Application of surface analysis for root cause failure analysis

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1. INTRODUCTION

Elucidating the root cause of failure in multilayer films can be quite challenging. Being able to obtain the elemental and chemical composition of failure surfaces greatly eases this task. Since the causes often involve contamination, additive migration, backside transfer, or improper pretreatment, analytical methods capable of analyzing the outermost molecular layers is vital. Two such methods are X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). The unique properties of these methods are readily demonstrated herein by four case studies taken from current industrial products.

2. DISCUSSION

2.1 X-ray Photoelectron Spectroscopy (XPS)

2.1.1 Background

X-ray photoelectron spectroscopy is based on the phenomenon that when a sample is illuminated by photons of sufficiently high energy, spontaneous emission of electrons occurs. This "photoelectric effect" was first observed in 1887 by Hertz[1]. It was not until 1905 that Einstein described the basic equation of the photoelectric effect, relating the kinetic energy of the emitted electron to the photon energy and the binding energy of the electron[2]. Using a mono-energetic x-ray with energy $h\nu$, the kinetic energy, E_K, of the emitted electrons will be related to the binding energy of the electron E_B by $E_K = h\nu - E_B - \Phi$.

The small correction term Φ is used to account for the combined work function of the sample and the spectrometer. Measuring the kinetic energy of the emitted electron permits calculation of the binding energy of that electron, i.e. the energy needed to strip the electron from the atom. Steinhardt and Serfass realized that this could be used to create an analytical tool for determining the elemental composition of surfaces[3]. Shortly thereafter Siegbahn observed that small shifts in the binding energies were indicative of the chemical state or oxidation state of the atom[4]. Siegbahn also coined the acronym ESCA for "electron spectroscopy for chemical analysis" to emphasize the fact that "XPS" spectra contained both photoelectrons and Auger electrons. To this day, the terms, XPS and ESCA, are used synonymously by practitioners even though it causes some confusion among lay users.

A schematic diagram of a typical commercial XPS spectrometer is shown in Figure 1. The key components are a monochromatic x-ray source, a sample holder, an electron energy analyzer, and an electron detector. Note that the entire system is housed in an ultra-high vacuum chamber. As a consequence XPS is typically restricted to vacuum compatible solids.

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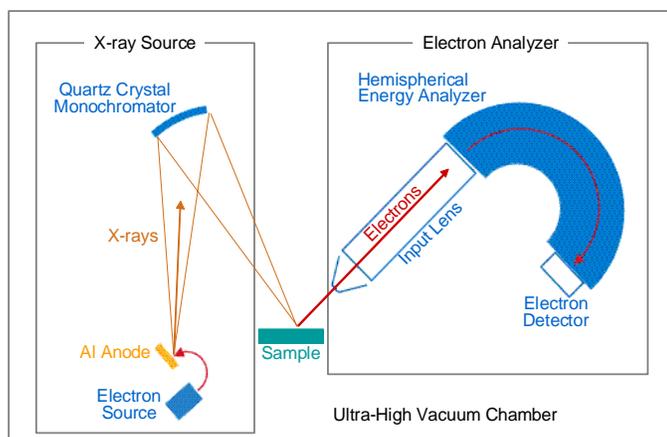
Figure 1. Schematic diagram of an XPS system.

Although perhaps not readily apparent, XPS is a surface analytical technique. Because the kinetic energy of the photoelectrons is relatively low ($< 2KeV$) they can travel only a few nanometers before undergoing inelastic scattering. Hence only those electrons originating within the outer few nanometers of the surface will be detected. Moreover the technique is quantitative in that the number of detected electrons is directly proportional to the number of atoms from which the electrons were emitted. These properties make the technique well suited for analysis of the surface of any vacuum compatible material.

