Metal Adhesion to PET Film

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Introduction

As the move from rigid packaging to flexible packaging continues the barrier of materials used becomes more important. In general, the use of metallized films, and more specifically, the use of PET films, to achieve the barrier needed for shelf-life has been increasing for a number of years.

There are several PET films from larger and larger groups of film manufactures for use in barrier (metallized) applications. This paper will discuss the adhesion of metal (aluminum) to PET films.

Adhesion

The interfacial region where metal atoms come into contact with the film surface may be simply classified as mechanical, diffusion, chemical, and combinations of these types. The type of interfacial region formed depends upon substrate morphology, contamination on the surface, chemical interactions, the energy available during interface formation and the nucleation behavior of the deposited metal.

In the case of metallizing PET film, the most important aspects of adhesion arise from mechanical and chemical bonding at the interface. The mechanical interface is characterized by an interlocking of the depositing metal with the rough surface of the substrate. The strength of this interface will depend upon the mechanical properties of the materials being brought together: metal and film. The chemical bonding depends upon the formation of chelates of the polymer oxygen atoms with the metal atoms (1 and 2).

Metal

When the metal atoms strike the surface during deposition, they lose energy to the surface and condense on the surface. During the condensation, the atoms have some degree of mobility on the surface defined by their kinetic energy and the strength and type of interaction between the atoms, clusters of atoms and the substrate surface.

The metal atoms / clusters will grow to form a continuous metallic film. It has been suggested that the atom density and growth mode determine the effective interfacial contact area and the development of voids in the interfacial region. Atom density and metallic crystal orientation formed during the deposition can be affected by environment (residual gas in the chamber), contamination, surface inclusions (filler), and deposition techniques. In addition to the effective contact area, the mode of growth of the metallic film will determine the defect morphology in the interface region and the amount of diffusion and reaction between depositing atoms and the substrate. All of these contribute to the mechanical adhesion of the metal film being formed on the PET film substrate and to the barrier properties of the final metallized film.

PET Film Surface

Chemical Bonds

Pet film surfaces have been characterized to include carbonyl, hydroxyl, and vinyl groups. These groups contribute to the surface energy of the PET film. In addition, there are crystalline and amorphous areas throughout the film. All of these have an affect on the adhesion of the metal to the PET film.

One of the advantages of PET is the surface groups available for chemical reaction (mentioned above). In the case of aluminum, a metal that forms a very stable oxide, reactions occur with the surface groups to form chelates. Hence, the surface is conducive to wet out by the aluminum being deposited and has the ability to react with the groups at the surface to give chemical adhesion. (Other metals that produce oxides would likely react in a similar manner.)

In polyethylene and polypropylene films which have a low surface energy affecting the metal wet out at the interface and no oxygen containing groups for chemical interaction, metal adhesion tends to be poor.

Mechanical Adhesion

The other component of the adhesion of metal to PET film is that of mechanical adhesion. As mentioned above, PET film has crystalline and amorphous areas. The adhesion of the metal depends partly on the amount and size of the spheralites (crystalline areas) in the PET film. The energy from the evaporated metal is used to melt the surface giving anchors for mechanical adhesion, and as mentioned above, that metal will react with the PET. The amorphous and crystalline areas react differently to the incoming metal. The amorphous areas allow the metal to 'drill' farther into the film surface than the crystalline areas. The metal penetration is about 30-40Å.

Adhesion Improvements

From the information above, we can say that the total adhesion (TA) of metal (aluminum) on PET film is the sum of the chemical (CA) and mechanical adhesion (MA). For PET film the metal adhesion is typically between 200-400 g/in.

$$\mathbf{TA = CA + MA}$$

In general, how can we increase the metal adhesion on PET and polymer films? Obviously, the total adhesion can be increased by increasing one or both of the components. How can this be done easily without affecting the overall properties of the PET film itself? Typically, the way most PET manufactures have done this is with chemical coatings. The coatings will allow increased chemical adhesion and / or mechanical adhesion in a cost effective manner.

> If you were to improve the chemical adhesion, then providing a surface that would allow increased levels of chelation or reaction with the aluminum would be key. A coating that has a significant number of hydroxyl or carboxylic acid groups would be expected to give superior metal adhesion.
>
> If you were to improve the mechanical adhesion, then providing a surface that would have significantly less crystallization and also melt at a lower temperature than the PET base film would be key. (It is important that the material not have too low of a melting point which may interfere with processing.) This would allow the metal to penetrate further and give improved mechanical adhesion.

