AIMCAL Technical Paper

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Paper Title:
Analytical tools for investigating pressure sensitive adhesive-silicone release interactions.

Introduction:
There are complex interactions that take place during the adhesive coating process on siliconized release liner at the silicone-adhesive interface. These silicone-adhesive interactions can differ based on adhesive and silicone technologies. This paper will look at how analytical techniques can be used to provide insights into the resulting release coating and how that coating impacts adhesive performance of pressure sensitive adhesives (PSA). Examples will be presented demonstrating the importance of rheology, spectroscopy and microscopy towards understanding various practical concerns. The analytical data will be correlated to specific adhesive performance issues to show why and when various analytical techniques should (and should not be) used to solve critical quality and performance problems.

Overview of Analytical Techniques:

Rheology Temperature Sweep Dynamic Mechanical Analysis (DMA): Rheology is one of the most common analytical tools used for pressure sensitive adhesives to evaluate a material's viscosity and viscoelastic properties as a function of time, temperature and shear rate. Pressure sensitive adhesives are viscoelastic materials, and rheology has been proven to be a very useful technique to evaluate performance and troubleshoot formulation problems. Typical rheological analyses undergo oscillatory modes to measure the material's response to strain. The storage shear modulus (G') can be calculated and used to describe or compare the cohesive strength and tan delta (i.e. the ratio of G"/G') can be used to describe the elasticity behavior of the adhesives. DMA will allow us to determine if there is any change in the composition of the adhesive and its relationship to performance.

Scanning Electron Microscope (SEM): Scanning electron microscopes use a focused beam of high-energy electrons to generate a variety of signals at the surface of solid state materials. The resultinginformation reveals the external morphology of each sample. It is a very useful technique to look at the interface of the substrate and adhesive in order to determine changes in failure mode, coverage and morphology of different substrates.

Fourier Transform Infrared Spectroscopy (FTIR): Fourier transform infrared spectroscopy is an analytical technique to identify organic materials. This technique measures the absorption of infrared radiation by the sample material versus the wavelength. The absorption bands help identify molecular components and structures. Pressure sensitive adhesives are often complex mixtures containing various solvents, resin, tackifiers, fillers and additives; it is critical to ensure consistent product quality to check the raw materials and finished product. It can be used to verify the composition of the construction, identify any changes in raw materials, or indicate possible contamination.

X-ray photoelectron spectroscopy (XPS): X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique to measure elemental composition on a sample surface. The purpose of this

technique is to identify the chemical composition of the substrate as well as any residual migration that can occur between the adhesive and substrate.

Energy-dispersive X-ray spectroscopy (EDS): Energy-dispersive X-ray spectroscopy (EDS) is also an analytical technique used for the elemental analysis. It penetrates deeper compared to XPS into the sample layer allowing the user to identify if the elemental composition is different than what is seen in the surface.

Case #1: Low Peel on Medical Tape

In this first example, we will look at a low adhesion issue regarding a medical self-wound tape using a solution acrylic PSA. The adhesive is coated onto a silicone release liner and transferred to the non-woven substrate. Performance data shows low peel values which initially points to be an adhesive issue, but it is critical to use analytical tools to identify the potential root cause in raw materials or process.

First, a Scanning Electron Microscope (SEM) was used in an effort to identify any surface differences between the finished self-wound tape, the tape backed with silicone liner and the un-coated non-woven substrate.