2.1.2 Quantitative analysis of erucamide migration

A film manufacturer was receiving complaints about sporadic adhesion failure with a corona treated polyolefin film. The film was known to contain low concentrations of erucamide and it was suspected that elevated storage temperatures might be causing additive migration to the surface. To test this hypothesis, samples were aged for up to 23 days at room temperature and for up to 9 days at 120°F. XPS was selected as the analytical method since it could easily quantify nitrogen from erucamide ($C_{22}H_{43}NO$) even when present at levels as low as a fraction of a monolayer. Analysis of the unaged and aged samples revealed the presence of carbon, oxygen, and nitrogen in all samples, see Figure 2. In all cases the nitrogen 1s spectra were consistent with the presence of erucamide.
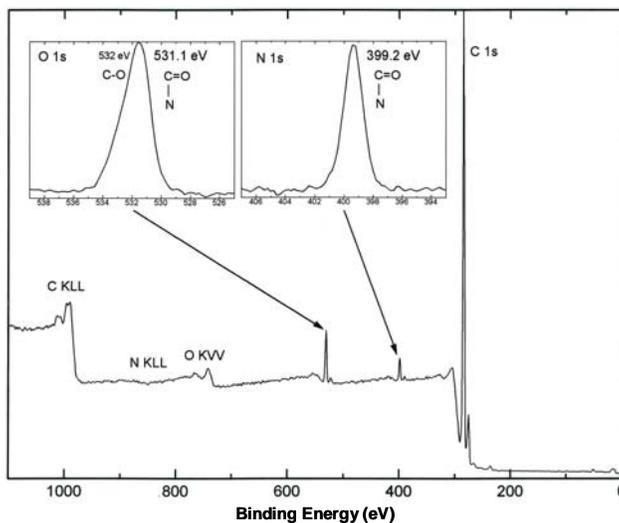

Figure 2. XPS survey spectrum and oxygen 1s and nitrogen 1s high resolution spectra for a film aged 9 days at 120°F.

As shown in Figure 3 migration was slow at room temperature, increasing by 60% after 23 days. In contrast migration was rapid at 120°F increasing 450% in 1.5 days. Since erucamide has a molecular formula of $C_{22}H_{43}NO$, a nitrogen concentration of 2.6 atom% observed after 9 days at 120°F means that 60% of all detected atoms originated from erucamide. This equates to a layer ~2 nm thick or roughly 8 monolayers. Clearly this film must be stored at temperatures well below 120°F to prevent erucamide migration and concomitant adhesion failure.
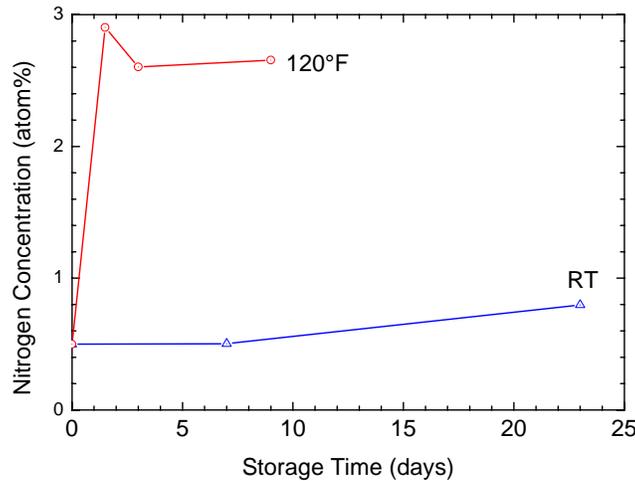

Figure 3. Surface nitrogen concentration as a function of aging for a polyolefin film containing erucamide.

2.1.3 *Locus and mode of failure in a multilayer label*

A PVC film was metalized under what was thought to be standard conditions and found to pass the 610 tape pull test. This metalized film was then used to produce finished labels consisting of a release liner, adhesive, PVC film, aluminum metalization, ink, and PVC top coat. A tape pull test of the finished labels revealed failure apparently between the PVC film and the aluminum metallization, see Figure 4. In contrast "Good" labels produced from a different metalizer exhibited failure mostly between the ink and top coat and with few areas failing between the PVC film and the aluminum metalization.
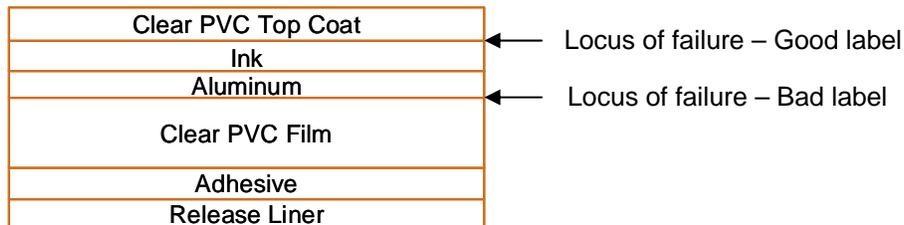

Figure 4. Schematic diagram of the multilayer label showing the locus of failure for Good and Bad samples.

