

# CHEMICAL ANALYSIS OF THE POLYESTER/METAL SURFACE OF A DELAMINATION FAILURE

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## Abstract

A polymer film lamination shows an unexpected delamination failure. The lamination is produced by adhesive laminating a previously printed metallized polyester film to a LLDPE sealant. In use the lamination is found to fail by delamination between the polyester film and the metal layer. Chemical surface analysis of the failure surface by X-ray photon spectroscopy (XPS) indicates a degraded polyester surface creating a weak boundary layer at the polyester/metal interface which is the cause of the delamination. Possible causes for the degraded polyester surface are discussed.

## Introduction

In the production of flexible packaging materials it is customary to prepare laminations of various products to make the final composite film structure. This is necessary as there is no single packaging material which is suitable for all applications and it is desirable as it affords the use of various techniques to prepare and combine the individual components. Today metallized films are used widely to provide both light, moisture and gas barrier properties to flexible snack packaging. The use of laminations supplies protection of the barrier properties of the metallized substrates as well as the ability to add additional features to the packaging material such as graphics or heat sealing layers.

The integrity of the packaging material will be related to the adhesion of the various layers of the lamination. Consequently, a great deal of effort and expense goes into developing material combinations which are fit-for-use and have particular delamination failure mechanisms. There is generally a peel strength target value which is measured to ensure conformance to product specifications, to ensure uniformity in the manufacturing of the various packaging components as well as the lamination process. When an adhesion failure occurs in a lamination, it is important to determine the cause of the delamination and the mode of failure. This is done to determine if the lamination failure is due to a failure in a component material or with the lamination process itself as the final laminated product has a greatly increased peel strength value over any single component. It is important

to determine the source and mode of the failure to see if the product is still fit-for-use. Also, it is necessary to ensure that the failure is not repeated and which component or which process step is responsible for the failure to determine if a product lot should be returned to the manufacturer and if there should be an economic claim to recover the cost of the failed lamination product.

In this investigation, during normal production of a standard product, there had been a sudden onset of a delamination failure of a printed, sealable metallized lamination product where the metal adhesion went from approximately 100 gm/in with little to 50% metal lift from the polyester surface to 100% metal lift with no measurable peel strength. In addition, some ink flaking was observed. It was desired to know the source of the poor metal adhesion and the ink flaking.

## Experimental

Three retained production samples of several commercial adhesive laminations were obtained from the laminator for investigation of the cause of the failures observed. The laminations examined were produced over a period of time in normal manufacturing operation and with various lots of component materials and showed both acceptable and unacceptable lamination performance. The lamination structure which was produced was a 6 color surface printed 92 gauge metallized PET (printed on the unmetallized side) which was then subsequently adhesive laminated with LLDPE sealant to the metal surface (figure 1). Bond strengths were measured by the laminator by directly separating the layers and measuring the peel force. Sample 1 was good showing typical bonding behavior, Sample 2 and Sample 3 showed the poor lamination bond strength and 100% metal lift performance

The XPS samples were prepared from the retained samples with an initiated delamination of the metal/film interface and were supplied to Evans East in East Windsor NJ, where they were further prepared for XPS analysis. This was accomplished by exposing previously unpeeled mating layers which were peeled revealing "fresh" areas of adhesion failure (Figure 2). Both sides of the failure were examined initially by low-resolution XPS survey scans to determine which elements were present.

High-resolution XPS spectra were acquired to determine the binding energy (i.e., chemical state) and concentration of the elements observed in the survey spectra. The quantification of the elements was accomplished by using the atomic sensitivity factors for a Physical Electronics Model 5700LSci ESCA spectrometer. The approximate escape depth ( $3\lambda \sin\theta$ ) of the carbon electrons was 80Å. Table 1 lists the atomic concentrations measured for samples 1, 2 and 3 on both the exposed aluminum surface and the exposed PET surface in the exposed regions of the delamination.

## Discussion

Laminated films are important in producing flexible packaging and it is expected that the lamination, once formed will remain adhered together. When a lamination fails it can be due to poor metal adhesion from a degraded or a contaminated film surface on which the metal was deposited, improper lamination process conditions or perhaps poor metallizing conditions. The mode of failure as well as the location of the lamination failure is used to determine the likely source of the failure. In many instances with metallized films it is expected that any delamination between the metallized film and the sealant will occur without transfer of the metal to the adhesive or if there is transfer that the peel strength will exceed a specified value. In many applications, acceptable peel strength of a metallized lamination is 100 to 300 gm/in with some metal lift being acceptable. Seldom is it acceptable (or "comfortable" to the customer) to have 100% metal lift in any metallized lamination, unless the peel strength is very high relative to the specification, because of the uncertainty that this raises about the "quality" of the metallized films and the barrier properties. In short it is generally expected that the metal should be difficult to remove from the metallized film surface. When the metal lift is 100% and the peel strength is low or not measurable, it is generally understood that the metallized film has failed due to the metal layer adhesion to the substrate film.