An approach that has been very successful historically is to chemically coat the PET film with a co-polyester. The coating, although very thin, gives a surface that allows chemical bonding due to the ester functionality and also mechanical bonding since the material melts at a lower temperature and has little crystallinity. By providing this type of surface the metal adhesion is increased to 500-600 g/in.

The available published data, taken collectively suggest that the above bonding scheme is correct. Using XPS, studies have been done to examine the interfacial area between the deposited metal and the substrate. These studies yield the following interpretation:

1. Upon evaporation of the aluminum metal onto the polyester film some surface degradation occurs. This results in vinyl and carboxyl endgroups being formed.

2. Subsequent reactions of the aluminum with the carboxyl endgroups yield a chelated species.

TEM evaluation of the co-polyester coated film sample and an uncoated control film indicated a difference in the depth to which the metal was deposited. It appears that the aluminum penetrates the co-polyester coating to a depth of approximately 50-75 Å. It is reasonable that the aluminum should penetrate the co-polyester more than the PET control sample based on the relative thermo-physical properties of the two polymers. Therefore, it appears that the increased adhesion to the co-polyester is due to enhanced mechanical interlocking.

Upon metallization, XPS spectra showed new oxygen functionalities were created; one due to aluminum oxide and others to aluminum-carboxylate-oxide species. From the known chemistry of PET and aluminum, these are chemically reasonable. For both the co-polyester coated PET and the uncoated PET these functionalities were observed. There was no significant increase in chelated species in the co-polyester samples versus the PET control film. Thus the increase in the adhesion of the aluminum to the chemically coated film is entirely due to the increase in mechanical adhesion(2).

When attempting to design a co-polyester for coating, it is not as easy as it sounds; the mechanical adhesion is improved by the atom(s) drilling down into the coated surface of the PET film. One would think that the lower melting point of the co-polyester would make an excellent adhesive layer. This is not necessarily the case. There is a melting point range that is optimum for metal adhesion and the production of the film. In addition, the coating should not crystallize. Crystallization would interfere in the mechanical adhesion and lower the total adhesion.

Also, one must consider the chemical adhesion. Although not the major factor in metal adhesion, it still makes a contribution to the total adhesion. When designing a co-polyester this must be considered.

Recently, a chemically coated film has been introduced that demonstrates improved metal adhesion of over 1000 g/in. This film, using what was learned from the studies mentioned above, employs a coating that allows increased mechanical and chemical bonding for this improved metal adhesion.

Barrier

The reason the adhesion of aluminum to polyester is important is to provide a barrier structure of sufficient strength to give the required shelf life for a package. Metallized film continues to provide a path from rigid packaging to flexible packaging and many millions of pounds are produced each year. In general, the metallized chemically coated films have the same barrier (oxygen and moisture) as their non-coated counterparts.

However, some coated films have shown slightly worse barrier properties than the uncoated film, yet have much better metal adhesion. This may beg the question of effective metal thickness: how much deposited metal is for barrier and how much for adhesion. If you significantly increase the penetration of the metal into a coated film giving increased metal adhesion, can this metal also contribute to the barrier properties or does the metal deposited after this provide the barrier properties. For example, an uncoated PET film with an optical density of 2.2 has an average metal thickness of 135 Å. If a chemically treat film is metallized with the metal having deeper penetration, i.e. increased metal adhesion, would the metal deposition have to be increased to

2.4 (155 Å) to account for the deeper penetration of the metal into the surface coating? If the metal penetration does not contribute to barrier, one would be led to believe this to be true.

Other questions: does the interaction of the metal and polymer surface affect how the metal layer grows and does this affect the barrier? As the metal deposits, does the coating or depth of penetration change the growth of the crystals on the surface and, hence, change the barrier?(3)

How Do I Measure the Metal Adhesion?

There are a number of tests that will measure the metal adhesion. However, what do they really measure? Where is the locus of failure? First, if the metal is not completely removed, you are not measuring the metal adhesion to the substrate. Can you calculate the adhesion and calculate from the percentage removed? For example, if a tape test measures 250 g/in adhesion when 50% of the metal is removed, does this mean that the metal adhesion is 500 g/in if all were removed?

Secondly, just because you pull the metal from the substrate, are you removing all of it or are there traces left behind? Thirdly, does the method somehow change the metal, therefore biasing the adhesion?