XPS was selected to examine the mating failure faces due to its ability to measure the composition of the surfaces and for its ability to distinguish different chemical bonds. The elemental compositions of the various mating faces are given in Table 1. The compositions of the PVC Film sides of the both the Good and Bad labels were similar to PVC. The compositions of the Top Coat sides of both samples were not, however, similar to each other. For the Top Coat side of the Bad label approximately 50% of all detected elements were due to metallic aluminum and aluminum oxide from the metalization and 10% were due to PVC. The remaining 40%

consisted mostly of carbon and oxygen with traces of tin, nitrogen, and sodium. In contrast for the Top Coat side of the Good label roughly 30% of all detected elements were due to PVC and roughly 25% were from metallic aluminum and aluminum oxide. The remaining 45% consisted of carbon and oxygen in ratio of ~2:1.

Table 1. Concentration of Elements Observed by XPS (atom%)

Sample	C	Cl	O	Al	Sn	N	Na
Bad – PVC Film	68.5	28.9	2.5	-	<0.1	-	<0.1
Bad – Top Coat	26.0	3.5	38.4	31.4	0.1	0.2	0.3
Good – PVC Film	71.8	25.5	2.7	-	<0.1	<0.1	-
Good – Top Coat	55.3	10.0	22.7	11.3	<0.1	0.7	-
PVC – theory	66.7	33.3	-	-	-	-	-

A detailed understanding of the failure surfaces is possible by inspection of the carbon 1s spectra shown in Figure 5. Note that the vertical lines in Figure 5 represent the approximate intensity of the C-C and C-Cl components due to PVC. The carbon spectra of the PVC film sides (left panel) of the Good and Bad label failures reveals that most of the carbon is due to PVC with small amounts due to compounds containing C-C and C-O bonds and to a much lesser degree O-C=O bonds. The Top coat side of the Bad label failure (solid line in right panel) contained peaks due to C-C, C-O, and O-C=O bonds. This is most likely an aliphatic-ester plasticizer from the PVC film.
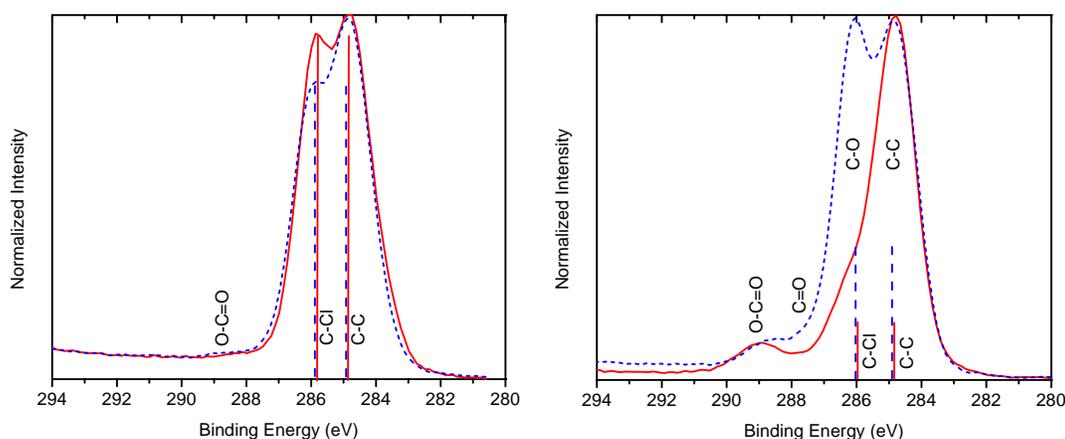

Figure 5. XPS carbon 1s spectra of the PVC film (left) the top coat (right) sides of the good sample (dashed line) and bad sample (solid line) after tape pull failure. The vertical lines represent the approximate intensity of the C-C and C-Cl components due to PVC.