The laminated product examined for this paper showed a range of performance from acceptable lamination performance for sample 1 to the unacceptable delamination for samples 2 and 3. In this product and process, a good lamination would be expected to exhibit measurable peel strength of 100 gm/in or higher with some metal lift from the PET surface (generally characterized at around 50%). However, with samples 2 and sample 3 there was found 100% metal lift with no measurable peel strength. In addition ink flaking was observed with samples 2 and 3 which is not typical of the standard commercial product.

There are several possible sources of the adhesion failure of the aluminum most of which relate to the

presence of a weak boundary layer on the film surface under the evaporated metal layer. It is also possible that poor metallization conditions such as poor vacuum or perhaps too cold a substrate surface can impact the metal deposition and the subsequent metal adhesion. If the failure is due to a weak boundary layer there should be evidence of degraded polymer or surface contamination on the delaminated film and metal surfaces.

XPS is a sensitive way to determine the chemical structure of the surface of a polymer sample. In addition it can be used to determine the transfer of material between two surfaces which are delaminated. This permits the determination of the mode of failure and potential sources of interfacial weakness which might be due to the presence of a weak boundary layer on the metallized film. In some metallization base films there are migratory additives which are added to improve film handling but which also are known to interfere with metal adhesion. However, these are generally only added to polyolefin films. Due to the polymerization methods and high extrusion temperatures, polyester (PET) films are produced without migratory additives and rely on non migratory additives such as silica particles for web handling improvements.

In the absence of migratory additives the principle sources of weak boundary layers on the polyester film would be degraded PET due to over treatment of the surface during film manufacture or during metallization if the metallized was plasma treated. The presence of degraded polymer could also be a result of excessive recycle in the film process or extrusion conditions which could cause excessive degradation of the PET during film extrusion (poor drying, excessive melt temperature etc). These extrusion conditions could cause the production of low molecular weight oligomers to be present in the PET film which could then diffuse to the film surface prior to metallization, thereby creating a weak boundary layer on the film surface. It is also possible that the metallization conditions themselves could degrade the film surface as the metallization brings energy to the film surface and can cause oxidation of the polymer surface. The lamination process itself would not be expected to affect the chemical composition of the surface under the metal deposit.

Examination of the failure surfaces with surface sensitive techniques such as XPS can determine if the film surface has been contaminated or chemically changed at some point from the both the elemental concentrations and from the high resolution XPS spectra of the polymer film surface. In particular it is instructive to examine the carbon and oxygen XPS spectra to determine the type and relative amount of chemical groups at the film surface. In a PET XPS spectra, we would expect to find equal concentrations of C-O and

C=O functional groups and the presence of more of one relative to another would be evidence of a chemical change or contamination at the polymer surface under the aluminum deposit.

Figure 3a and 3b shows the typical high resolution oxygen and carbon 1S spectra for a PET polymer surface. In figure 3a we note the symmetrical peaks for the C-O and C=O 1S spectra due to the equal number of C-O and C=O functional groups in the PET molecule.

Figures 4a ,4b, 5,a, 5b, 6a & 6b show the high resolution XPS oxygen and carbon 1S spectra for the exposed PET surfaces of samples 1, 2 & 3 respectively. It is clear from these figures that the PET surface of samples 2 & 3 has been chemically changed from the native PET polymer surface.

All of the aluminum surfaces showed the presence of carbon and oxygen (table 1) in which the XPS high resolution spectra showed to be predominantly C -O groups in samples 1, 2 & 3 and with some C=O also present in sample 1. Samples 2 & 3 also showed an increase over sample 1 in  $Al^{+3}$  concentration relative to Al metal on the aluminum surface, perhaps indicating a chemical attack of the aluminum interface by the PET film surface.

## Conclusions

It is clear from the XPS analysis of the good (sample 1) and bad (samples 2 & 3) laminations that the metallized PET surface of samples 2 & 3 have been chemically modified in some fashion which is increasing the concentration of C-O species at the film surface. This is perhaps indicative of an increase in acid O=C-OH and/or glycol C-OH end groups on the PET surface. This would imply that the PET surface has been reduced in molecular weight or that it contains an increase in reduced molecular weight PET which would be consistent with the presence of a weak boundary layer at the PET film/metal interface giving rise to the decreased bond strength and the increased metal lift in laminations 2 & 3. This chemical change of the PET surface was not seen in sample 1 which exhibited acceptable lamination bond strength.