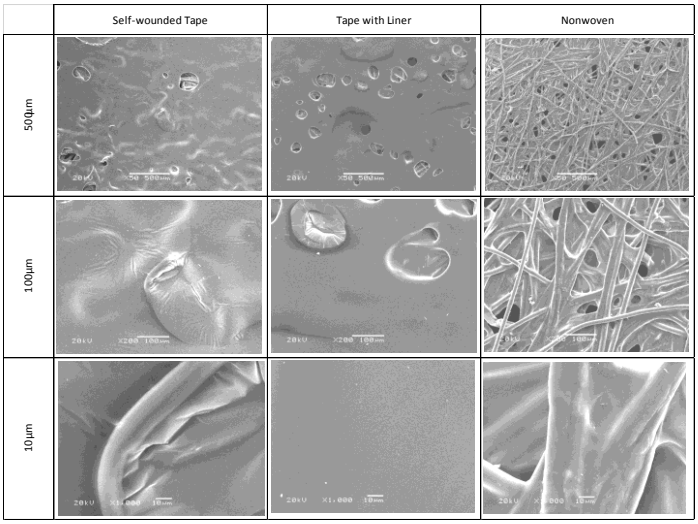
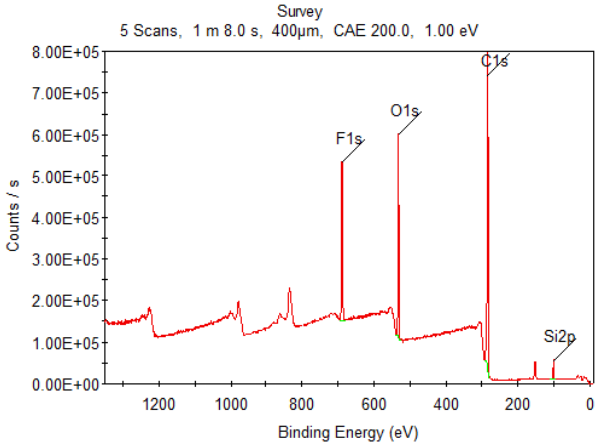


Figure 1 – Images of coated adhesive surfaces and nonwoven

SEM images aimed to point differences in the coating surfaces of two control and complaint samples as well as the uncoated nonwoven. There are no major differences between these two; the sample laminated liner has a slightly higher number of non-woven fibers exposed. This helped to eliminate the idea that there could have been any morphological issues with adhesive coating.

Further samples were submitted for Energy Dispersive Spectroscopy (XPS) in order to analyze any interaction that may occur between the adhesive surface, the self-wound non-woven, and the release liner.



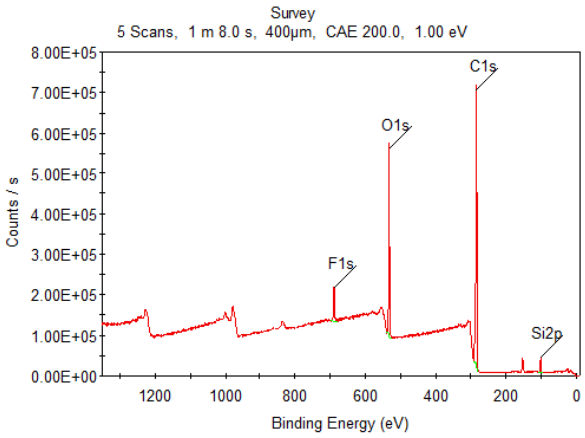
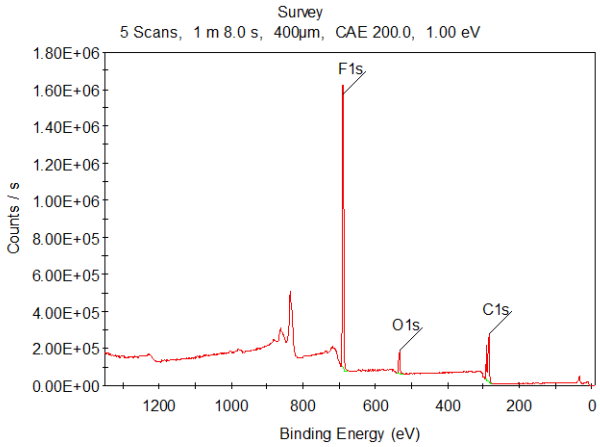


