# ADDING VALUE TO VACUUM COATED PRODUCTS BY IMPROVING METALLIZED FILMS PROPERTIES AND FUNCTIONALITIES

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**Introduction**

The demand for metallized film with increased functionality is steadily growing. The trend of replacing more sophisticated films with less valuable materials is not new: down gauging, layer reduction, foil replacement in a growing number of applications, use of mono-materials of compostable films are all consolidated trends in the most advanced and innovative flexible packaging industry. This paper will describe and discuss various solutions implemented in recent years to add functionalities to the vacuum coated films for high volume requirement, such as metallization. For all most popular polymers, there are potential growth opportunity in improving selected properties such as gas and moisture barrier and adhesion . Although polymer composition and pristine treatment usually represent the pre-condition to achieve high quality and performance in the vacuum coated product, this paper will discuss strategies and solutions implemented during the vacuum coating process which contribute to improve metallized film functionality.

The spectrum of tools actually or potentially existing for the industry are schematically listed below, subdivided into three substrate treatments sequence :

A Pre treatment

- Plasma pretreatment
- In Vacuum coating
- Substrate surface planarization and seeding

B Deposition

- Vacuum Level
- Cleanliness
- Deposition control
- Stoichiometry
- Plasma activation

C Post treatment

- On-line coating
- Off-line coating
- Post-plasma treatment

This paper will briefly survey the current status of the technology and concentrate on a few selected solutions which, in the author's experience, represent new and valuable opportunities for the industry to improve product quality.

## 1- Processes and technologies

1.1 - With "pre-treatment", we mean all modifications of the original material surface which aim to improve the metal deposition step ; they include different kinds of coating and energy activated surface modification.

Coatings perform the function of covering and stabilizing loose species on the polymer surface : many authors (an example, ref.( 1)) and researchers have pointed out the presence of particles from the production environment or from the human activity which would interfere with the vacuum deposited material possibly creating micro-cracks and pervious sites. Short polymer chain or additives blooming to the surface are also responsible for creating unevenness. Surface planarization and porosity filling is another function performed by a pre-coating process. Examples of coating proposed in recent years are (citations have been deliberately limited to works presented at recent Aimcal Conferences) :

Air, off line coating (2), (3)

Energy curable coatings applied in the vacuum chamber (5), (7)

Melamine coating in the vacuum chamber (6)

Plasma Pre-treatment is well established in vacuum coating : the material crosses the ionized gas, undergoing to ions and electrons bombardment . This energetic impact of charged particles modifies the film surface property by a scavenging and cleaning action. Moreover it can functionalize the surface affecting the surface polarity and activating nucleation points for the depositing species. It is considered in many cases a powerful tool to increase the bond between the polymeric surface and the vacuum deposited layer but its success depends on the material type and on the careful control of power intensity to prevent polymer damage with a consequent property loss. The plasma treatment effect on barrier properties is, somehow, less universally recognized and it is still more material dependent than the adhesion promoting one. In the next paragraph, we will illustrate and discuss success stories on use of plasma treatment on diverse materials and conditions.

Substrate material planarization and deposition “seeding”. This category, which is basically a special kind of pre-coating , includes a number of different processes characterized by the generation of a “thin” layer prior to deposition creating a more suitable base for the thin film growth. An example is the seeding effect of silver to promote enough bond for zinc deposition on polypropylene in capacitor film manufacturing. Or the “gettering” effect of metal deposited from magnetron sputtering treatment which plays role in improving adhesion and barrier. Another solution consists of creating an oxidation monolayer precursor prior to the functional layer deposition. This paper will illustrate the results of a recent project with industrial aluminium metallization.

1.2 The deposition of Aluminium coating is functional to the quality of the barrier layer and both machine design and process control give a significant contribution to the achievement of a good result. This topic has been the subject of one of our previous work recently presented also at an Aimcal Conference (8). It was based on data from the shop floor and actual production showing the impact of process parameters (Vacuum level, winding quality, cleanliness, coating thickness and uniformity) as well as treatment and evaporation control on metallized film barrier properties . Some authors (9) suggested the advantages of plasma activated evaporation which, in particular for reactive evaporation to produce Aluminium oxide, would be instrumental to increase reaction efficiency and speed and create a , somehow, more compact thin layer structure due to a more energetic environment. This paper will illustrate the latest results mainly related to reactive evaporation for AlOx production , concentrating on the efforts to achieve a resilient product which can withstand the converting operation.

