

Multilayer Packaging Film Characterization

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INTRODUCTION

Flexible packaging films function as barriers to extend shelf life of food products by protecting them from the environment. These films can be single layer or multi-layer constructions. Polyolefins (polypropylene and polyethylene) account for the majority of the packaging film market (~65% in 2009). Multi-layer film processing methods include monolayer or coextruded film extrusion (blown or cast), coextrusion blow-molding, profile coextrusion, thermal lamination, and coating. Packaging applications include sleeves, pouches, bags, and shrink films. Each layer imparts specific properties: heat sealability, gas barrier, printability, toughness, puncture resistance, moisture resistance, etc.

Understanding the construction/composition of films is beneficial for a variety of reasons:

- Reverse engineering to identify an alternative source
- Patent infringement litigation support
- Failure analysis to determine root cause (e.g., delamination, ink bleed, processing defects)

LAYER CONSTRUCTION

Layer construction can be investigated using cross-sectional analysis. Cross-sections can be prepared in several ways, including razor blade cut, microtome, cryo-microtome, ion milling, cryo-ion milling, focused-ion beam (FIB), and plasma FIB, depending on film thickness and if relatively soft/tacky adhesive tie layers are present. With the latter, cryogenic processes are necessary to prevent smearing, tearing, plastic deformation and pullout. Cross-sections can also be prepared at different angles to artificially increase layer thickness.

Depending on the film manufacturing process, optical microscopy (OM) and/or scanning electron microscopy (SEM) can be used to determine the number/thickness of layers in cross-section. Typically, films that are laminated or coated have more well-defined layer interfaces that scatter light and can be readily observed by OM.

Often SEM is used to visualize and distinguish layers when the following situations apply:

- Layers have distinctly different elemental composition
- Layers 'cut' differently due to differences in their mechanical properties

Most polymers are comprised of carbon, hydrogen, oxygen, and nitrogen. If the layers are composed of polyolefin(s) (carbon-based), individual layers will be difficult to differentiate by SEM imaging since they will have a similar grayscale in backscatter electron mode. Polymers such as FEP, PTFE, and PVDF will have a lighter contrast (lighter grayscale) compared to polyolefins due to the presence of fluorine, a higher atomic number element. Nylon and EVOH materials contain oxygen in their backbones, thus they will show contrast relative to polyolefins or halogen-containing polymers.

Figure 1 shows an SEM image of a film cross-section that was prepared by mounting a film piece in epoxy and cutting with a microtome to create a relatively flat/smooth surface. Four distinct layers were observed based on differences in electron density. Energy dispersive spectroscopy (EDS) was performed to confirm that the darker layers contained primarily carbon, the lighter layers contained carbon and oxygen, and layer 4 also contained nitrogen.

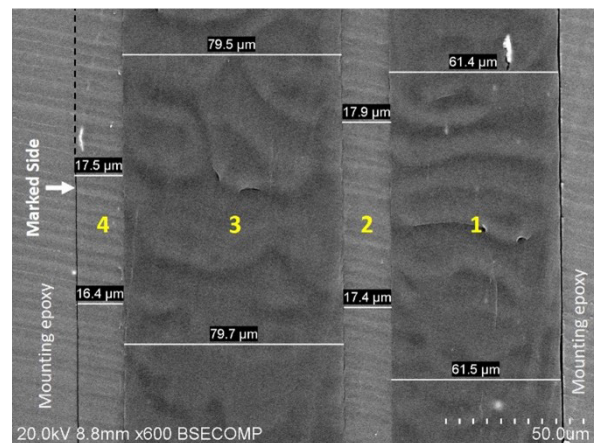


Figure 1. SEM image of a four-layer packaging film cross-section in backscatter electron mode

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LAYER COMPOSITION

Once a cross-section is prepared, there are several complementary techniques that can be used to assess chemical family of each layer, and the choice of technique depends on layer thickness.