The Top coat side of the Good label failure (dashed line in right panel) has an interesting spectrum. At first glance it appears to be similar to PVC but this is not a correct interpretation since the sample contains only 10 atom% Cl and hence, only a small portion of the intensity around 286 eV can be accounted for by PVC. The remaining intensity at 286 eV is due to C-O bonds. Hence the Top coat side of the Good label failure contained roughly equal amounts of C-C and C-O bonds with smaller amounts of C=O and O-C=O bonds. These bonds are evidence of the oxygen plasma treatment of the PVC film prior to metalization. These peaks are much less intense on the corresponding Bad surface. Combined, these results indicate that the Bad label exhibited failure at the PVC film – aluminum interface and this interface contains an aliphatic-ester plasticizer from the PVC film. The Good label exhibited failure *within* the plasma modified

PVC film – aluminum *interphase*. Most, if not all, of the oxygen-containing organic species appear to be due to the plasma modification. Note that both samples contained traces of tin, probably from a tin-based stabilizer. The concentration of tin is however sufficiently low that the stabilizer most likely plays no significant role in adhesion failure. These results indicate that the Bad PVC film was improperly pretreated. A subsequent review of the plasma modification records revealed that the power was approximately five times to low for the bad sample.

2.2 Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

2.2.1 Background

Secondary ion mass spectrometry is based on the phenomenon that charged particles (atomic and molecular ions) are emitted from a surface that is bombarded by high energy ions. Many of the early advances in SIMS and in particular static SIMS were performed by A. Benninghoven and his group in the late 1960s and 1970s[5]. It was quickly realized that the analysis must be performed under "static" conditions if molecular information was to be obtained. When the primary ion dose is kept below ~10^{12} ions/cm^2 the probability that two primary ions will strike the same location is low and the surface remains unchanged or static during the analysis. The consequence of this is that the emitted ions originate from virgin material and hence the ions are characteristic of the original surface.

In order to apply static SIMS to organic materials, high mass resolution is needed. This is best accomplished using a Time-of-Flight detector. This experiment proceeds as follows. A very short (10^{-12} sec) pulse of primary ions strikes the sample creating a pulse of positive and negative ions as well as neutral fragments. The ions are subjected to an extraction field V$_e$ of several thousand volts. This imparts each ion with a fixed kinetic energy, E$_k$, given by E$_k = qV_e$, where q is the ion charge which is typically 1. The kinetic energy can also be expressed as E$_k = \frac{1}{2} m v^2$ where m is the mass of the ion and v is its velocity. Since the kinetic energy is the same for all ions the velocity of each ion will be inversely proportional to its mass. By allowing the accelerated ions to fly through a field-free tube and then measuring their arrival time at a detector at the end of the flight tube, the ions mass can be calculated. Hence, a TOF-SIMS spectrometer requires a pulsed ion source, an extraction field, a flight tube, and a detector capable of detecting the arrival of each individual ion. One common TOF-SIMS design is shown in Figure 6.
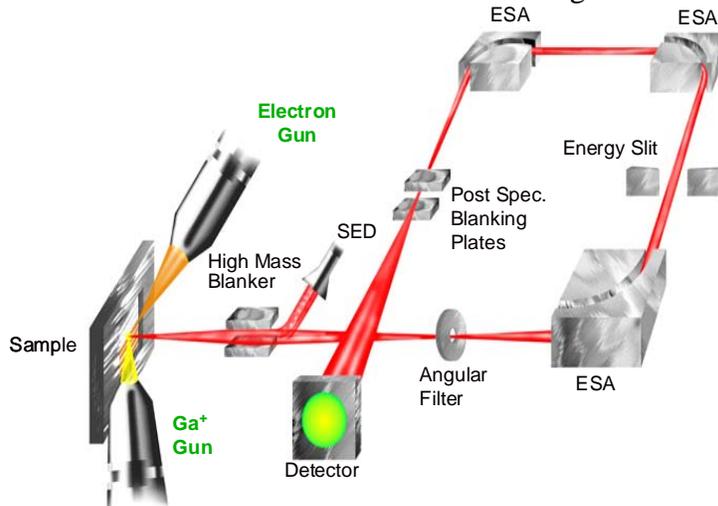

Figure 6. Schematic diagram of a TOF-SIMS system.