Conclusion

The metal adhesion on PET film and the barrier that is obtained is certainly a complex subject. The principles discussed in this paper give some direction to the needs of a PET film. There are a number of other variables that contribute to the overall barrier of the film and ultimately, the laminated structure that have not been covered, from the metallizing process itself to the handling of the film in manufacture of the laminate.

References

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Metal Adhesion To PET Film

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Discussion Points:

- ✓ Introduction
- ✓ Adhesion
- ✓ Metal on PET film
- ✓ Metal adhesion improvements
- ✓ Metal adhesion measurements
- ✓ Metal adhesion and barrier
- ✓ Conclusion / questions

Why is metal adhesion important?

- Flexible packaging-
  - now used in all segments of the food packaging industry
  - growth of flexible packaging - very strong over the last ten years
  - with this growth comes concerns about package integrity:
    - longer shelf life
    - fresher, better tasting products
    - more convenient packaging

- One of the films that has contributed to this growth is polyethylene terephthlate (PET) film and in particular, *metallized PET films*.

Improving metal adhesion

Metallized PET (MPET), and other films, have been used in many applications as a replacement for foil and have effectively allowed flexible packaging to replace rigid packaging.

The adhesion of the metal and the barrier properties of MPET are related:

- to the film surface
- the interaction of the metal with the surface
- the way the metal builds structure beyond the surface
- the thickness of the metal deposited.

Efforts to improve the adhesion of the metal on films have yielded a number of chemically coated film products.

Adhesion:

The phenomenon in which surfaces are held together by interfacial forces

Forces of adhesion:

