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Case Study
Identifying Films Layers of a Blood Bag

Released by:

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Job Number: JXXXXX

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Date

Client Name
Company Name
Address

Phone
Email

Dear Valued Client,

Please find enclosed the test results for your sample described as:

1. Blood Bag

The following tests were performed:

1. Fourier Transform Infrared Spectroscopy Microscopy (FTIR-Micro)
2. Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDX)
3. Pyrolysis Mass Spectrometry (PYMS)

Objective

Thin films used in packaging can often contain far more complexity than their simple appearance may suggest. These samples may contain multiple layers, sometimes only a few microns thick, in order to maximize the favorable properties that can be gained from the different chemistries of each layer.

In this study, a blood bag was found to have two different chemistries when analyzing the inside and outside of the bag. Further investigations revealed even more layers, all of which may play important factors in the final properties of the sample. The goal of this case study was to investigate the blood bag by multiple methods in order to identify and measure the various layers present in the sample.

Summary of Results

A summary of the layers for *Blood Bag* is shown in **Table 1**, with a cross-section in **Figure 1**.

The *Blood Bag* sample was found to have four separate polymeric layers: two polyethylene layers and two polyamide layers, one of which contained a secondary polymer, such as polyvinyl alcohol. FTIR-micro was used to map a cross-section of the *Blood Bag* and identify the bulk chemistry of each layer, and was even able to discern the differences between the two polyamide

layers. SEM-EDX was used to obtain more accurate thickness information on each layer of the film, and could be used to identify which layers contained significantly more C, N, and O. Finally, selective dissolution was applied to successfully separate the four layers into additional films, which were then analyzed by PYMS to confirm the identifications made by FTIR-micro and provide more definitive polymer identifications beyond bulk chemistry. Additionally, PYMS was able to identify a mixture of polyamides present in the fourth layer, which were indistinguishable from each other with FTIR alone.

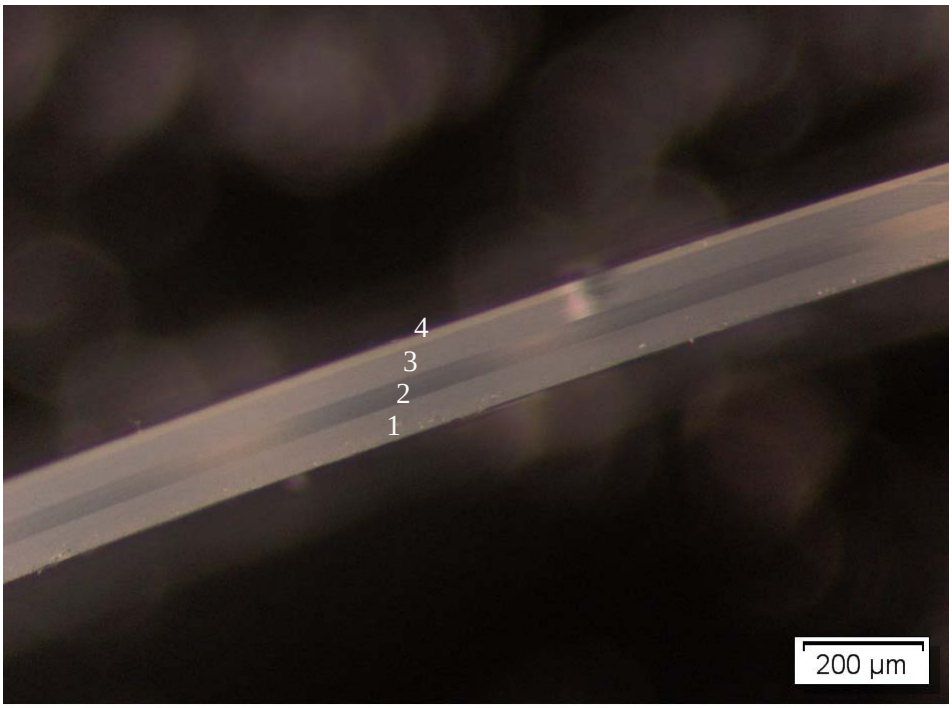

Figure 1: Cross-section of *Blood Bag* with numbered layers

Table 1: Summary of Analysis for *Blood Bag*

Layer Number	Approximate Layer Thickness by SEM (µm)	FTIR Identification	Layer Major Elements by EDX	Solvent In Which Layer was Insoluble	PYMS Identification
1	39	Polyethylene	C	HFIP	Polyethylene
2	39	Polyamide/PVA	C, N, O	TCB	Nylon 6/PVA
3	41.5	Polyethylene	C	HFIP	Polyethylene
4	11.6	Polyamide	C, N	TCB	Nylon 6,6/Nylon 6

Initial Investigation

The *Blood Bag* sample, shown in **Figure 2**, was initially tested using attenuated total reflectance mode FTIR analysis. However, it was found that the inside and outside surfaces produced significantly different FTIR spectra, as seen in **Figure 3**. This prompted further investigation into the composition of the bag, analyzing the number and chemical composition of the layers.