1.3 - Post treatment includes all processes implemented after the thin layer deposition aimed to preserve or to improve the product quality, in particular, the barrier properties.

In-vacuum coating would be the ideal solution to protect the thin film, for example vacuum deposited aluminium, by a transparent organic layer immediately after the deposition : it would protect the pristine condensed metal from any mechanical damage, including microscratching or from chemical attack from contamination etc. Energy curable chemical processes have been described by several authors (5) (7). They consists of depositing a monomer by in-chamber spraying or by a special coating process , immediately followed by an energetic source for instant curing and crosslinking (in the mentioned works it is an electron beam gun or a plasma source) with the formation of a polymeric protection on the vacuum coated film. Another approach is the evaporation of melamine on the vacuum coating layer prior to film winding (6), forming a transparent and protective layer without any further treatment . These products generally do not increase the metallized film barrier but they prevent its deterioration by mechanical or chemical effects, which, for most of applications, would be equally important.

Plasma post-treatment has been proposed as being able of performing different actions depending on the requirement : a consolidation of the deposited layer to create a more compact texture with improved property; plasma bombardment with an oxidizing gas could also create a controlled very thin oxide layer to protect the barrier coating from further oxidation or contamination and finally it would be useful to complete stoichiometric oxidation in the case of reactive evaporation in the AlOx process. (4) Therefore plasma post treatment is, potentially, a powerful tool to complement an high quality deposition but, according to the Author's experience and information, the concept needs to be fully proved at the industrial level.

The atmospheric coating function would be to protect the metallized surface from damages during the converting processes (such as, slitting, printing, laminating, bag making) and from the slow, but, at times, continuous oxidation progress occurring after deposition , which limit the "shelf life" of metallized film prior to be worked into final products. This ideal solution is, however, very seldom justified, on economical ground, for commodity film for flexible packaging. There are, however , efforts to develop coating products which have intrinsic barrier properties intended to upgrade metallized films and to extend the most popular products application ranges. Likewise, the clear barrier films such as Aluminium or silicon oxide coated products, need a protection which could ideally compensate and eliminate the intrinsic oxide brittleness, possibly causing , if unprotected, major barrier properties deterioration when stretched during converting or handling. There are already solutions recently reported (2) which are being introduced in the industry, looking for technically consistent solutions and very cautious about their cost compatibility. Next paragraph will describe experience and results of our Company's effort to develop partnership project to comply with all the industry requirement.

## 2 New Solution and Results.

This paragraph illustrates two development projects aimed to upgrade the most used metallized films, that is Bi-oriented Polypropylene (Bopp) and Polyethylene Terephthalate (Pet). in particular, the first project target have been the improvement of bopp oxygen barrier by pre-treatments; the second case refers to clear barrier Pet by Aluminium Oxide (AlOX) coating and the results of efforts to achieve and maintain consistent and resilient barrier properties .

a) **BOPP pre-treatment** : bi-oriented Polypropylene film for metallization are usually fabricated by extruding, in its basic version, three layers : the PP omopolymer core is sandwiched between an outer, metallizable skin designed to provide adhesion for the deposited metal and an inner sealable layer. The metallization side is usually corona or flame treated to increase the metal-polymer bond and its composition and formation are known to be crucial for the final product property, not only for the bond strength but also for the barrier.
Our experience confirmed that in-vacuum bopp surface modification immediately preceding the metal deposition can have significant effect for the metallized film properties improvement: we illustrate results of plasma treatment and "tie layer" application for a number of different film type, all experience characterized by being done on industrial metallizers at shop floor level conditions.
**The plasma treatment** conditions used for this project are :
Type of plasma : AC hollow cathode plasma treater 80KHz 10-20 Kw
Gas : Air or Argon-O2
Treatment dose : 0.8 -1 Kjoule/m2
The treater design and process condition represent an optimization supported by a two years' industrial experience (8 ) and it includes :

- An higher frequency power supply designed to minimize arc and to guarantee a continuous treatment.
- An high treatment dose : the tests have demonstrated that higher plasma power is beneficial for the barrier properties, depending on the bopp surface composition and energy.
- A larger plasma zone to guarantee sufficient "residence time" even at high web speed.
- Treater box design to prevent back treatment

**<u>The "Tie Layer"</u>** consist of a nano-thin metal oxide deposition which can possibly perform any of the following actions or a combination of all : surface planarization like a coherent coating; generation of a highly adherent intermediate surface to promote higher metal bond; condensation "seeding" due to its high surface energy . The tie layer is formed prior to the bulk metal deposition by creating a controlled oxidation zone in the vacuum machine without interfering with the regular alluminum deposition.