Technique	Lateral Resolution or Spot Size	Information
Fourier-transform infrared spectroscopy (FTIR)	40 – 50 μm	Functional group ID (infrared light source, based on light absorption at specific wavelengths)
Raman spectroscopy (Raman)	1 μm	Functional group ID (laser light source in near-IR or visible region, based on light scattering)
NanoIR (AFM-based)	30 nm	Same as FTIR + topography
Time-of-flight secondary ion mass spectrometry (TOF-SIMS)	100 – 400 μm	Ionized fragments, molecular and elemental composition

Bulk techniques such as differential scanning calorimetry (DSC) and pyrolysis GC/MS can be used to identify specific homopolymer and copolymer types in the stack-up. For semicrystalline polymers, different types will have distinctly different melting temperatures (e.g., 105-115 $^{\circ}\text{C}$ for LDPE vs. 135 $^{\circ}\text{C}$ for HDPE). Polymers can also be pyrolytically decomposed to isolate and identify monomers/comonomers, oligomers, and isomers that are unique to specific polymer types.

EXAMPLE 1

FTIR and Raman spectroscopy were used to determine layer composition of the four-layer film shown in Figure 1. Based on FTIR spectra, the polymer family of layer 4 was a good match for nylon 6, an aliphatic polyamide. Based on Raman spectra, layer 4 also showed the presence of an aromatic polyamide. Unlike FTIR, Raman is more sensitive to polarizable functional groups (e.g., aromatic groups); aromatic groups scatter light more intensely than CH groups by Raman. Thus, layer 4 was consistent with MDX6, which is commonly blended with nylon 6 for gas barrier applications. Mechanical properties were also measured to establish baseline properties for purposes of finding an alternative source.

EXAMPLE 2

NanoIR was used to determine layer composition of a three-layer film. Based on SEM analysis, the middle layer had a thickness of approximately 5 microns. Figure 2 shows topographical (height) and chemical maps that span across all three layers. Chemical maps were created by positioning a cantilever on the surface, irradiating the sample with infrared light at a fixed frequency, and detecting cantilever displacement. The material expands and displaces the cantilever tip when it absorbs IR due to bending and stretching of specific molecular bonds. Amide and alkene (C=C) functional groups at 1050 cm^{-1} and 1645 cm^{-1} were unique absorption peaks that confirmed the presence of nylon and ethylene vinyl alcohol (EVOH), respectively. It was determined that the film was comprised of nylon outer layers and an EVOH middle layer.

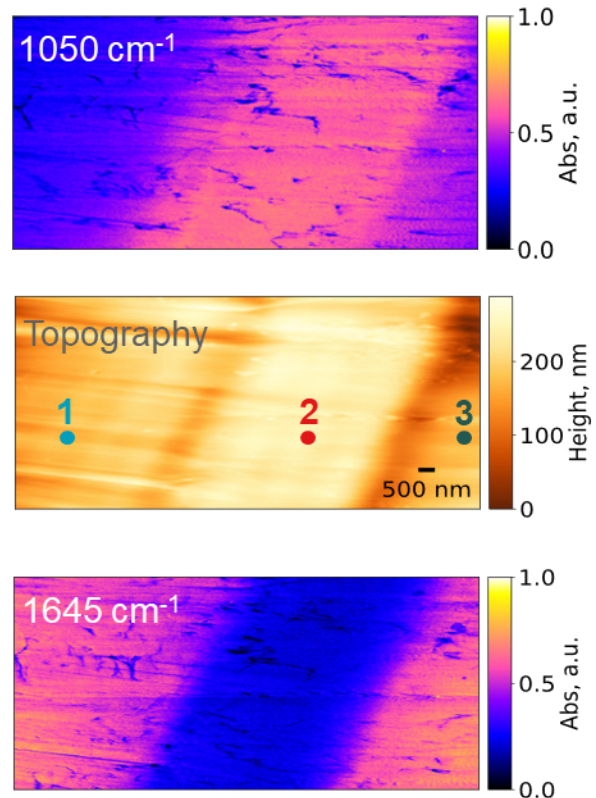


Figure 2. NanoIR color maps (left) and spectral overlays with reference spectra (right) confirming three distinct layers

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FAILURE ANALYSIS CASE STUDY

An investigation was performed to assess root cause of ink transfer from packaging film to the surface of a perishable food product at the heat seal. Packaging film was sourced from two vendors (Vendor A and Vendor B), heat sealed using the same process, and the ink transfer issue was only observed in product with film from Vendor B. The film was constructed with an outer web (PET barrier) with blue ink printed on the backside that was bonded to an inner web (heat seal) using an adhesive. The ink is sandwiched between film layers during the heat sealing process as shown in Figure 3. Based on FTIR analysis, both films had PET outer web and ethylene vinyl acetate (EVA) inner web layers.