Figure 2 a, b -Surface of the self-wound roll

Surface of adhesive laminated with release liner



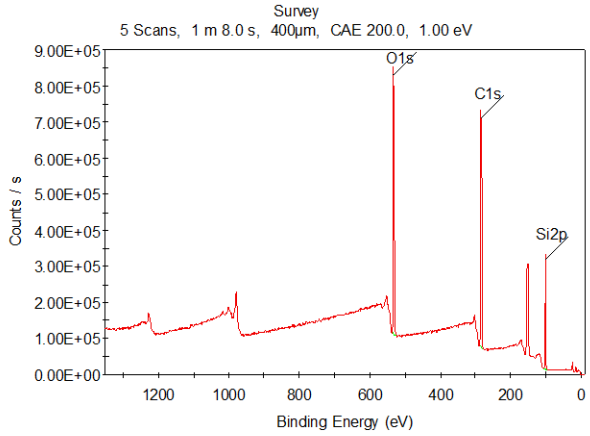


Figure 3 a, b - Surface of uncoated nonwoven

Surface of release liner

From the images above we can see high fluorine concentration in the surface of the non-woven, while the release liner didn‘t have any traces. Of the two coated samples, the self-wound roll has much higher fluorine content than the one laminated to the release liner. This points to the idea that the adhesive could be removing the fluorocarbon treatment from the surface of the uncoated non-woven.

The SEM and XPS data leads us to hypothesize that that adhesive failure is due to the migration of flourine from the nonwoven into the adhesive. To further support the hypothesis of fluorine migration, the samples were submited for EDS to identify any difussion of fluorocarboned treatment from the non-woven to the adhesive surface.

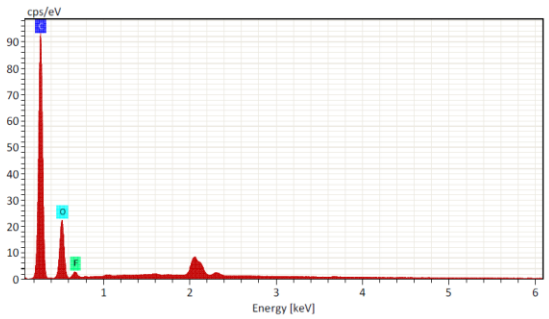


Figure 4 – Nonwoven spectra

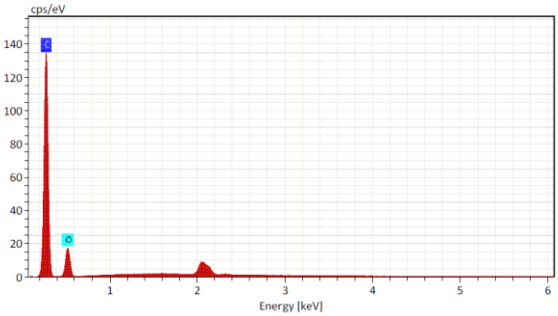


Figure 5 – Self-wounded roll spectra

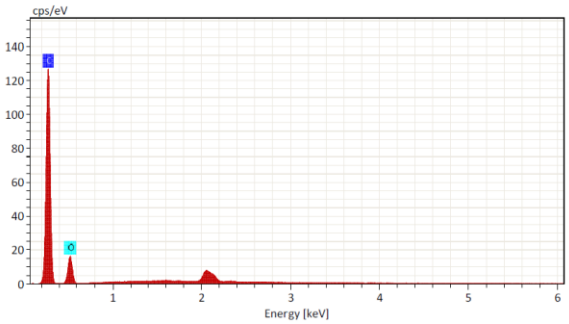


Figure 6 – Sample laminated to release liner spectra

From EDS we can see that there is presence of fluorine in the surface and inside the non-woven. Further, there are no traces of fluorine inside the adhesive in either of the two coated samples. Therefore, there is no diffusion of the fluorocarboned treatment from the non-woven through the adhesive surface.

Case #1 Results: Analytical techniques used for this case proved to be very useful in identifying the root cause. First, it was confirmed that the fluorine (fluorocarbon) source is the non-woven, as the release liner has no presence of this element. Second, from XPS, there is higher concentration of fluorine on the self-wound roll, indicating that it can be removing the fluorocarbon treatment from the uncoated side of the non-woven. Third, from EDS analysis we can see there is no diffusion of the fluorine from the non-woven through the adhesive towards the surface. Lastly, there is no major difference in the adhesive coating from either sample. Since fluorocarbon compounds are used as release agents, the presence of fluorine in the self-wound finished medical tape can help explain the low adhesion issue.