In this project the two pre-treatments have been used separately and in combination : although they are intrinsically different in the action mode on the surface, they have often a synergic effect on improving the film properties as the following graphs will illustrate .

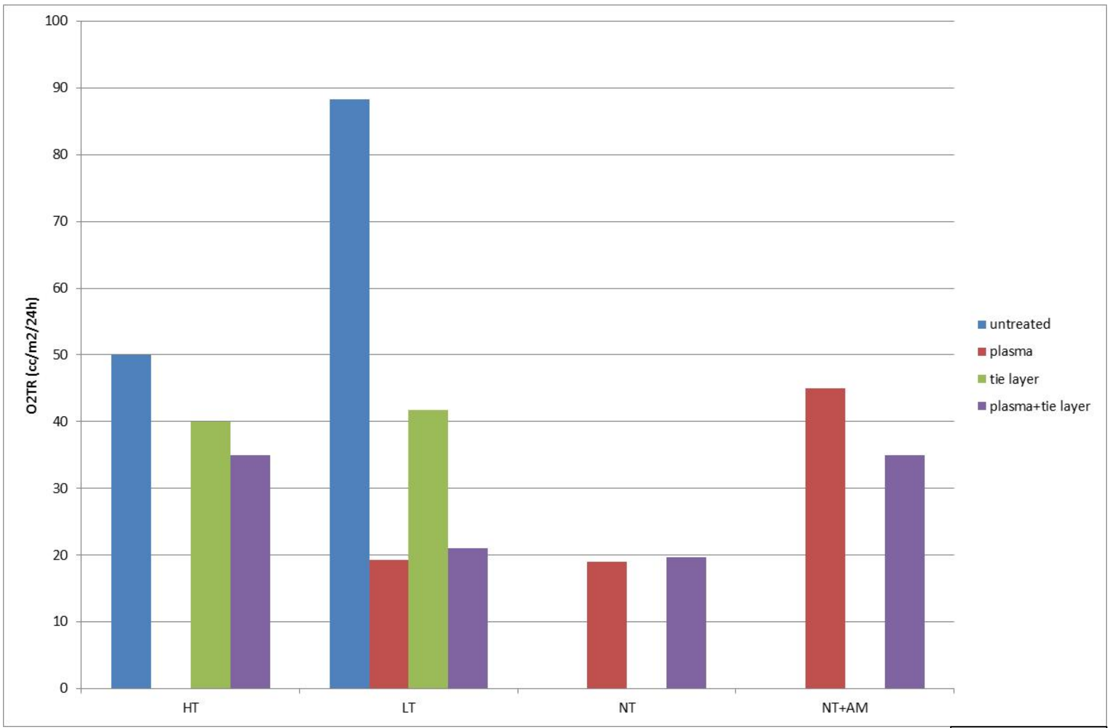
A picture of the behavior of different BOPP films is shown in the graphs number 1 and number 2, for barrier and adhesion, respectively, in which multiple film trials have been divided according to the original bopp film surface property, identified by acronyms which , broadly correspond to the following properties :

NT : no treatment ; the bopp film has been deliberately metallized without any corona or flame treatment: surface tension < 35 dyne-cm