Figure 2: *Blood Bag* sample

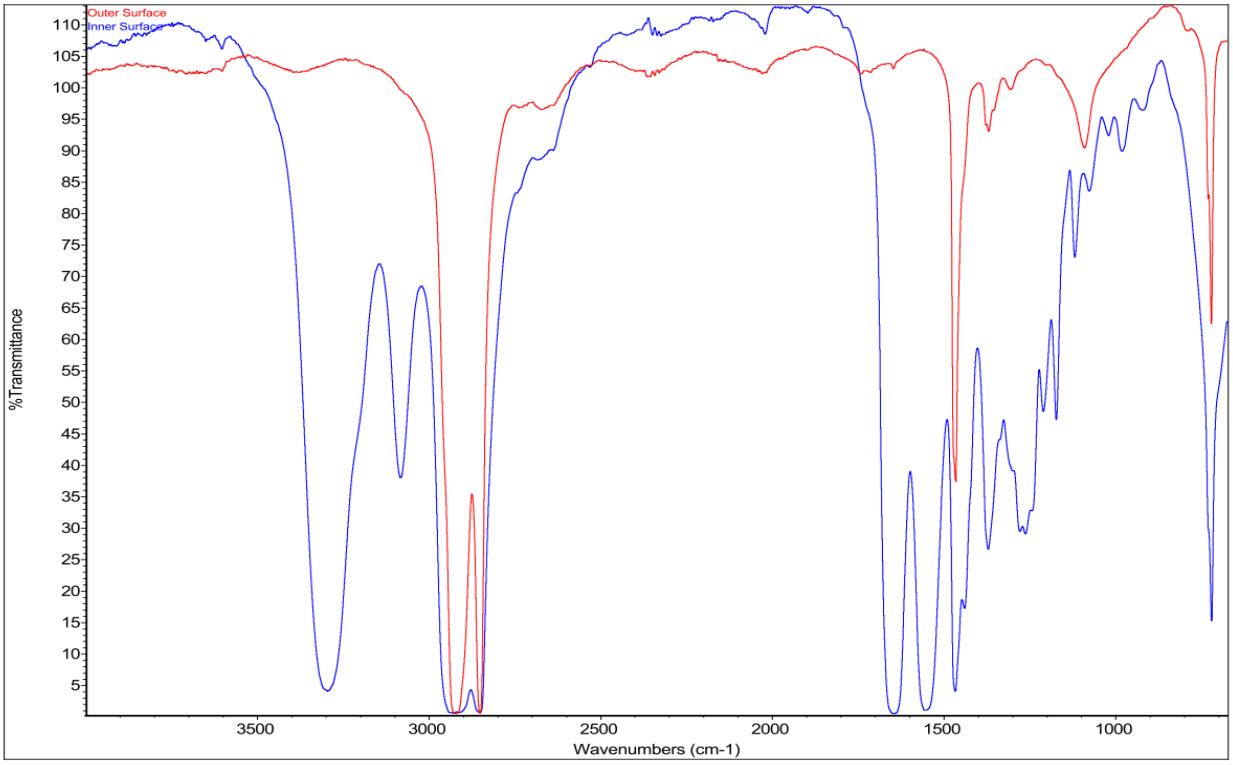

Figure 3: FTIR spectra of inner (blue) and outer (red) layers of the *Blood Bag*

Sample Preparation and Optical Microscopy

The sample was cross-sectioned using a scalpel and imaged by optical microscopy. As seen in **Figure 4**, the *Blood Bag* was found to comprise four layers visible my optical microscopy. The layers were large enough to be measured, summarized in **Table 2**, although Scanning Electron Microscopy is recommended for smaller layers for higher accuracy, as seen in **Figure 12**.

Table 2 **Layer Thickness by Optical Microscopy**	
Layer	Thickness
1	54.56
2	37.34
3	47.79
4	15.28

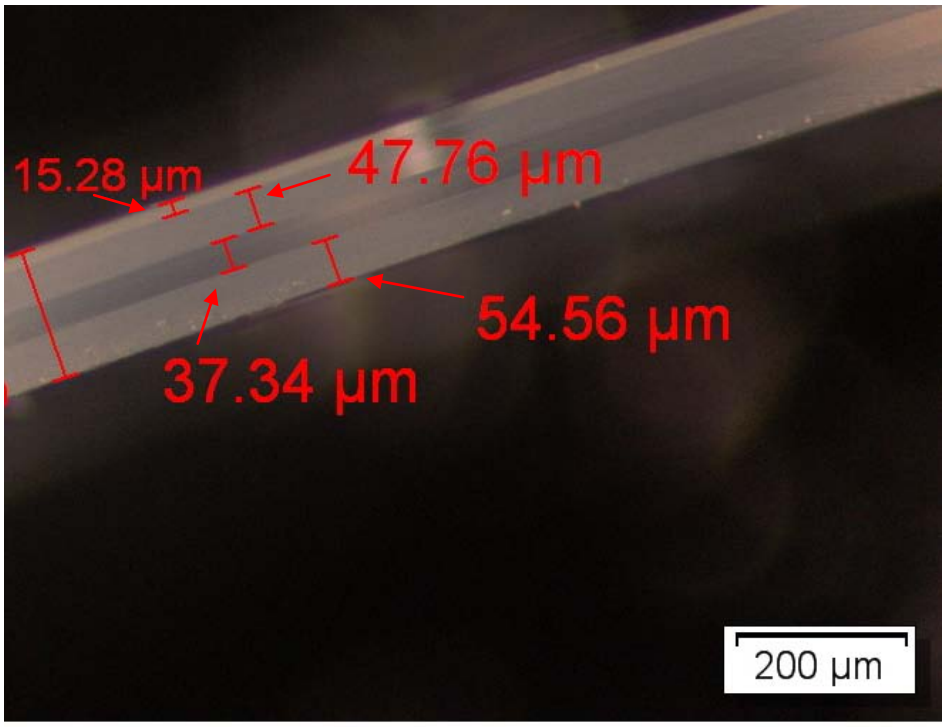

Figure 4: The cross-sectioned *Blood Bag* with layer measurements

FTIR-MICROSCOPY

A wedge-shaped cross-sectional piece of the sample was cut and compressed in a diamond cell, producing a sample of suitable transparence for mapping with transmission mode FTIR, as shown in **Figure 5**. The sample was then analyzed with FTIR transmission mode line mapping, the map of which is shown in **Figure 6**.

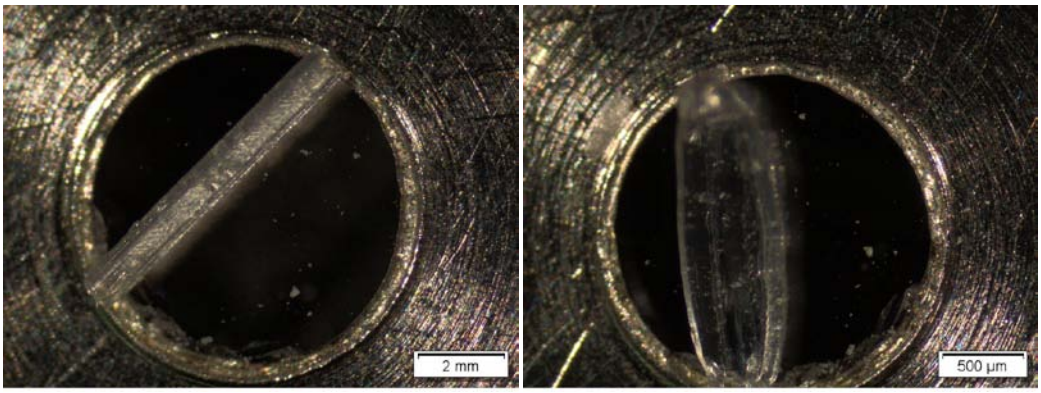

Figure 5: Cross-sectional wedges of *Blood Bag* on a diamond cell before (left) and after (right) compression