⇒ **Mechanical - interlocking**

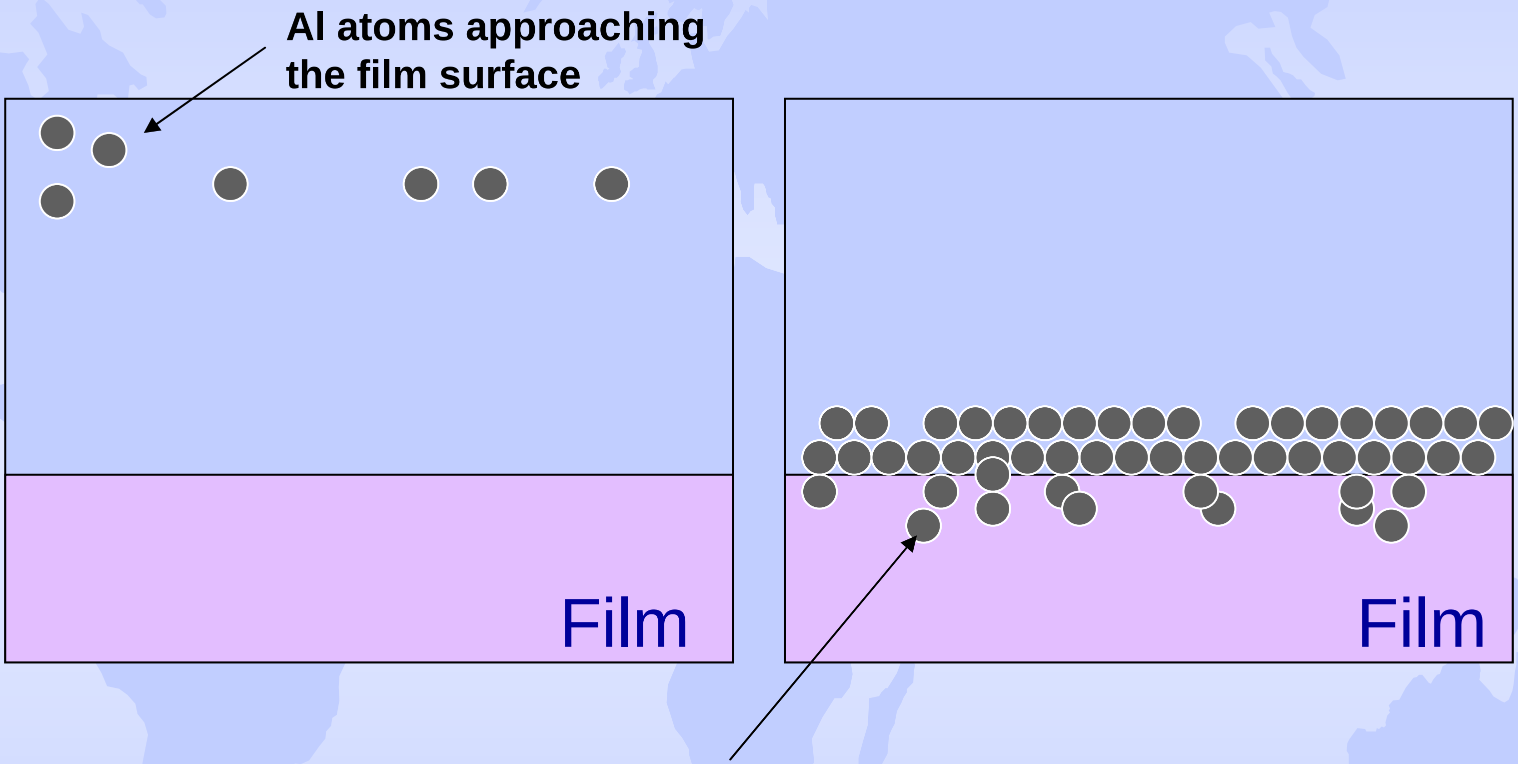
⇒ **Chemical - bonding**

⇒ **Secondary - dispersion forces**

$$TA = a MA + b CA + c SA$$

How much each contributes yields the total adhesion of the metal on the polymer surface

Bonding: Mechanical

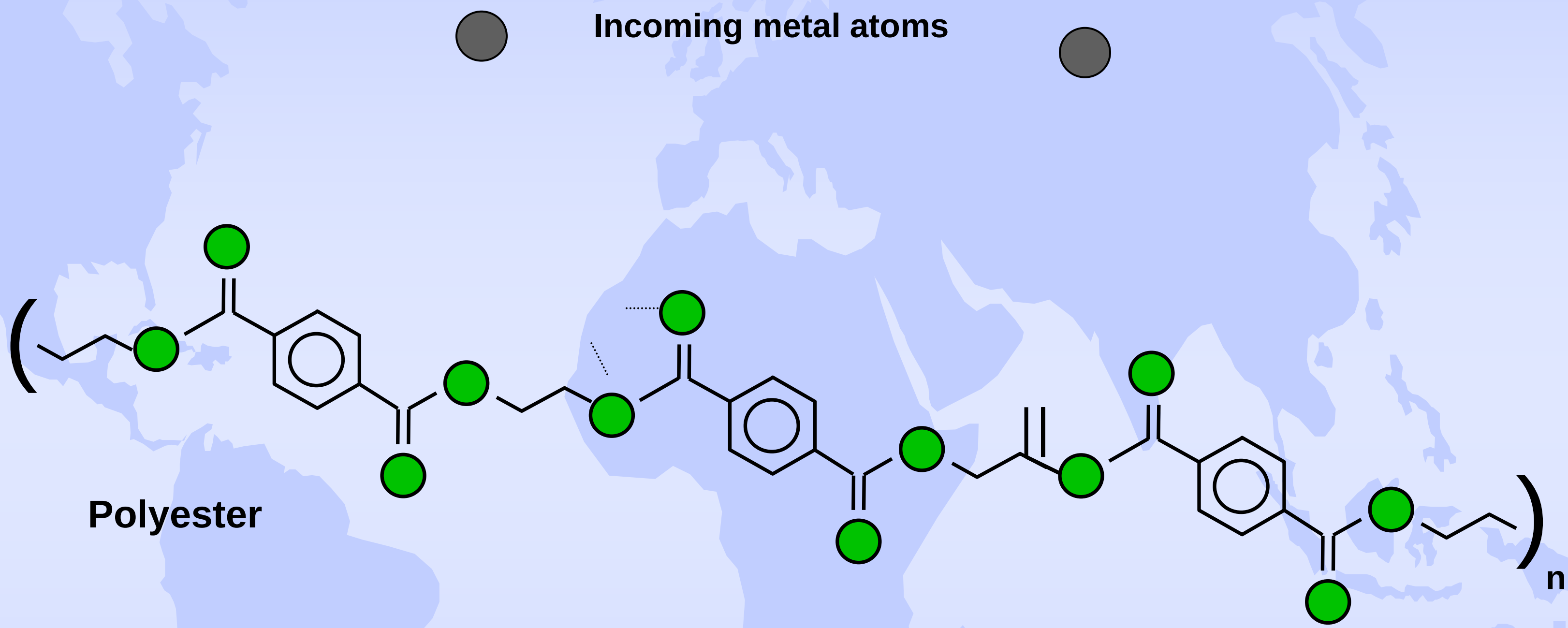


In the case of evaporated metal, there is an <u>interlocking</u> between the film and the metal- generally yielding good adhesion

