10^{-5}$ mBar and the winding zone ranges between $9x10^{-2}$ and $8x10^{-3}$ mBar. The plasma treater is located in the winding zone and the pressure was monitored in the plasma treater using a Baratron capacitance manometer gauge (Figure 1). Gas was added to the plasma zone using mass flow controllers to control the flow of two different gases providing adjustable gas ratios.

The film used for all of the trials was a standard commodity grade 12 μm PET film by Trias Sentosa (ASTRIA film single side corona treated). The web was 1250mm wide and plasma treated/coated on the corona side.

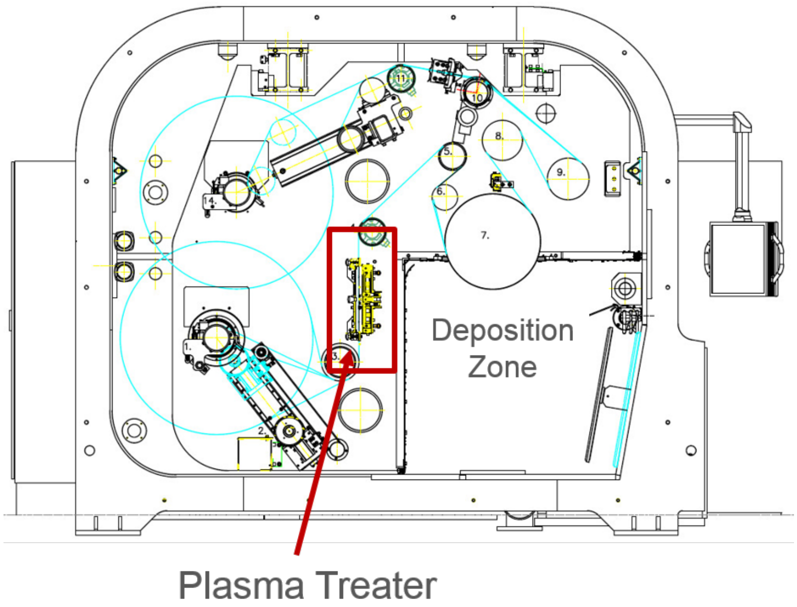

Figure 3: Cross section of the Bobst K5000 Metalliser. Indicated with the red box is the location of the plasma pretreater.

Results and Discussion

Plasma pretreatment of the PET film was performed and the film was left uncoated. These samples were assessed for any changes in surface characteristics after plasma treating at typical production speeds. Following SEM evaluation at 20,000X magnification there were no significant visual differences between the polymer surfaces. This would be expected with the small amount of plasma dwell the film would have been subjected to. To be able to visualise any nanotopographical changes on the film surface atomic force microscopy would need to be performed at high resolution (1 x 1 μm)

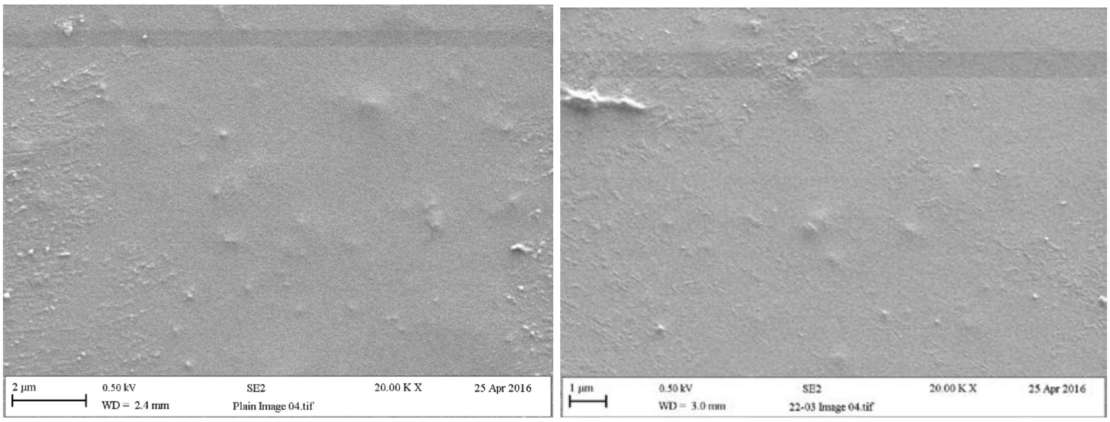

Figure 4: SEM micrographs (at 20,000 X magnification) displaying lack of difference between plain film (left) and plasma pretreated film at a production speed (right).