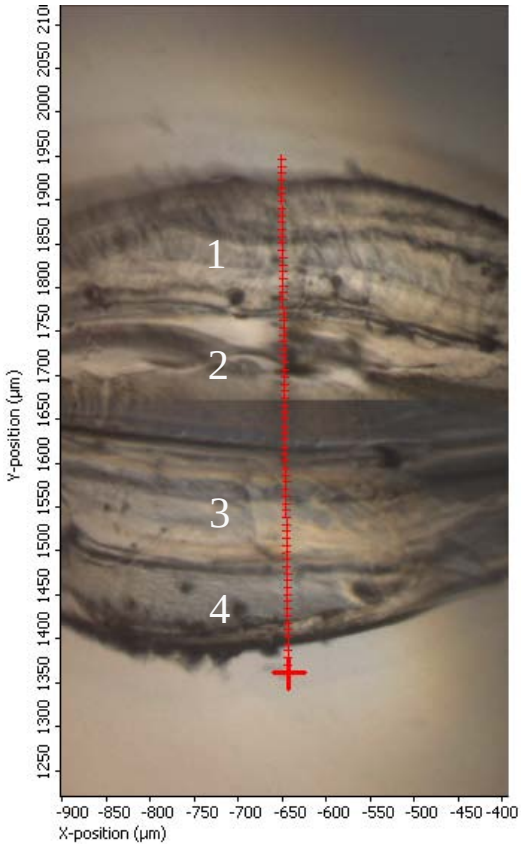

Figure 6 - FTIR micrograph of *Blood Bag* mapped area (dotted red line) with numbered layers

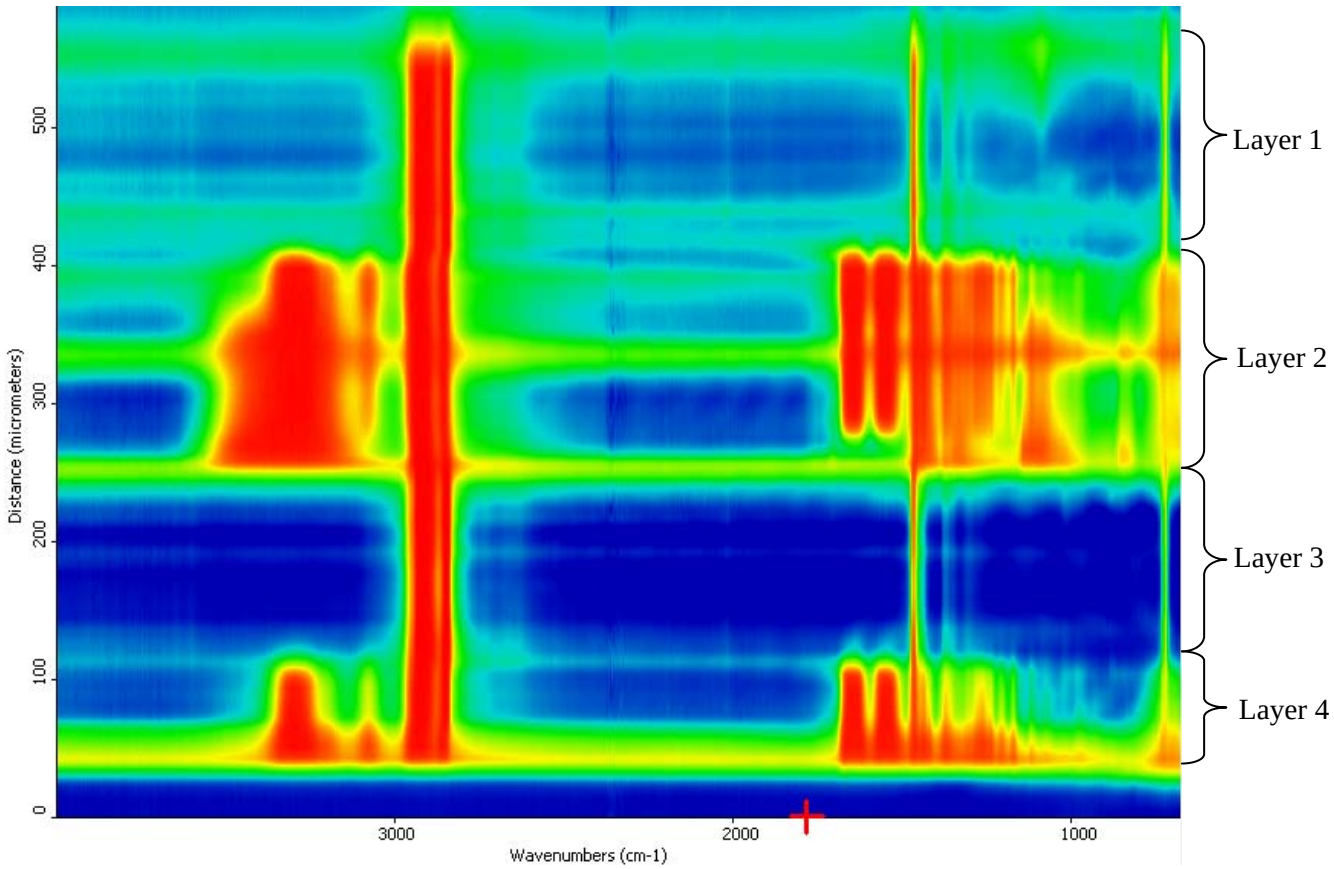

Figure 7: 2D FTIR line map of *Blood Bag*. Blue represents weak transmittance while red represents strong transmittance

The 2D FTIR line map in **Figure 7** shows where along the line map (red dotted line in **Figure 6**) the spectra intensities change for each wave number. In addition to the FTIR micrograph, this confirms that the FTIR spectrum is changing from layer to layer. Four discrete regions with continuous spectra are visibly, which is consistent with the four layers identified visibly by optical microscopy. The layers have been noted on the right side of **Figure 7**.

FTIR spectra were selected from each region, which are shown in a stacked overlay in **Figure 8**. The stacked overlay shows that layers 1 and 3 show similar spectra, as do also layers 2 and 4. Possible functional group identifications based on wavenumber are listed for all the samples in **Table 3**.