Based upon the nature of the lamination failure at the metal/polymer interface and the XPS evidence of a modified PET surface, it is reasonable to conclude that the lamination failure observed in samples 2 & 3 is due to an inferior quality metallized film and not due to the adhesive or lamination conditions. The source of the poor quality films is either the metallizing or the film manufacturing process.

Furthermore, because samples 2 & 3 with the poor lamination bond strength samples also displayed poor ink adhesion it is likely that a weakly adhered boundary layer is also present on the opposite film surface.

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Sample	O	N	C	Cl	Si	Al	K
Sample#1 aluminum surface	29.4	0.7	59.4	ni	3.0	7.6	nd
Sample#1 exposed PET	29.4	nd	69.8	ni	0.1	0.7	nd
Sample#2 aluminum surface	25.5	1.4	68.3	0.2	1.0	2.8	0.6
Sample#2 exposed PET	29.5	0.4	68.6	0.1	0.2	0.7	0.5
Sample#3 aluminum surface	29.8	1.2	56.5	0.1	2.2	9.4	0.8
Sample#3 exposed PET	26.5	0.9	69.8	nd	2.4	0.4	nd

Table 1: Elemental analysis of three lamination samples at the PET/aluminum interface

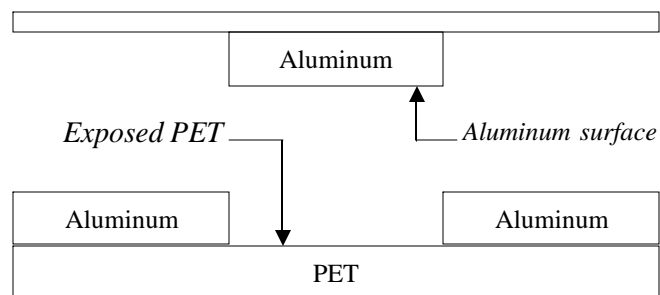


Figure 2: Schematic diagram of delaminated lamination and locations of the XPS surface analysis.

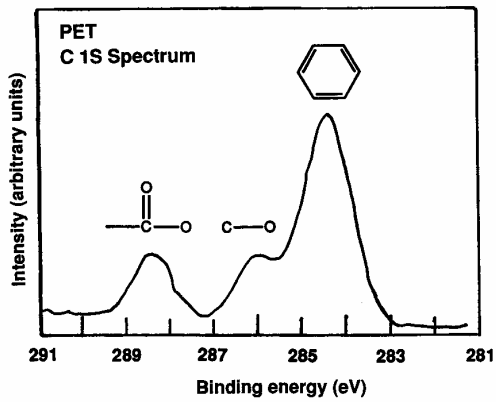


Figure 3a: Oxygen 1S spectrum for PET

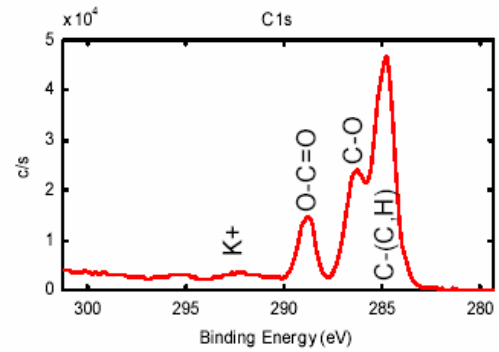
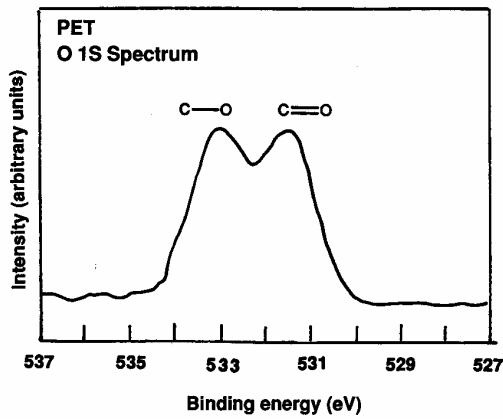
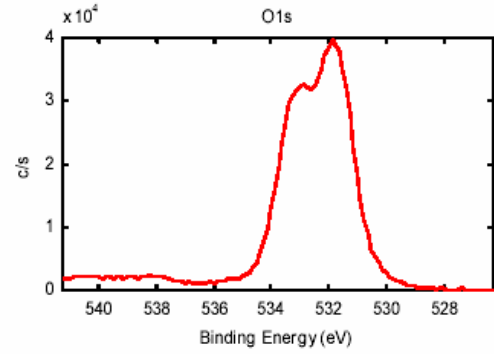