Case #2: Low Tack on Specialty Labels

The second example deals with a low tack issue on a label for high temperature application using a solution acrylic PSA. After production of the adhesive, the quality control data showed low tack for a specific adhesive batch compared to the performance of previous batches. Samples of the adhesive (both control and complaint material) were obtained, coated for performance testing, and submitted for various analytical tests. As a starting point, samples were submitted for Rheology DMA (Temperature Sweep) in order to identify any compositional differences between the complaint and control batches. Rheology may give an indication of whether the composition and/or raw material quality impacted the product performance.

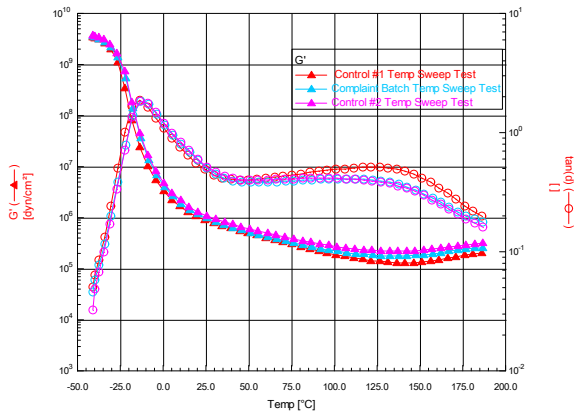
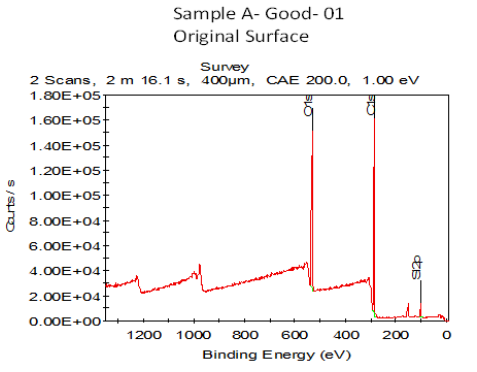


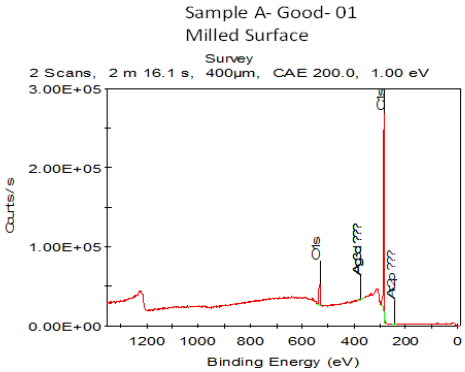
Figure 7 – Rheology DMA III case 2

The overlay plot shows shear modulus G' and tan delta (i.e. the ratio of G"/G') for the control and complaint lots. The curves for the complaint lot fall between the curves of the control batches as well as the peak tan delta (Tg) meaning that the complaint adhesive shows no major compositional differences from the control.

After obtaining inconclusive results from DMA, both lots were submitted for metals testing (in order to verify the type and amount of crosslinker) and both appeared to have the exact same amount. Further, the samples were submitted for XPS in order to look for silicone on the surface of the adhesive layer to see if there was a difference between the control and complaint adhesives. Two samples of the control and complaint adhesive were submitted. The adhesive surfaces of the samples were scanned by XPS initially for silicone and then milled in situ with argon ions for 5 minutes and then scanned by XPS again to see if any silicone remained on the surface.