Layers 1 and 3 were found to be consistent with polyethylene. Layers 2 and 4 had several peaks in common with a polyamide, such as Nylon. However, the spectra for layers 2 and 4 exhibited some significant differences in peak shape and the fingerprint region of the FTIR spectra. This suggests the two layers are related to polyamide but one may be modified or contain a co-polymer. For example, layer 2 contains a more intense peak at 1100 cm^{-1} and a wider peak around 3300 cm^{-1}. Consequently, some significant similarities are seen when comparing the spectrum of layer 2 to polyvinyl alcohol (PVA), seen in **Figure 9**. By contrast, layer 4 shows a very clear match to polyamide, without any significant peaks unaccounted for, seen in **Figure 10**.

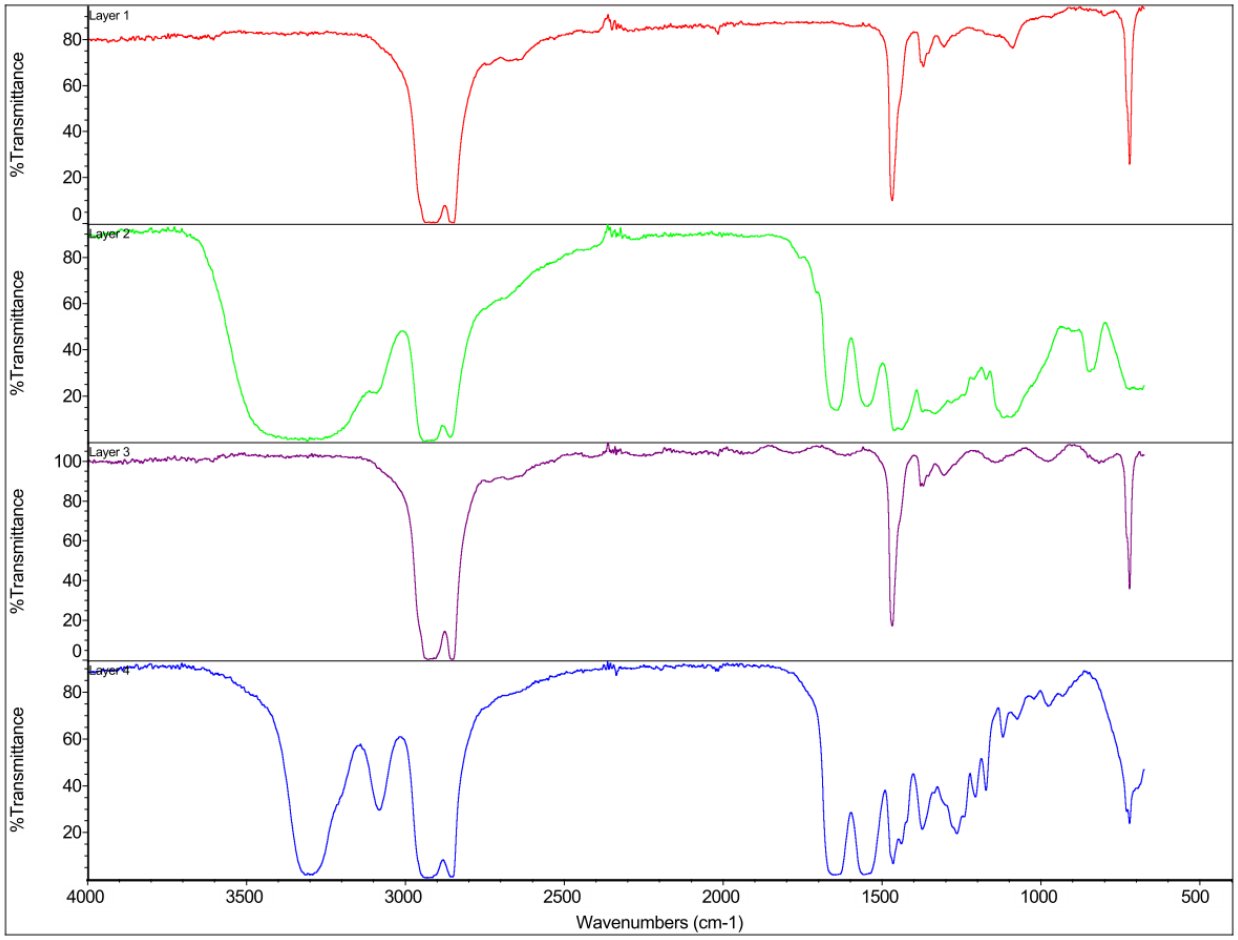

Figure 8: Stacked FTIR spectra of *Blood Bag* layer 1 (red), layer 2 (green), layer 3 (purple), and layer 4 (blue)

Table 3
FTIR Peaks and Identifications Of *Blood Bag* Layers

IR Frequency (cm^{-1})				Functional Group
Layer 1	Layer 2	Layer 3	Layer 4	
-	3308, 3090	-	3312, 3080	NH stretch
2917, 2850	2935, 2858	2930, 2850	2924, 2856	CH stretch—aliphatic
-	1641	-	1653	C=O stretch
-	1544	-	1558	N-C=O stretch
1467	1462	1467	1464	CH_2 bend
1369	1331	1369	1372	CH bend
-	1116	-	1263, 1118	CN stretch
1088	844	-	1073	C-O stretch
719	719	719	720	CH_2 rock