Raman and FTIR (Fourier Transform Infared Spectroscopy) were used to investigate any difference in spectra with these two methods. Due to the plasmas effect on the film being at the surface and the two methods testing at a certain depth within the bulk of the sample no differences were observed between plasma treated and untreated film on the spectra (results not shown).

The most beneficial data was obtained from adhesion testing metallized samples that had been plasma treated with different conditions. This method also represents a real outcome of a standard metallised film in a production size machine. Adhesion testing is also a method directly relatable to the quality control processes film producers would use in the laboratory of a production facility.

Increasing the power density applied to the modified treater affects the treatment intensity of the plasma. A greater plasma intensity aids the adhesion of Al to PET, the issue of overtreatment is not as important for PET than other films such as CPP and BOPP. Overtreatment can cause a layer of low density molecules on the surface, that are loosely bonded to the bulk of the substrate, where the aluminium adheres to the substrate by the weak bonds of the top layer.

In this study increasing the power density provided an almost linear increase in adhesion (Figure 3). It is unclear whether or not at the higher power the adhesion is leading to a plateau. Further work would involve going beyond what was tested to calculate when the breakdown of the film would be observed, by monitoring the adhesion values. Plasma treating at any power provided a significant improvement in adhesion compared to the untreated film.

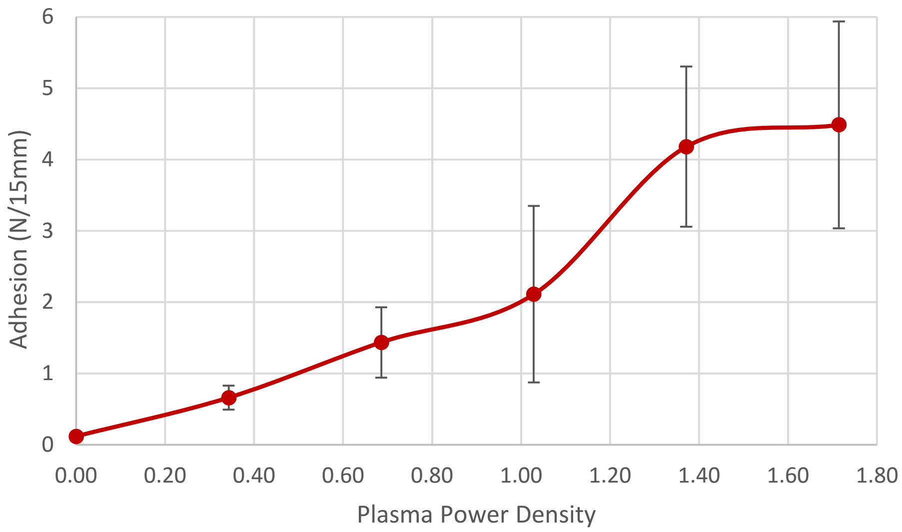

Figure 5: Plasma power density in relation to adhesion. High power density produced high adhesion samples.

Plasma treating the film with different gas types also had an effect on the water contact angle. Following testing of the film using dyne pens it was found that the dyne level was too great to be measured accurately using dyne. Using water contact angles on aged samples it was shown that inert plasmas produced the least wettable surface and reactive plasma produced the most wettable (Figure 4). It is discussed in literature that using reactive plasmas introduces oxygen groups onto the surface of the film that are responsible for strong covalent oxygen bonds between the aluminium and the substrate (C-O-Al) [3].