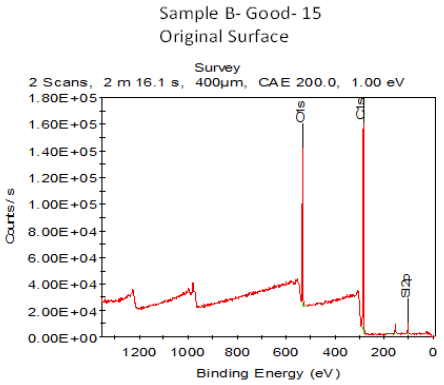


Element	C	O	Si
Concentration(at%)	72.51	22.35	5.13

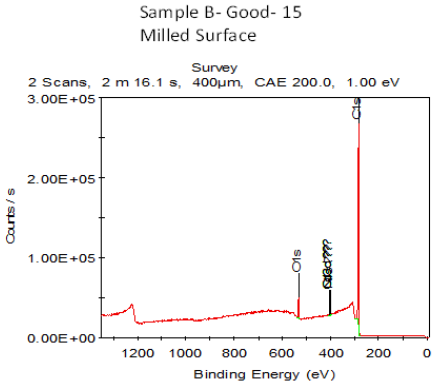


Element	C	O	Si
Concentration(at%)	65.42	4.42	N/A

Figure 8 – XPS images control sample 1

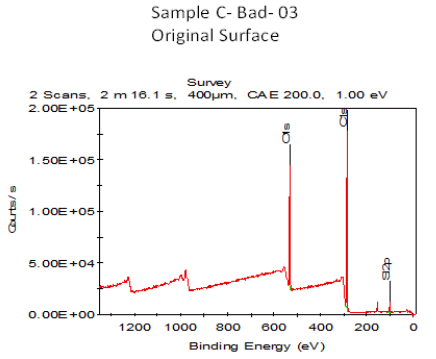


Element	C	O	Si
Concentration(at%)	75.36	20.82	3.82

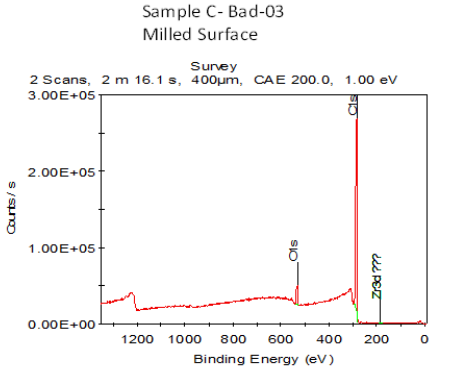


Element	C	O	Si
Concentration(at%)	94.52	4.61	N/A

Figure 9 – XPS images control sample 2

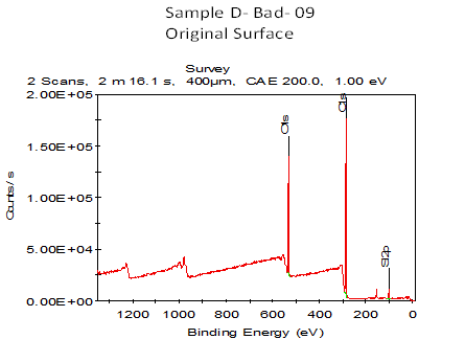


Element	C	O	Si
Concentration(at%)	74.79	20.96	4.24

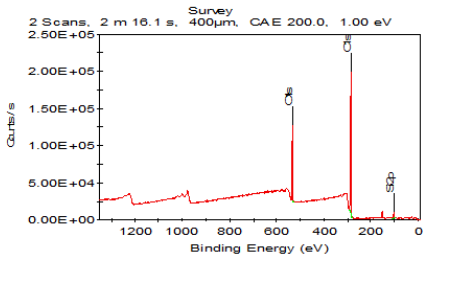


Element	C	O	Si
Concentration(at%)	95.92	4.08	N/A

Figure 10 – XPS images complaint sample 1



Element	C	O	Si
Concentration(at%)	75.2	25.37	4.43



Element	C	O	Si
Concentration(at%)	77.37	18.17	4.46

Figure 11 – XPS images complaint sample 2

As can be seen from the scans above, all samples showed relatively the same amount of silicone residue on the initial adhesive surface; however, after ion milling, only sample D (complaint sample) still had silicone on the milled adhesive surface. This seems to indicate that on one sample the silicone has actually penetrated deeper into the adhesive layer, which can result in lower tack values.