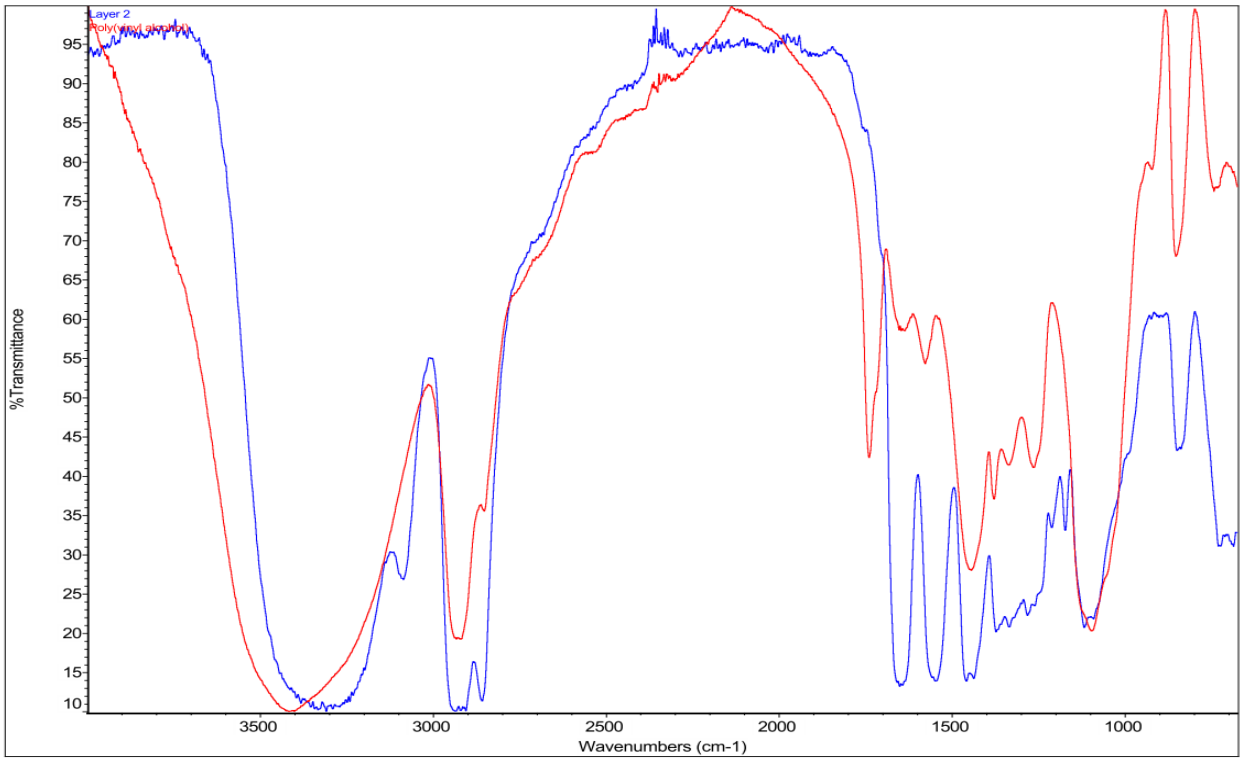

Figure 9: FTIR spectra of *Blood Bag* layer 2 (blue) and PVA (red)

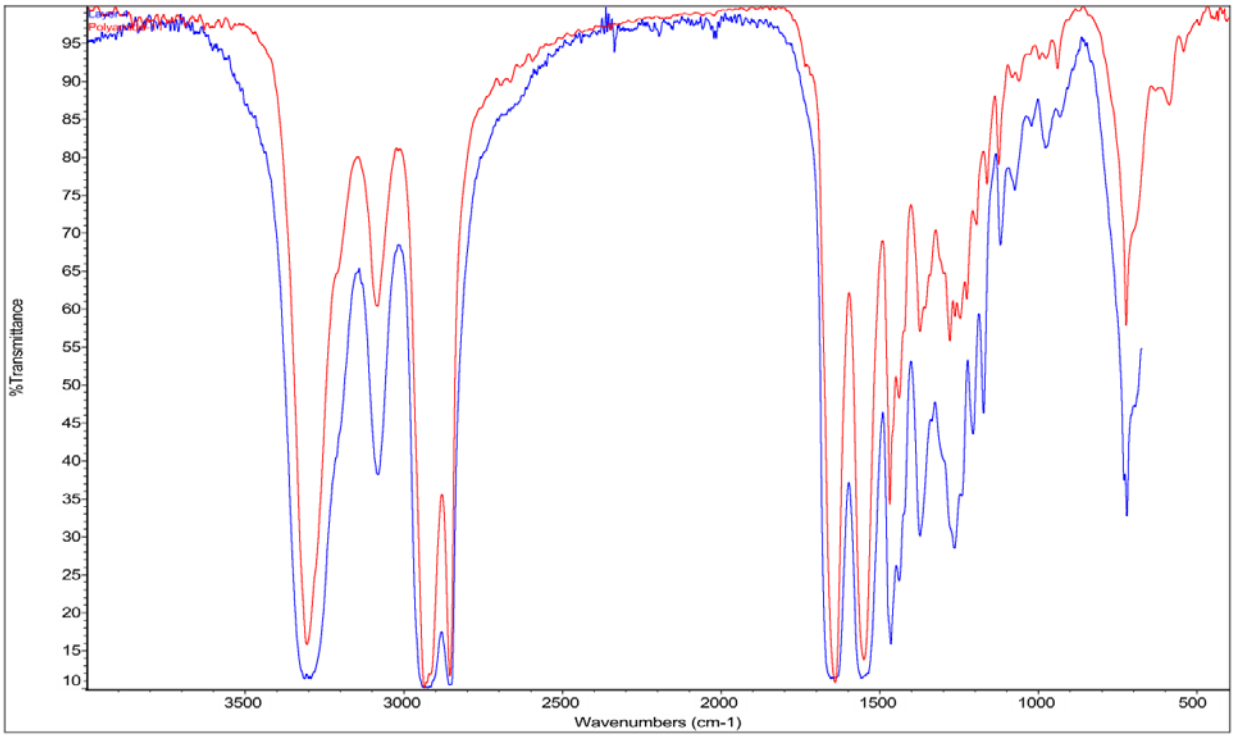

Figure 10: FTIR spectra of *Blood Bag* layer 4 (blue) and polyamide (red)

SEM/EDX

Figure 11 shows the secondary electron (SE) and backscattered electron (BSE) images of the samples. The images were then measured, as shown in **Figure 12**, to obtain another measurement thickness for each layer. The values are slightly different compared to the optical microscope imaging in **Figure 4**, which shows how SEM offers a higher level of accuracy in film measurements.

The sample was then analyzed by EDX mapping, looking for the distribution of carbon, nitrogen, and oxygen in the sample. The EDX elemental maps for the *Blood Bag* can be seen in **Figure 13**. As can be seen, layers 2 and 4 contain significantly higher amounts of nitrogen and layer 2 contains significant amounts of oxygen. This is consistent with the FTIR analysis, which found those layers to be consistent with polyamides and layer 2 to contain an additional component consistent with EVA. While EDX analysis is generally useful for distinguishing inorganic species and is only a semi-quantitative method, the slight differences in oxygen and nitrogen content can be seen and used to support the FTIR analysis.