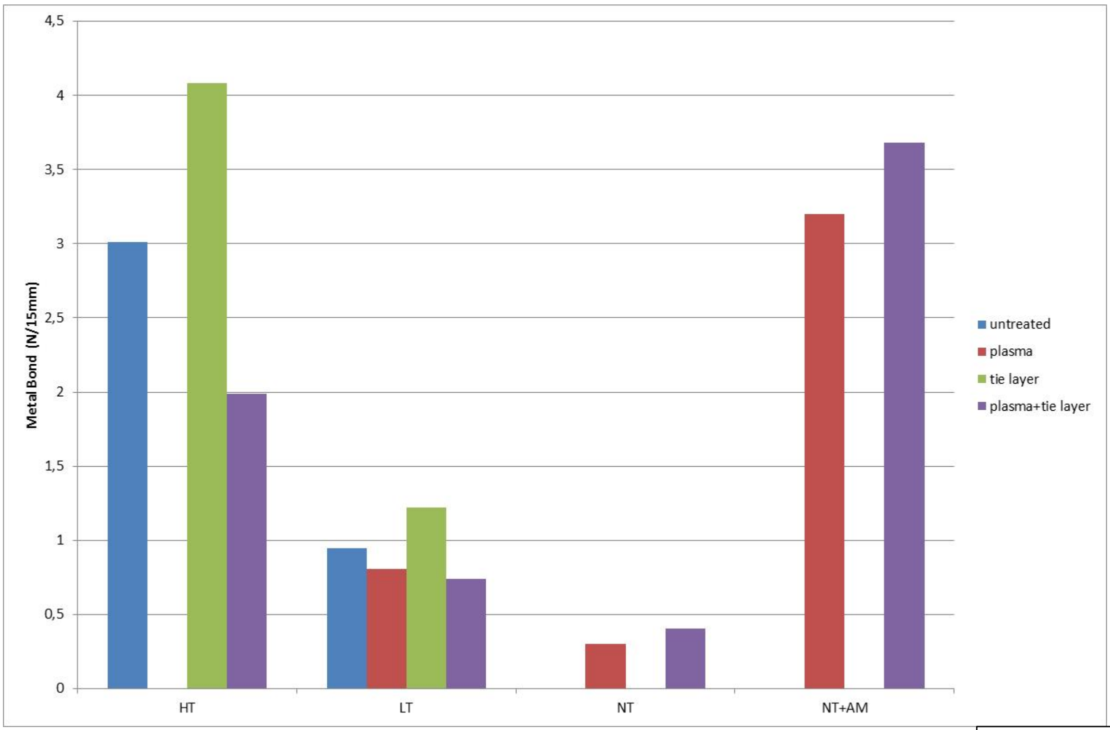
LT : low corona treatment surface tension < 38 dyne/cm

HT : "Medium/High" corona or flame treatment surface tension >40 dyne cm

NT + AM : a few types of film had been extruded with a special skin, characterized by lower temperature melting co-polymer intended to promote metal adhesion ; non treated.




Graph 1




Graph 2

The bopp pre-treatment case, represented in this graph , demonstrate that the polymer film property and the nature and effectiveness of pre-metallization treatments are strictly correlated , main points resulting from the study are :

- Plasma is a very powerful tool to achieve high barrier properties (O2TR <15/10 cc/m2/day is bopp benchmark) especially when the film has a low initial treatment
- Low treatment means, in general, moderate to low metal bond , therefore, in principle, high barrier goes together a limited bond: the combination of plasma and tie layer can optimize the intrinsic adhesion or barrier tradeoff.
- Co-polymer skins for high adhesion are moderate barrier solutions: the tie-layer can improve the barrier while retaining an high metal bond.
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b) **Clear barrier with Polyester film (AlOx)** AlOx coated Pet is produced by a process defined "reactive evaporation" because oxygen gas, introduced into the evaporation section of a metallizing machine, mixes and reacts with the metal vapour forming Aluminium oxide. The compound deposits on the polyester film surface as a thin and transparent layer, significantly increasing the polymer original barrier properties. While the AlOx to Pet cohesion bond is generally good, the two materials behave differently if subjected to mechanical stress causing the brittle barrier layer to crack when stretched , potentially losing its barrier property. This represent the often emphasized disadvantage of the AlOx coating on the assumption that the barrier loss can occur by processing it into the final product due to the mechanical stress created along a typical sequence of slitting, printing, laminating and bag making . This section will illustrate the current status of our work to minimize the risk of AlOx coated film damage during subsequent working operation. There are two steps , each one representing a different level of product performance : 1- the deposition and reactive process control during the vacuum coating; 2- the protection of the vacuum coated layer by a subsequent atmospheric top coating.