Case #2 Results: Some differences were noted between the complaint and the control lot. From an adhesive composition perspective, the control and complaint adhesive appears to be the same and consistent between batches. On the other hand, XPS testing did indicate that there is the potential that the release liner in use may be the cause of the performance difference noted.

Case #3: Low Tack in a Foam Tape Application

The last example deals with a loss of tack in a double sided foam tape using a rubber-based PSA. It was suspected that there may be a transfer of silicone from the release liner to the adhesive surface. Multiple complaint coated samples were tested against one control sample. First, the control and complaint adhesive compositions were evaluated by FTIR.

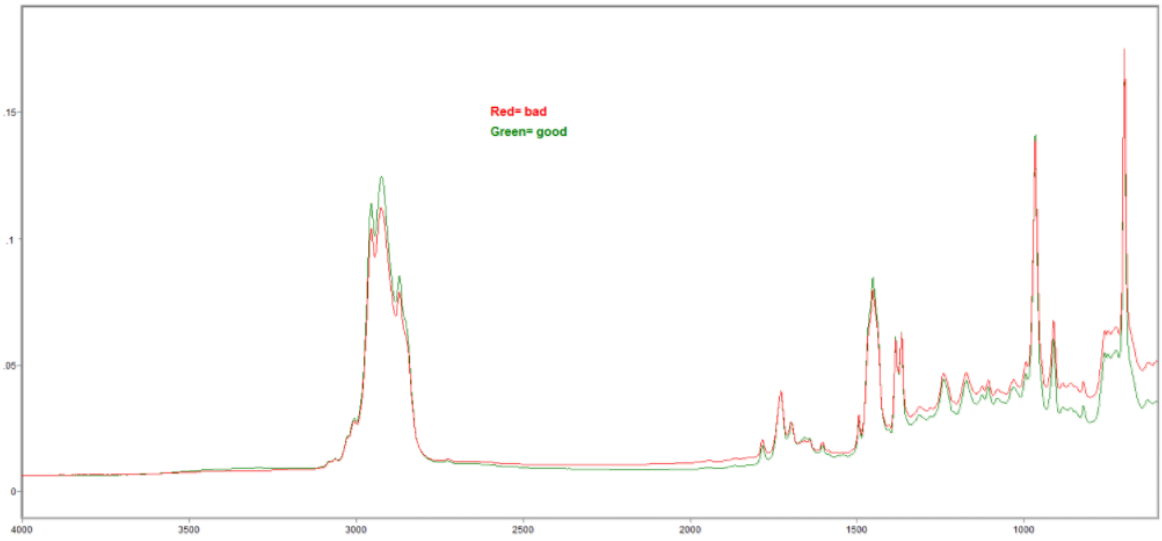


Figure 12 – FTIR image case 3

Infrared spectra of the complaint adhesives was very similar to the adhesive on the control sample. There was no evidence of any notable differences in the composition of the adhesives.

Since the FTIR data showed that the complaint samples were very similar to the control, the next step was to analyze the samples via SEM in order to evaluate the morphology of the coated surfaces.