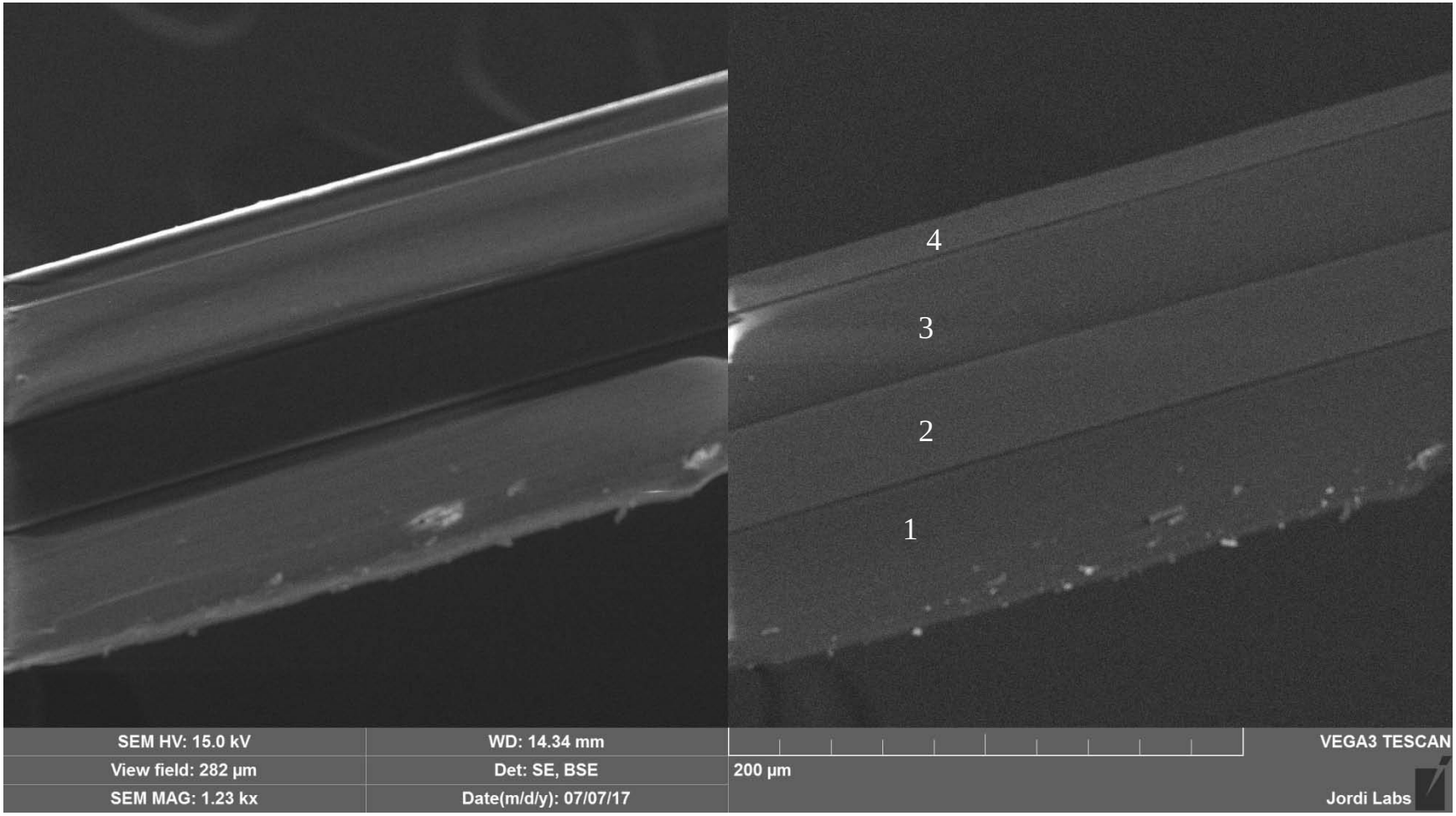

Figure 11: SEM SE (left) and BSE (right) images of *Blood Bag*, with numbered layers