The advantages of this type of instrument are that characteristic ions emitted from the outermost 1-2 monolayer can be measured with high mass resolution and accuracy and with very high sensitivity. By using a microprobe primary ion beam that is rastered over the surface, micro area analysis and ion imaging are possible. In fact it is common to record the spatial location, creation time, and mass for all of the ions generated during an analysis and then to filter the data off-line thereby creating retrospectively TOF-SIMS spectra from selected areas and TOF-SIMS images showing the distribution of selected ions.

2.2.2 Backside transfer of Irganox® 1010

Antioxidants are often added to polyolefin films at low concentrations. However migration and segregation can lead to surface concentrations much higher than bulk levels. When this occurs and the product is in the rolled form, backside transfer is possible. This scenario was suspected for a metalized bilayer polyolefin film. The sample consisted of a base film that contained Irganox® 1010 with a polymer skin free of Irganox® 1010. The reverse side of the base film was metalized with aluminum. It was assumed that encapsulation of the Irganox-containing layer would contain the compound. To test this, samples were examined by TOF-SIMS. TOF-SIMS was selected due to its high sensitivity and molecular specificity.

Irganox® 1010, i.e. tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)] methane has a molecular formula of $C_{73}H_{108}O_{12}$ and a molecular weight of 1176.78 amu. Analysis of the pure material indicated that is makes an intense negative ion by hydrogen extraction (M-H⁻) at mass 1175.78 amu. It also forms intense fragment ions due to loss of $C_{14}H_{23}O$ (M-207.17) and $C_{17}H_{25}O_2$ (M-261.18), see Figure 7.
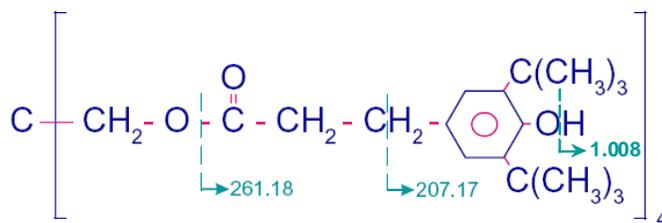

Figure 7. Molecular structure of Irganox® 1010 showing the dominant fragmentation points.

TOF-SIMS analysis of both sides of the metalized film confirmed the presence of Irganox® 1010 as shown in Figure 8. This data clearly shows that Irganox® 1010 migrated to the polymer surface during processing and was transferred to the metalized side during storage after reroll.
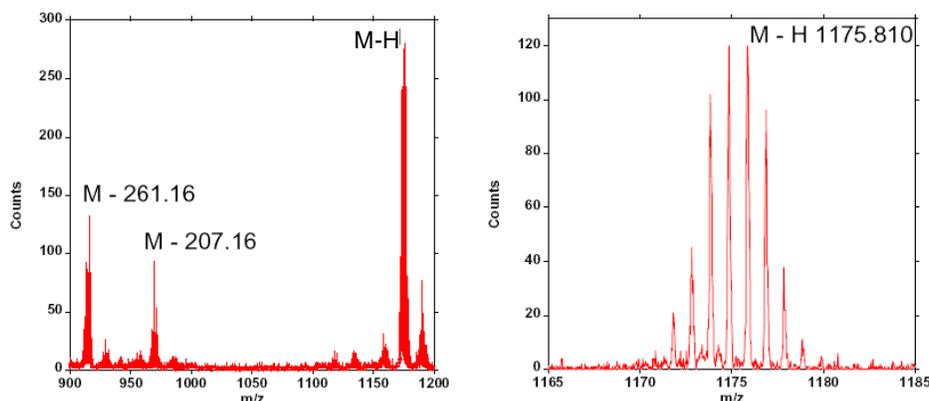

Figure 8. Negative ion TOF-SIMS spectrum of the aluminum side of a metalized multilayer film.

2.2.3 Ghost image on a refrigerated food package

In some instances a common product can work fine for many applications only to fail when used in a novel situation. This is precisely the case for a printed film used to package refrigerated food. This film had the required chemical and physical properties but had a cosmetic defect in which a ghost image of the printing was visible when water condensed on the film. Needless to say this was unattractive and could lead to the customer rejecting the product. The only background provided prior to analysis was that the film was a polyolefin.