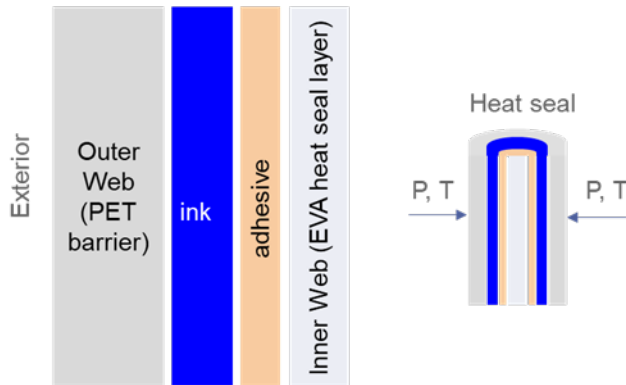


Figure 3. Schematic of food packaging film and heat seal layer stack-ups

Upon examination of the heat seals on packaged products using Vendor A and Vendor B films, it was observed that Vendor A seals were intact, and Vendor B seals had large tears/holes as shown in Figure 4.

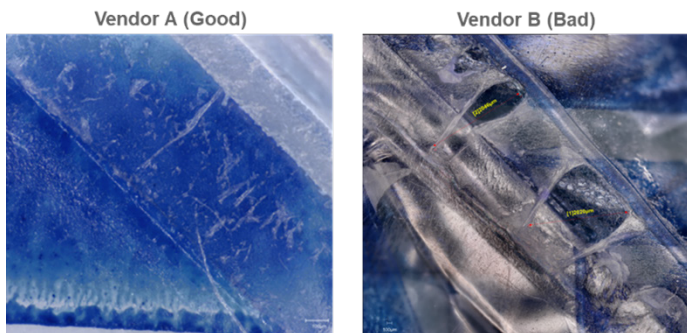


Figure 4. Optical images of the heat seals on packaged food products using film from Vendor A (left) and Vendor B (right)

Interlayer bond strength was also evaluated on coupons removed from packaged products at unsealed locations. The outer and inner webs were intentionally delaminated at one end of each coupon using chemical or mechanical separation; Vendor A film was well-bonded and required soaking in an organic solvent to initiate delamination, whereas Vendor B film delaminated readily using tweezers. Once the delamination was initiated, the inner and outer webs were pulled apart (~90° peel) at a fixed crosshead speed. As shown in Figure 5, Vendor B film webs peeled apart easily at a low load (adhesive failure mode) and Vendor A film exhibited breakage of the webs (cohesive failure mode) at ~5X higher load.

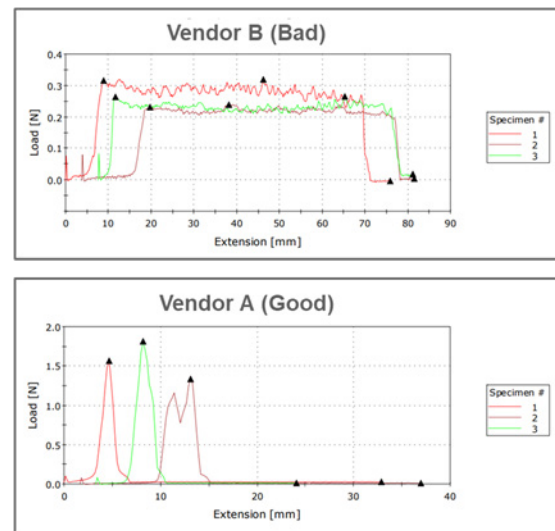


Figure 5. Interlayer peel strength results for Vendor B (top) and Vendor A (bottom) films

It was determined that Vendor B film had poor interlayer bonding that led to excessive flow and tearing of film during the heat sealing process, providing a path for the ink to migrate into the food product. Contributing factors to Vendor B film failure could include differences in adhesive chemistry, adhesive coverage, and/or surface treatments associated with film manufacturing.

SUMMARY

Multi-layer packaging films can be characterized using a variety of techniques to determine number of layers, layer thicknesses, and chemical identification of individual layers. Spectroscopy, thermal analysis, mass spectrometry and microscopy can be combined to provide a comprehensive picture of the film construction. A thorough understanding of key differences may be critical for developing novel packaging systems, determining root cause of failures, and assessing intellectual property concerns.