Bonding: Chemical

- **Covalent –– exchange of electrons between atoms**
- **Ionic –– interaction between ionic crystals (loss of electron)**
- **Metallic –– may be classified as covalent, but with much greater mobility of electrons which contribute to the bonding (not applicable at the interface, however, as the metal layer builds this becomes important)**

Bonding: Chemical

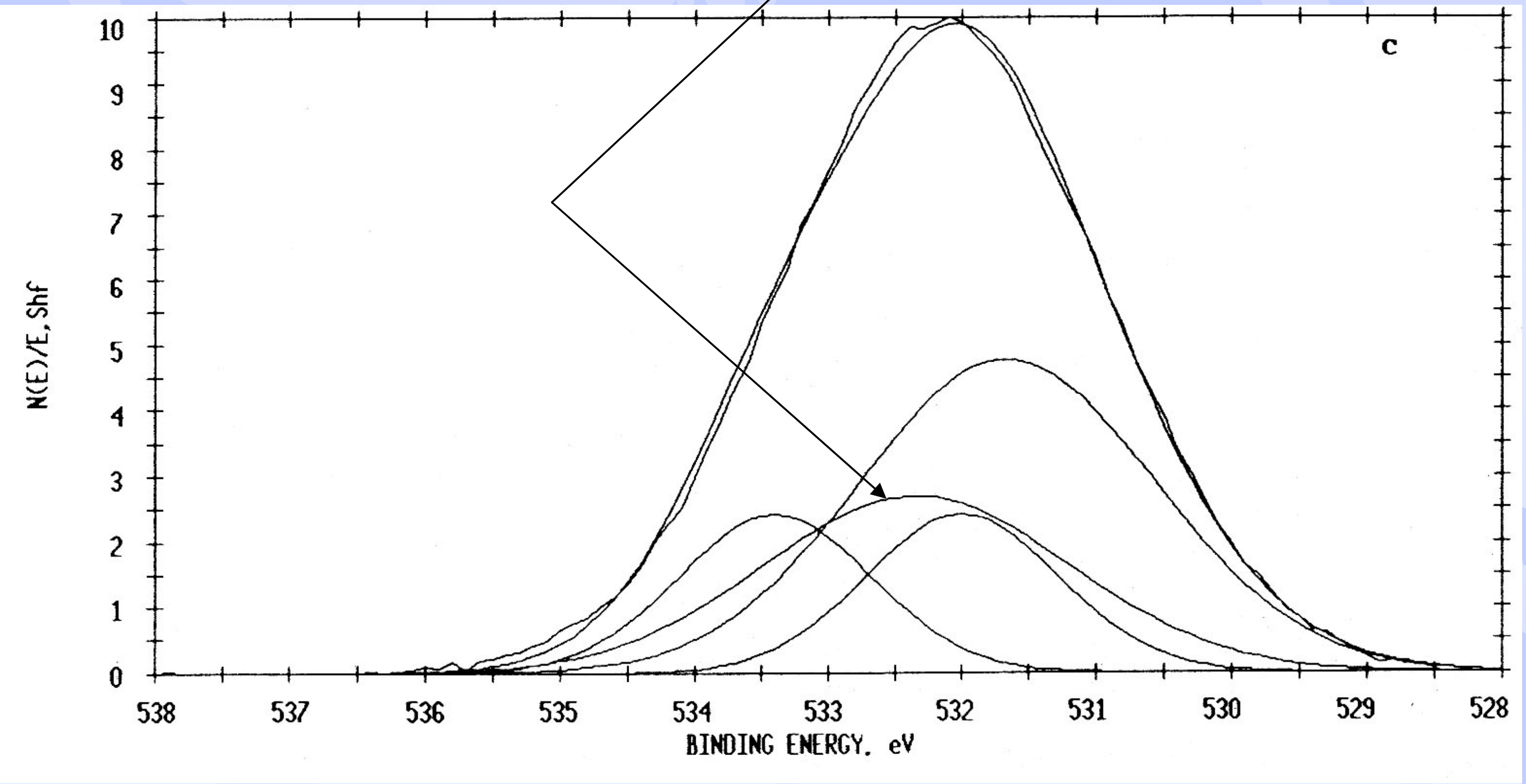


The interaction of the polymer chain with the incoming metal atom can result in a few reactions:

- chelation with the oxygen atoms
- chain breaking and reaction with the end groups formed

Bonding: Chemical

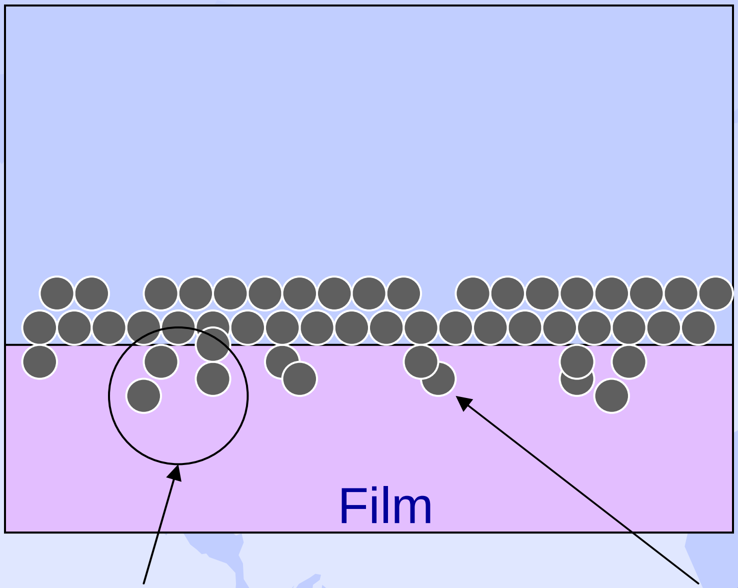
From XPS analysis, there are aluminum-chelated species formed at the PET – metal interface



The covalent bonds produced at each metal atom / cluster contributes to the bonding

Result: metal adhesion is in the 200-400 g/in range

Bonding Perspective



Mechanical interlocking-
Metal atoms drilling into the film surface

Chelation – reaction of the metal atoms with the polymer

As the metal atoms strikes the surface, they lose energy to the surface and condense on the surface. The metal atoms / clusters continue to grow into a continuous film.

Atom density and metal crystal orientation formed during the deposition will be affected by

- the residual gas in the chamber
- surface of the substrate
- deposition techniques.

These in turn affect the barrier and adhesive properties.

Bonding Summary

The total adhesion is the sum of:

-**The major component: MECHANICAL**
- -The depth the aluminum atoms penetrate into surface is important
- -According to TEM analysis of metallized PET film, the depth of penetration is in the 30-40Å

- The minor component: CHEMICAL
- - The reaction of the metal atoms with the PET chain
- - From XPS analysis, there are aluminum-chelated species formed

Improved Bonding

If the total adhesion is the sum of the mechanical and chemical adhesion:

$$TA = {}_aMA + {}_bCA$$

How does one improve the metal adhesion on PET film:

- can increase the mechanical factor or the chemical factor or both
- however, cannot affect the physical properties of the base film

Historically, PET manufactures have chosen to use chemical coatings. A typical coating is a very thin layer of a co-polyester.

Why a co-polyester polymer coating:

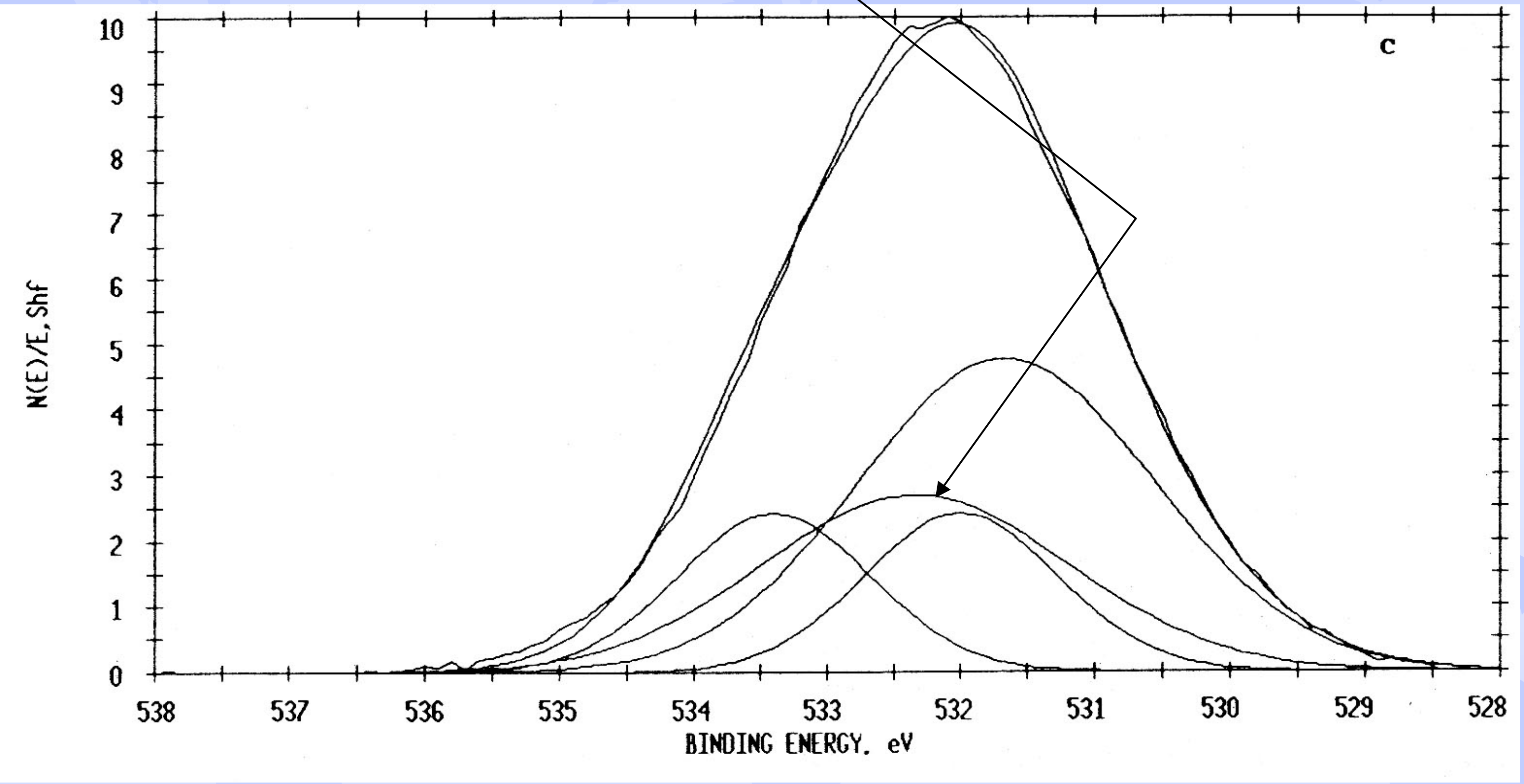
The co-polyester has some advantages:

- chemically similar to PET – good adhesion to the base film
- it has sites available for chelation with the aluminum metal
- it is amorphous – increase the penetration of the metal into the layer. (Crystallinity impedes the penetration.)
- it melts lower than PET film – allowing increased penetration into the film layer

If this is correct, improved metal adhesion should result

Chemical bonding contribution:

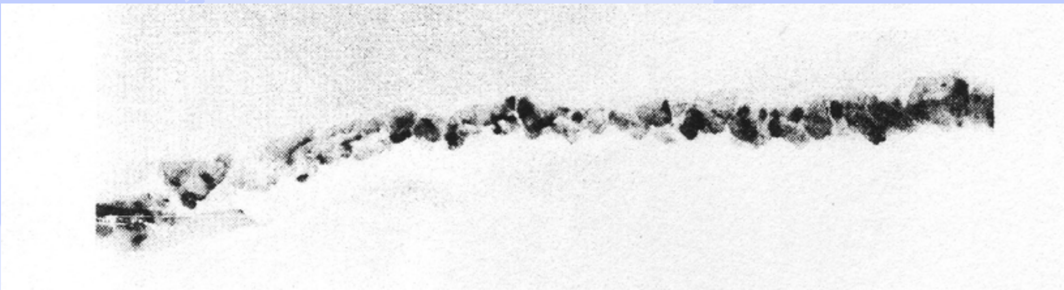
From XPS analysis, there are organo - aluminum species formed



Interestingly, uncoated and coated PET film exhibit the same level of reactivity. So one should expect about the same chemical adhesion contribution to metal adhesion as uncoated film.

Mechanical bonding contribution:

According to TEM analysis of metallized chemically coated PET film, the depth of penetration is in the 50-60Å vs. 30-40Å for uncoated film.