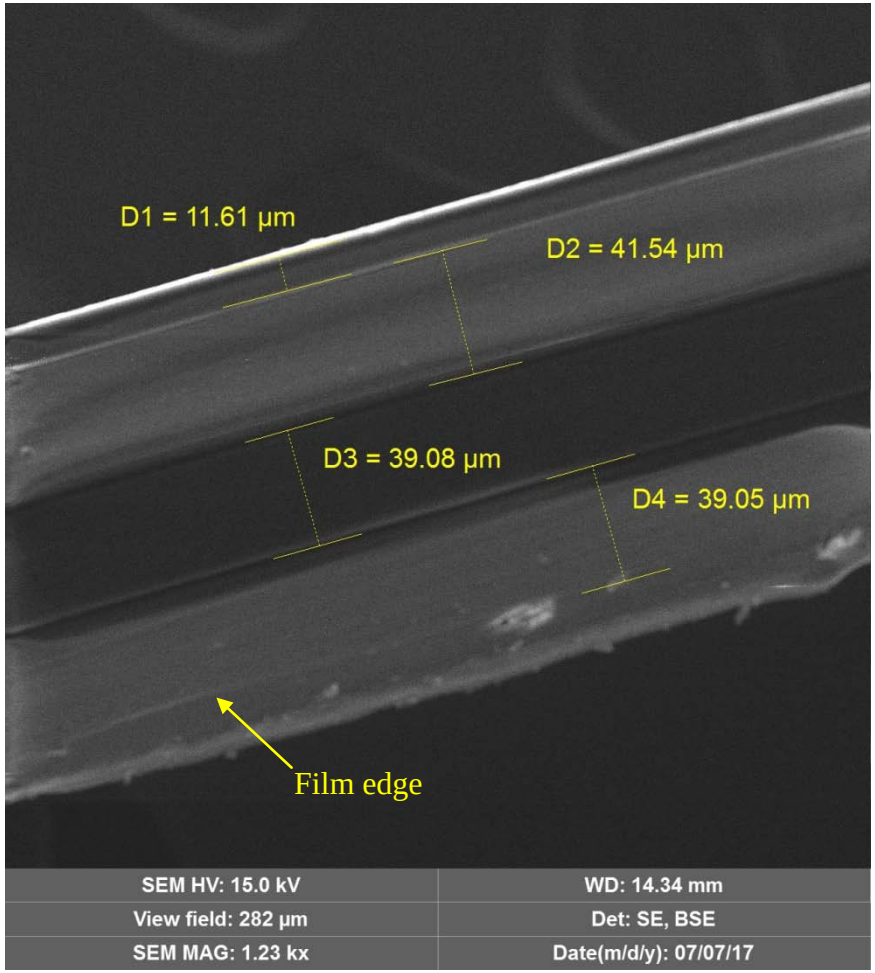

Figure 12: Measured SEM SE image of *Blood Bag*

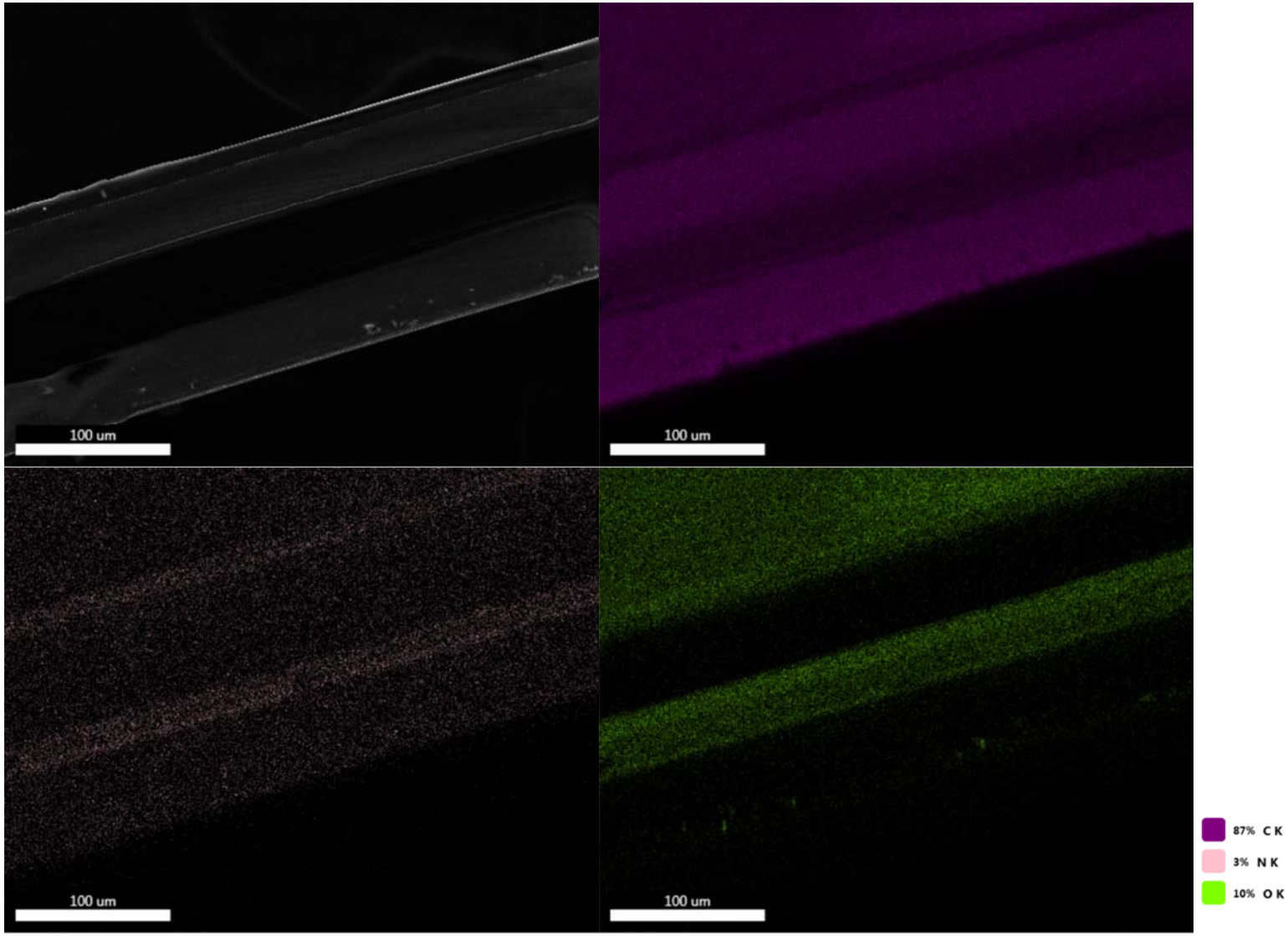

Figure 13: Individual EDX Element Maps for *Blood Bag*, showing the mapped area with SEM imaging (top left), carbon map (purple, top right), nitrogen map (pink, bottom left), and oxygen (green, bottom right)

Pyrolysis Mass Spectrometry (PYMS)

While the bulk chemistry of the film has been further revealed by FTIR and SEM-EDX, PYMS performed on the individual layers can provide a more definitive identification of the polymer layers. To achieve separation, a portion of the *Blood Bag* sample was immersed in HFIP. The film partially dissolved and two smaller films remained. These films were then tested separately by PYMS.

Analysis by PYMS was conducted using a double shot technique. The double shot experiment consists of heating a sample to release volatiles which were then cryogenically trapped and then analyzed by GCMS. Following completion of the 1st pass analysis, the remaining portion of the sample was then heated above the decomposition temperature rapidly and pyrolyzed components were passed into a gas chromatography column and analyzed by mass spectrometry. Prominent peaks found in PYMS typically include fragments of the polymer as well as monomer, antioxidants and other additives. Sample peaks were compared with over 796,613 reference compounds using the NIST/EPA/NIH mass spectral search program.

No prominent peaks were seen for the HFIP-insoluble films during the first pass, but the second pass produced two chromatograms shown in **Figure 14**. The two films were found to be consistent with each other, based on the chromatogram peaks, and the fragments observed were consistent with polyethylene. This is consistent with the findings by FTIR, which found layers 1 and 3 to be consistent with polyethylene, both of which would not be expected to dissolve in HFIP.