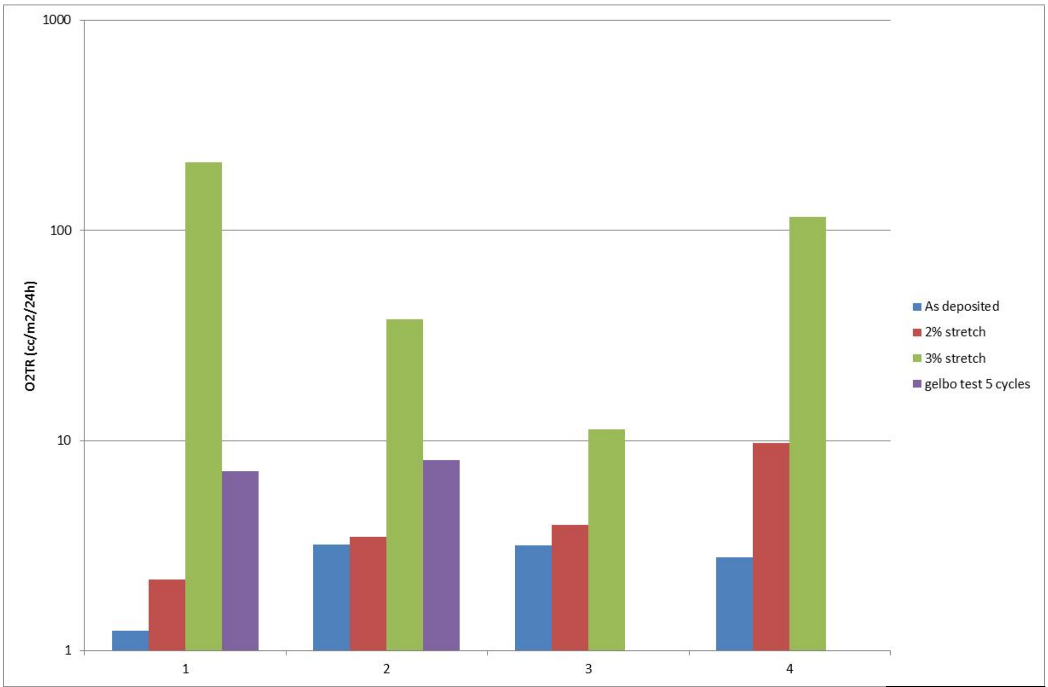
1 - The graph n.3 represents the average results of four different type of very common Pet film : each of them have been metallized with reactive evaporation process to deposit AlOx thin film. The process conditions are the same in all cases :

- o AlOx thickness : approximately 10 nm
- o Deposition speed : 550 – 600 m/min
- o Aluminium evaporation : < 1 gr/min per evaporator

- Plasma treatment : used in approx. half of the trials; it seems to have only marginal effect on the product properties and we do not have considered it as a variable for this study.

It is a "conventional" reactive evaporation process, with no use of plasma in the evaporation section (no "plasma activation", as cited above) , but the setting and control of the parameters governing the metal vapour oxidation are instrumental to guarantee consistent and resilient barrier properties. The two main criteria are : thin film thickness and sub-stoichiometric oxidation.

A very thin, coherent film thickness can be controlled by a precise reaction gas feed and distribution and by sensitive optical measurement of the transparent layer.
A sub-stoichiometric Aluminium oxidation has demonstrated to produce a more mechanically stable barrier than a fully oxidized film : this observation leads to the need of a very accurate process control to optimize the trade-off between good barrier and transparency.
The graph represent the barrier change due to mechanical stress : the tests consist of applying a force to produce a controlled AlOx film strain. It is apparent a progressive increase of permeation on the stretched material : until 2%, the barrier loss is limited for all films representing average values of multiple trials; over 2%, and even more at 3%, some film tend to lose almost entirely the barrier property showing that the barrier layer has been catastrophically damaged. For two film types, the graph show also the comparison with "Gelbo" test (a combination of film stretching and twisting, considered a rather severe representation of typical film conversion operations) : in both cases, the gas transmission increases but most of the barrier properties are saved. The comparison between stretching and "Gelbo" tests confirms the fact that also the former represent a simulation of severe handling condition : in fact, for 12 micron Polyester the force applied to get 2% elongation equals a stress of about 80N/mm2 or a tension of almost 1000N for 1 meter wide width, well above all standard values for converting operation.