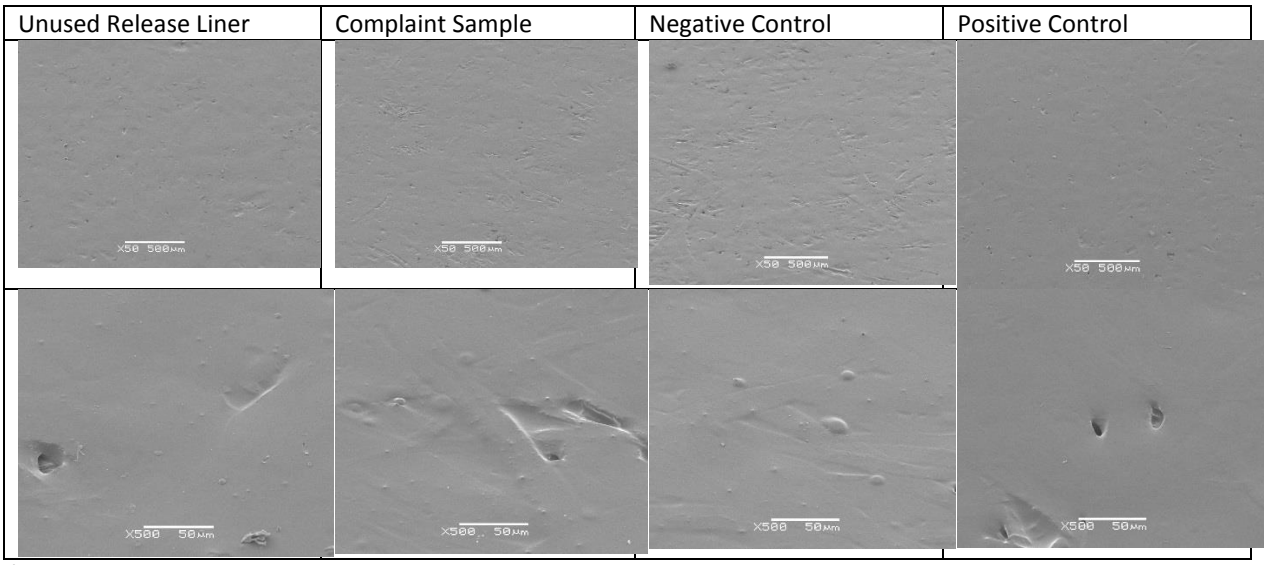


Figure 13 – SEM images case 3

Based on the SEM images above, the surface morphology is relatively consistent between the complaint and control samples. There is no evidence that liner morphology is the cause of the low tack issue. Additionally, the release liner side as well as the back side of the tapes were examined using an X-ray Photoelectron Spectrometer (XPS). Each of the surfaces examined were found to contain silicon. Constant silicon levels as a function of sample (i.e. control vs. complaint) were observed, with no distinct correlations differentiating between control and complaint samples.

By submitting the samples for multiple analytical tests, the concern over suspected silicone-adhesive interaction was eliminated and a higher focus was placed on identifying other plausible root causes within the product construction. Samples were further analyzed via Gel Permeation Chromatography (GPC) to understand if there may have been an issue with raw material molecular weight variation.

Case #3 Results: Consistent silicone transfer was observed from both sides of the liner from both Control and Complaint tape constructions. The liner does not appear, based on data available, to be the root cause of the issue. Knowing when and how to use analytical techniques to prove that the root cause did not lie with adhesive-silicone interface was very helpful as it helped steer the investigation in the right path.

Conclusion: Analytical techniques have proven to help troubleshoot issues that may occur during the adhesive coating process on siliconized liner at the silicone-adhesive interface. Some techniques are more effective than others depending on the type of issue encountered. The most important thing is to first identify any change in composition in the adhesive or raw material associated with the application (FTIR, DMAIII). Second, it is important to consider any morphological differences between the good and bad samples (SEM) and, lastly, to dig deeper into the elemental composition at the silicone-adhesive interface (XPS) and into deeper layers in the sample (EDS).

References:

1. Chen, T. T. (n.d.). STRATEGIES FOR RHEOLOGICAL EVALUATION OF PRESSURE SENSITIVE ADHESIVES (pp. 1-13, Tech.).
2. Energy Dispersive X-Ray Spectroscopy (EDS). (n.d.). Retrieved August 16, 2017, from http://www.mee-inc.com/hamm/energy-dispersive-x-ray-spectroscopyeds/
3. Swapp, S. (n.d.). What is Scanning Electron Microscopy (SEM). Retrieved August 7, 2017, from https://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html
4. XPS / ESCA. (n.d.). Retrieved August 05, 2017, from https://www.phi.com/surface-analysis-techniques/xps-esca.html

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