Having little information to guide the analysis, control and ghost image areas of the film were examined by XPS. As shown in Table 2 the control and ghost image areas contained carbon and oxygen while the ghost image area also contained traces of nitrogen and silicon. Clearly the outer surfaces were not contaminant free polyelefin.

Table 2. Concentration of Elements Observed by XPS (atom%)

Area	C	O	N	Si
Control	84.8	15.2	-	-
Ghost Image	89.9	8.5	0.6	1.2

High resolution carbon, oxygen, and nitrogen spectra provided a more detailed assessment of the film, see Figure 9. The carbon 1s spectrum revealed that the control area had three distinct types of carbon bonds, C-C, C-O, and O-C=O. The presence of C-O and O-C=O was consistent with an ester, however the C-O peak was larger than the O-C=O peak meaning that an additional C-O source was present. The carbon 1s spectrum of the ghost area indicated that, relative to the control area, the ghost area had a larger fraction of carbon atoms as C-C and C-Si bonds. The nitrogen 1s spectrum was consistent with an amine or amide and the silicon 2p spectrum was consistent with a silicone. Unfortunately the exact structures of the compounds on the control and ghost area could not be extracted from the XPS data.
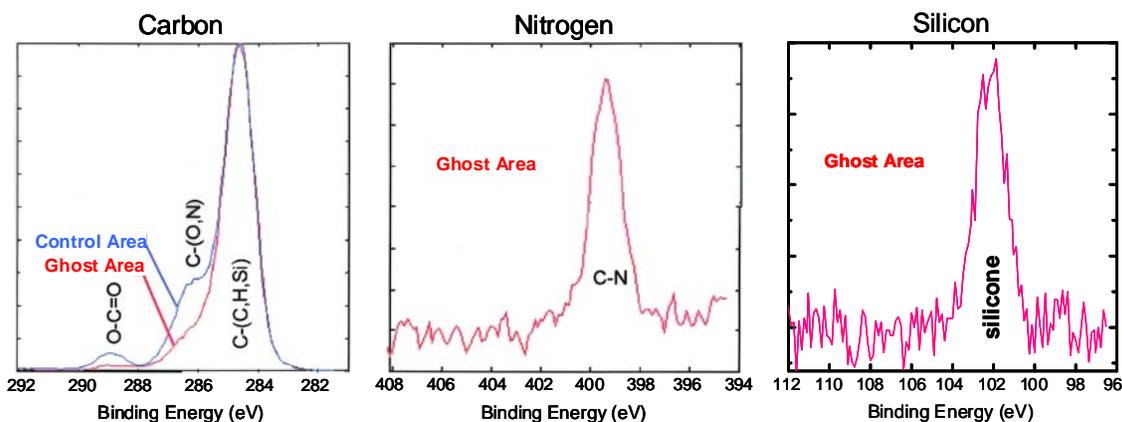

Figure 9. XPS carbon 1s, nitrogen 1s, and silicon 2p spectra of control and ghost image areas of a refrigerated food package.

TOF-SIMS analysis of the film readily clarified the XPS data. As shown in Figure 10, the positive ion TOF-SIMS spectrum of the control area contained intense ions attributed to glycerol monooleate (GMO). The positive ion TOF-SIMS image of GMO specific ions indicated that the GMO coverage was uniform. GMO being a monoester of glycerol contains one ester group and two hydroxyl groups. This explained the O-C=O and C-O bonds in the XPS spectrum.