Metallized, co-polyester coated PET film
Metal penetration = 50-60Å

Metallized, plain PET film
Metal penetration = 30-40Å

Conclusions:

- Chemical bonding about the same as in uncoated film
- Mechanical adhesion is improved due to deeper penetration of the metal

Result: Metal bonds in the 500-600 g/in range

Greater Metal Adhesion

How would one design a coated PET film that yields over 1000 g/in of metal adhesion…

Mechanical adhesion:

- optimization of the melting point
- does not crystallize

Chemical adhesion:

- choose monomers that promote increased chemical bonding

There are a number of tests that will measure the metal adhesion.

- **What do they really measure?**
  - **Where is the locus of failure?**

Ideally, one would like to pull all the metal from the film.

This does not always happen; only part of the metal is removed.

If the metal is not completely removed, are we measuring the metal adhesion to the substrate?

Can you calculate the adhesion from the percentage removed?

For example, if a tape test measures 250 g/in adhesion when 50% of the metal is removed, does this mean that the metal adhesion is 500 g/in if all were removed?

Metal adhesion measurements

What does this tell us about the failure?

- can it be that a layer of PET is coming with the metal…
  which is more of a cohesive failure of the PET layer?

- or, a layer of metal or metal chelate is staying with the PET…
  which is cohesive failure of the metal surface?

Just because you pull the metal from the substrate, are you removing all of it or are there traces left behind?

Does the method somehow change the metal, therefore biasing the adhesion?

- A heat seal method
  - type of material used
  - temperature of seal
  - time

Barrier and Metal adhesion

	Average Adhesion (g/in)		Average Barrier O2TR (cc/m2/day-atm)	WVTR (g/m2/day)
Plain PET	200		0.8	0.5
Co-polyester #1	600		0.8	0.6
Co-polyester #2	1000		0.9	0.6

There does **not** appear to be a significant correlation between metal adhesion and barrier.

However, there is a correlation between barrier and surface roughness

	Average Adhesion (g/in)		Average Roughness (Ra)	Average Barrier O2TR (cc/m2/day-atm)	WVTR (g/m2/day)
Plain PET	200		33	0.8	0.5
Smooth surface PET	200		10	0.5	0.3

Conclusion

The metal adhesion on PET film is certainly a complex subject:

✓ We have visited the mechanism of the metal / PET interaction

- mechanical adhesion
- chemical adheison

✓ I have given a brief overview of the PET film requirements to obtain improvements in metal adhesion.

✓ I have shown that barrier and film surface roughness correlate well, while metal adhesion does not seem to correlate.

✓ There are a number of other variables that contribute to the overall barrier of the film and ultimately, the laminated structure:

- the metallizing process itself to the handling of the film in manufacture of that laminate.

Thank You

PRESENTED BY

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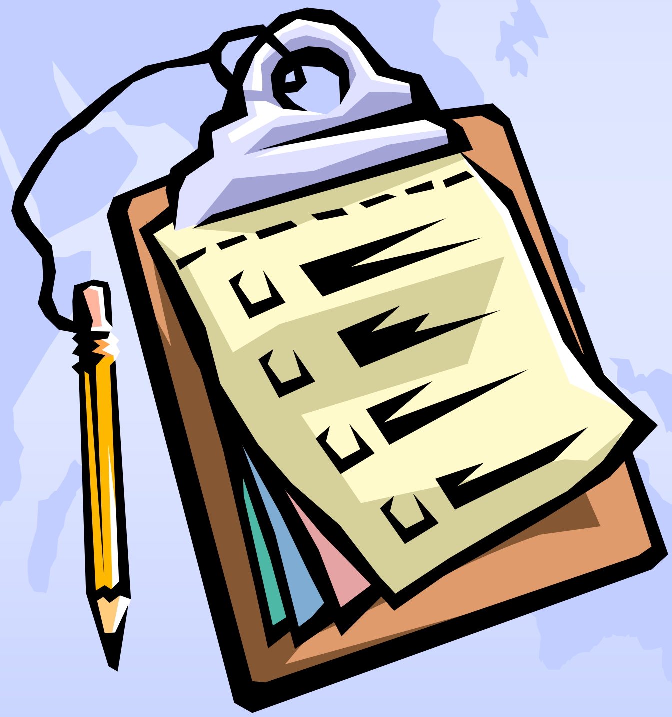

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