Figure 5a & 5b: O1s and C1s spectra of exposed PET from sample #2 spectra showing excess C-O relative to typical of PET polymer surfaces

Figure 3b, Carbon 1S spectra of PET polymer

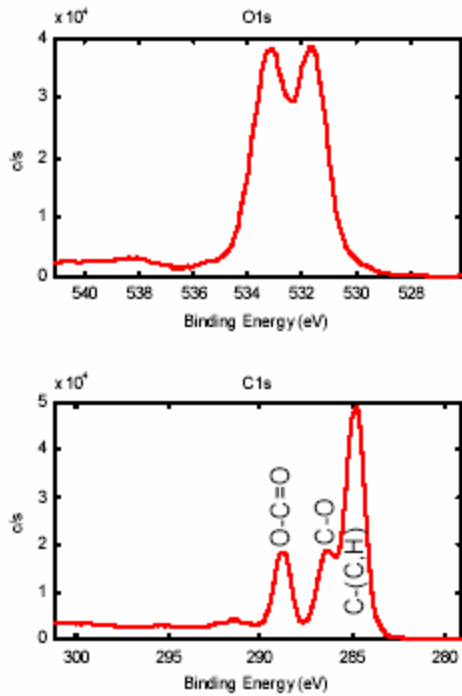


Figure 4a & 4bb, O1s and C1s spectra of exposed PET from sample #1 showing spectra typical of PET polymer surfaces

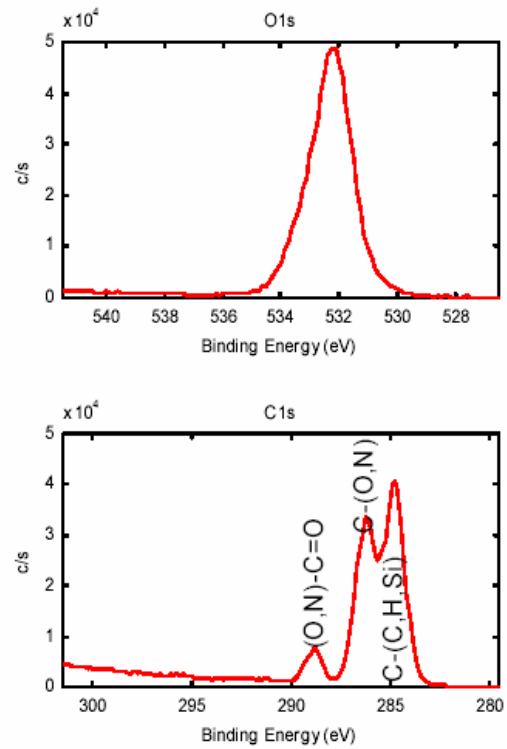
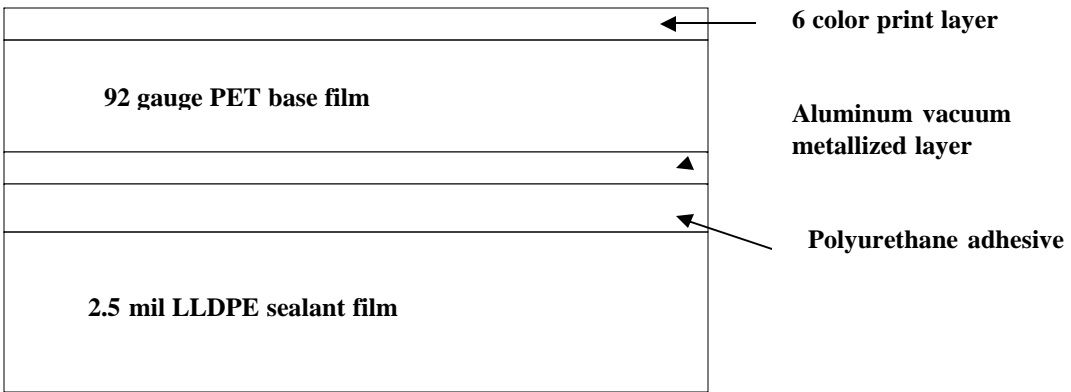


Figure 6a & 6b: O1s and C1s spectra of exposed PET from sample #3 spectra showing excess C-O relative to typical of PET polymer surfaces



**Figure 1: Schematic diagram of the sealable printed, metallized adhesive lamination showing the delamination at the PET/Aluminum interface**

**Key Words:** metallized film, adhesion, lamination