The positive ion TOF-SIMS spectrum of the ghost image area contained ions attributed to GMO as well as polydimethyl siloxane (PDMS) and stearamide. The presence of PDMS explains the silicon peak at 102.2 eV in the XPS spectrum. Likewise stearamide explains the presence of the nitrogen peak at 399.4 eV. The TOF-SIMS image of stearamide specific ions indicated it was localized to specific areas. Combined these results indicate the polyolefin film was coated with glycerol monooleate and that stearamide was the dominant contaminant in the ghost area and was the cause of the ghost image.
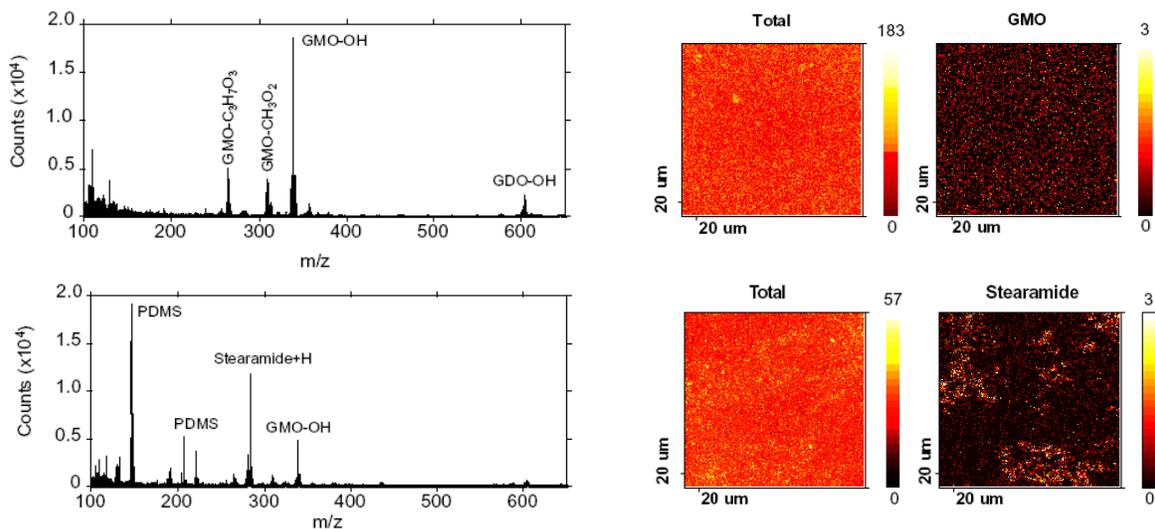

Figure 10. Positive ion TOF-SIMS spectra (left) and positive ion TOF-SIMS images (right) of a control area (top) and ghost image area (bottom) of a refrigerated food package.

3. CONCLUSIONS

The root causes of many polymer film failures can be due to additive migration, backside transfer, improper pretreatment, or foreign contamination. Differentiating these causes is greatly simplified by measuring the surface composition of the product in question or the mating faces of adhesion failures, or of component retains or witness samples. Analytical methods for such tasks need to be able to examine any solid surface while limiting the analysis depth to a few monolayers. XPS and TOF-SIMS are uniquely suited to these analyses and when combined offer a complete understanding of surface and interface chemistry. XPS excels at quantitative analysis of not only elemental composition but more importantly chemical bonding. Its wide applicability means that it is often a first look technique. TOF-SIMS excels at compound identification and imaging. Being a relatively new technique TOF-SIMS databases are small but growing rapidly. As such analysis of control samples and/or pure materials is often required.

Selection of the appropriate technique can often be based on what is known of the sample and what is required. If little is known about the sample it is often most productive to start with XPS analysis. If however the goal is to obtain unambiguous identification of a specific compound or if spatial distribution information is required, TOF-SIMS is the method of choice. In many instances either method would be acceptable but in other instances only the benefit of hindsight makes the choice clear. As an aid to technique selection some of the more important characteristics of these methods are summarized in Table 3.

Table 3. Selected Characteristics of Two Common Surface Analysis Methods

Method	XPS	TOF-SIMS
Sample Type	Organic/inorganic/metallic (high vacuum compatible)	Organic/inorganic/metallic (high vacuum compatible)
Information Obtained	Elemental composition and chemical bonding	Chemical bonding and molecular weight
Quantitative Analysis	Yes, best with standards	Difficult, requires standards
Typical Maximum Analysis Area	2 mm x 0.8 mm	300 µm x 300 µm
Minimum Analysis Area	15 µm	2 µm (analysis) 0.2 µm (imaging)
Sampling Depth	<10 nm	<1 nm
Detection Limit	0.04 – 1.0 atom%	1 ppma, 1×10^8 atom/cm^2
Imaging	Yes, limited	yes, rapid

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