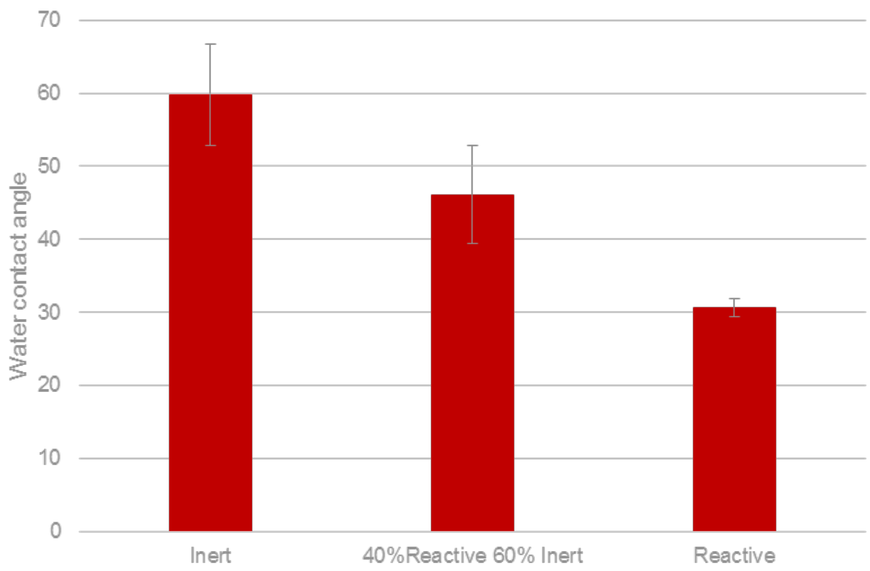

Figure 6: Water contact angles in relation to the Inert/Reactive gas ratio used for plasma treatment. The lower contact angle corresponds to a more wettable surface.

Metallized film was produced using plasma treatment with varying amounts of reactive gas. Increasing the reactive gas content although potentially increasing the oxygen containing groups on the surface of the films, decreased the adhesion values in this particular study (Figure 7). The differences were not statistically significant due to the size of the error bars therefore more trials would need to be run to provide a conclusive result on what effect oxygen containing plasmas of different concentrations are having on the adhesion.

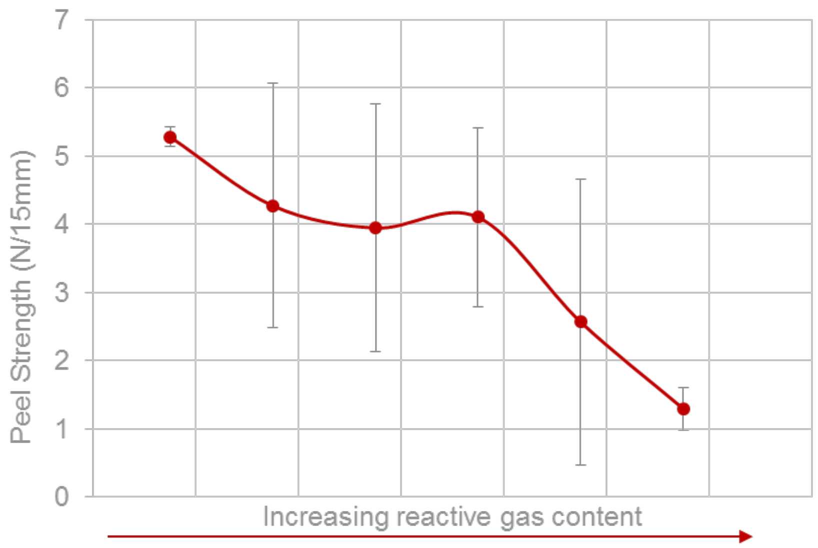

Figure 7: Relationship between peel strength and plasma oxygen content, decreasing in value as the oxygen content is increased.

Conclusions

Within the body of work a classification system for the peel test characteristics was developed to cover the four main adhesion strength peel characteristics commonly observed throughout a test area.

Observing the film surface using SEM, no visual differences of the surface could be observed at 20,000 X magnification, further work may include atomic force microscopy to obtain high resolution images of the nanotopography. Adding reactive gases to the plasma increased the wettability of the PET surface, suggesting oxygen groups have been added or created, however this did not relate to adhesion in this case. Increasing the power density resulted in a linear increase in adhesion. To conclude, it was evident that the plasma treatment of film to provide adhesion needs to be optimised for each application and, depending upon the requirements of the end user, where adhesion may need to be sacrificed to some extent to achieve the best barrier.

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