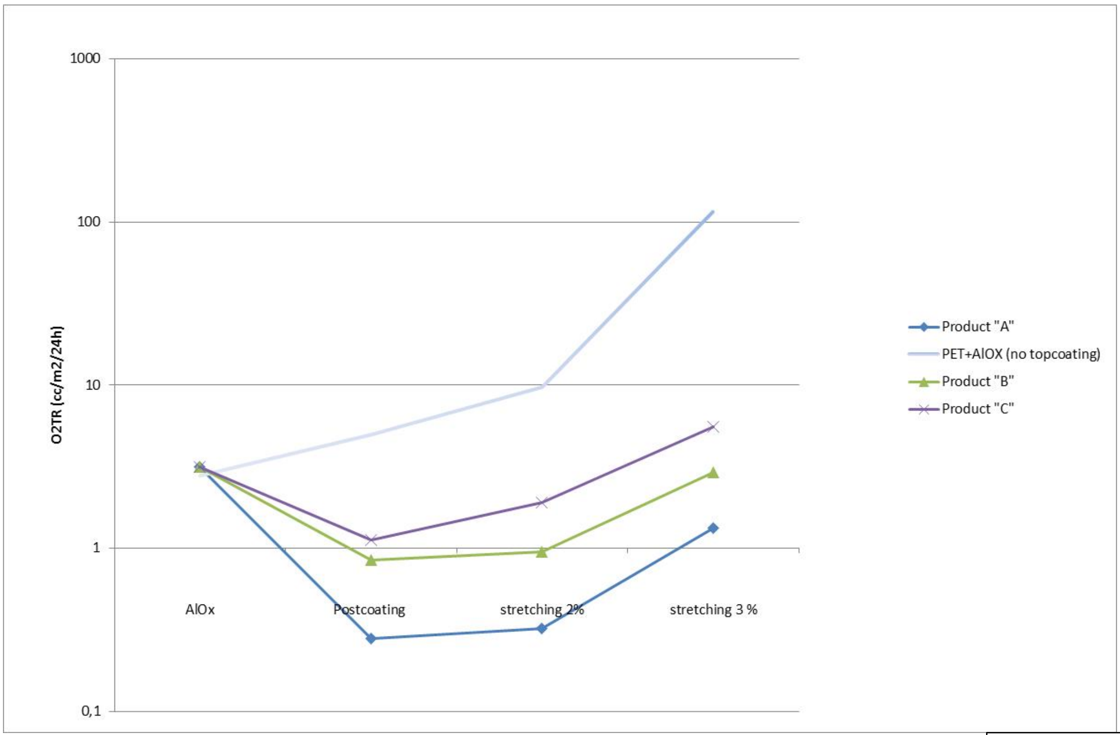

Graph 3

2 – An improvement of the AlOx coated film resistance to mechanical stress can be achieved by a protective coating : paragraph 1 describes various solutions recently proposed to safeguard the original AlOx barrier or even to increase it and the search of an optimized solution for most of the requirement is still an ongoing work. This paper contributes

to this effort by illustrating and discussing the preliminary results of a project still in progress to find a coating product which is chemically compatible with AlOx and can consistently increase the stability of clear barrier films.  General requirement are :

- Compatible with Aluminium oxide and with good adhesion
- Fully transparent
- Eco-friendly and food compatible , water base
- Barrier and mechanical property  to compensate for AlOx micro-cracks
- Low  application weight for low product cost
- An higher level requirement would be retortability

The graph n. 4 shows the average results of multiple trials: after testing a number of formulations, designed for the purpose of barrier and protection, we show here the results of three  products("A", "B" and "C") looking more promising and providing layer protection and better barrier.




Graph 4

All the three coating are water based formulations, applied by standard gravure cylinders ; weight is approximately 1 gr/m2 on dry basis.        All three lacquers reduce the AlOx oxygen permeability and guarantee the barrier consistency without reasonable level  under mechanical strain.   The ongoing work will find out if there is a single solution for the use on all kind of films and will identify the optimized product in term of application weight, cost and availability.

**Summary and Conclusions :** Among the number of solutions recently proposed  to upgrade properties and performance of the traditional aluminium metallized films, this paper has shown the results of extensive trials on different kind of films mainly aimed to improve the barrier performance. The metallized BOPP and the AlOx coated Pet have been represented here in more details: for the former polymer, we have shown the results of pre-treatment by plasma and of a tie-layer deposition; for AlOx Pet, the focus has been on protecting the clear film barrier with a top coating, formulated to salvage the properties by compensating the effects of possible AlOx micro-cracking under mechanical strain.  While optimization work is going on to provide more consistent and economically viable industrial solutions, this work confirms the need of a joined efforts from base film makers and process-machines provider to achieve superior product properties.

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