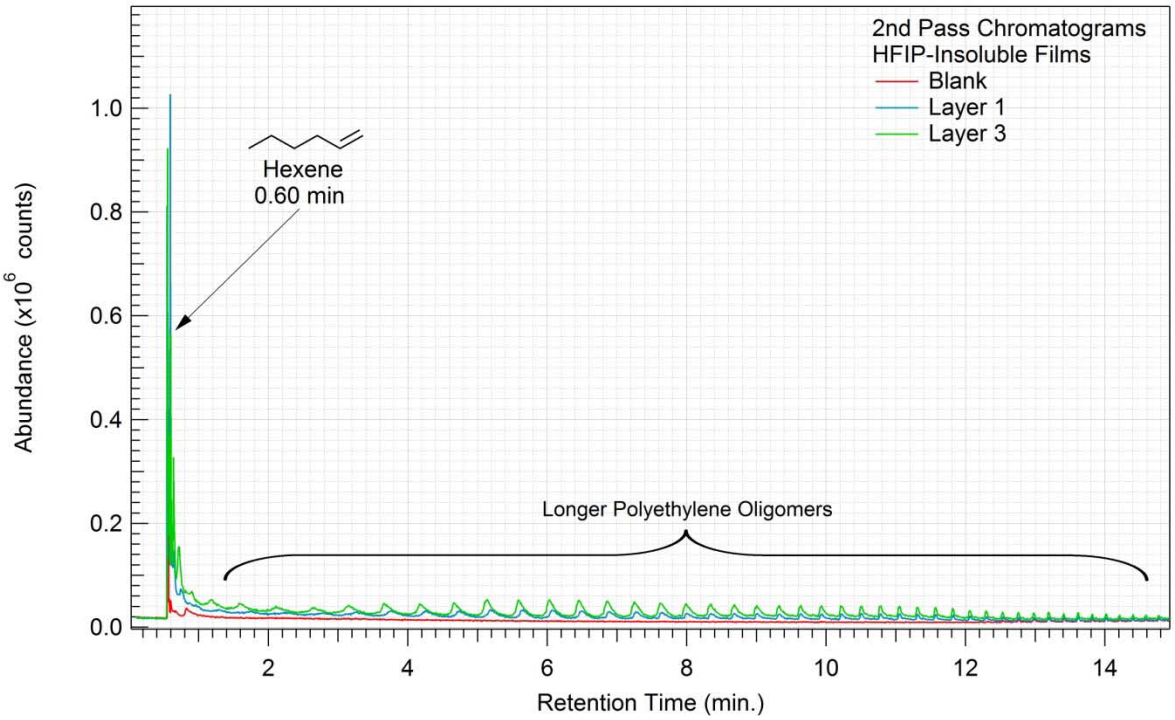

Figure 14: PYMS Chromatograms of HFIP-Insoluble layers from *Blood Bag*

To isolate the other layers, a new portion of the *Blood Bag* film was placed in hot TCB to dissolve the polyethylene layers. Once again, the film partially dissolved and two smaller films remained, which were easily separated. These films were tested separately by PYMS.

No prominent peaks were seen for the TCB-insoluble films during the first pyrolysis pass, but the second pass produced two chromatograms shown in **Figure 15**. Both films were found to have peaks consistent with polycaprolactam, otherwise known as Nylon 6.

However, one of the films was found to have degradants related to PVA, which were absent from the other polyamide film. The film without PVA fragments was also found to have unique fragments related to the polyamide Nylon 6,6. This is consistent with the FTIR results, which identified both layers 2 and 4 being related to polyamide, but with layer 2 containing an additional co-polymer, such as PVA. FTIR-micro would be unable to discern that both Nylon 6 and Nylon 6,6 were present in layer 4, but the application of PYMS allows for the two polymer species to be determined.

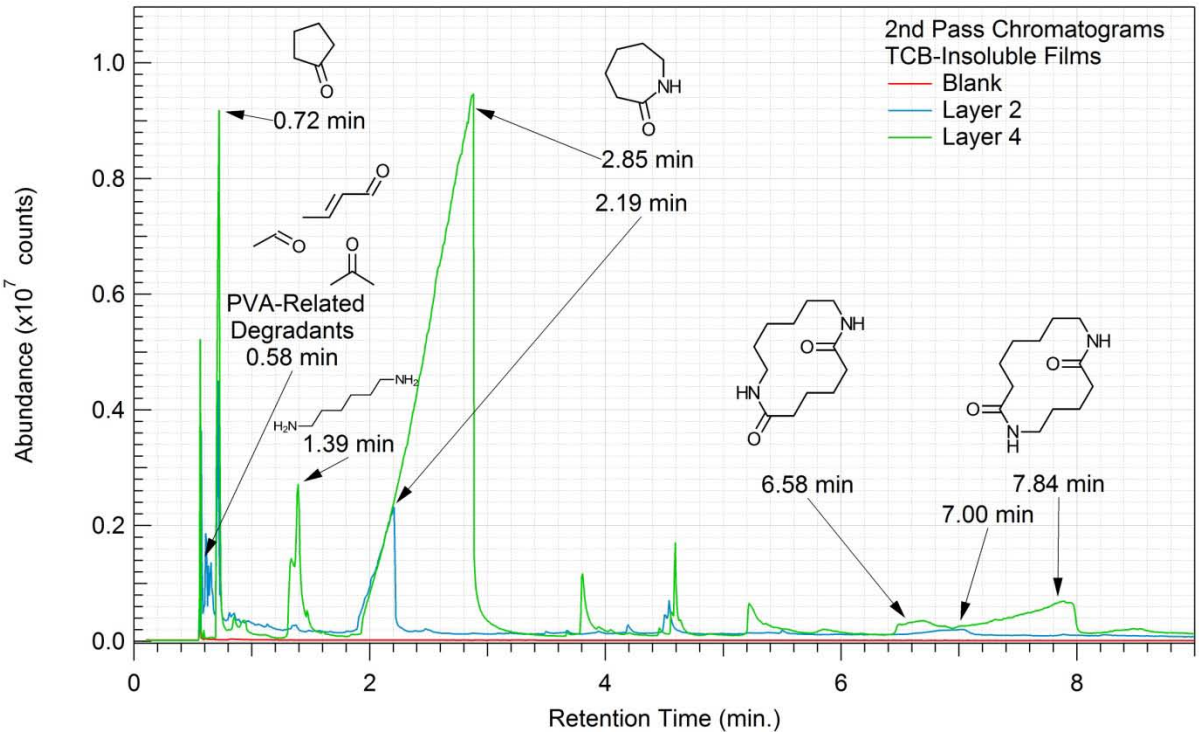

Figure 15: PYMS Chromatograms of TCB-Insoluble layers from *Blood Bag*

Analysis Conditions

This section of a Jordi report provides information on the methods used including instrument type, temperatures, solvents, sample preparation, etc. The specific conditions have been removed for this case study.

Closing Comments

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Jordi Labs specializes in polymer testing and has 30 years experience doing complete polymer deformulations. We are one of the few labs in the country specialized in this type of testing. We will work closely with you to help explain your test results and solve your problem. We appreciate your business and are looking forward to speaking with you concerning these results.

Sincerely,

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