

## CORRELATING ADHESIVE SURFACE ANALYSIS TO ADHESIVE PERFORMANCE

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### **Introduction**

Adhesive surface chemistry is known to influence adhesion properties. This influence can be realized through design of the polymer (changing the monomer ratios or monomers used) or formulation (such as with the use of tackifiers). Surfactants, silicones or other additives can also alter the surface chemistry, although their presence may not be intentional. These latter types of species can be referred to as “nonpolymeric components”, although nonpolymeric is not strictly true. There are two main sources of nonpolymeric component changes: changes in the surface chemistry due to process changes, such as polymerization or coating conditions; or changes in the surface chemistry as a result of contamination. Study of these nonpolymeric components and their influence on surface chemistry is the focus of this article.

Formulation of water-based label and specialty tape adhesives typically requires the use of surfactants to control dynamic surface tension and aid in coatability of the adhesive, which is often dependent on the type of coater and substrate used. Unfortunately, the use of these surfactants has been shown to impact the performance of the dry adhesive films<sup>1</sup> and therefore their use requires formulators to have a thorough understanding of surface chemistry in both a wet and dry state.<sup>2</sup> Surfactants are also used in latex polymerization and are nearly unavoidable in water-based latex polymers.

Contamination is another widespread issue in surface chemistry. Species of low surface energy or solubility can collect at a surface or interface and significantly alter performance of an adhesive. For example, contamination of a water-based latex adhesive with a surfactant can significantly alter the surface chemistry. Additionally, in systems where an adhesive is stored against an easy release material, such as silicone release liner for specialty tapes or labels, or release coats on masking tapes, material from the release surface can remain with the adhesive after separation leading to a decrease in peel and/or tack.

Deliberate changes to the polymer chemistry can result in performance differences. In some cases, such as through cross-linking, the bulk properties of the material can be changed significantly, whereas the surface chemistry of the material is largely unaffected. In other situations, such as through monomer design, both bulk and surface chemistry can experience significant changes, which can alter both the modulus and the adhesive forces of the adhesive to a substrate.

Characterization of the relevant surface chemistry for differences in peel and tack measurements is most useful when it defines the chemistry of the uppermost few molecular layers. Specialized tools designed to probe this thin surface layer include secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) (also known as electron spectroscopy for chemical analysis (ESCA)), which are sensitive to the top 2 and 10 nm, respectively. Together they can provide a molecular description of the chemistry in intimate contact with the substrate. SIMS data provide molecular and elemental information, with straightforward chemical imaging capabilities. XPS yields quantitative elemental and chemical state information. Although there are other surface-related techniques such as IR and Raman, they often probe too deeply into the bulk and/or lack the sensitivity or chemical specificity to properly define a surface in a complicated matrix.

Our previous work has shown the effect of the substrate surface chemistry and morphology on adhesive properties.<sup>3</sup> For this investigation, we examined the effects of contamination and process changes to the same adhesive within a series.

## **Experimental**

### Adhesives and Peel Testing

Samples were prepared by direct coating the specified adhesive on 2 mil PET facestock and drying for 5 minutes at 80°C in a forced air oven. The target coating thickness for the adhesives was approximately 1 mil (~25 µm). The samples were covered with release liner and allowed to condition in a controlled humidity and temperature environment according to PSTC standard conditions. 180° peels were evaluated via PSTC-101 test method.<sup>4</sup> For both sample sets in this paper the base polymer was an aqueous acrylic.

### XPS

XPS data were acquired using a monochromatic Al K $\alpha$  source on a Thermo K-alpha instrument. Acquisition data points were from four 400 micron oval areas from each adhesive surface. The data are presented as the average and standard deviation of those data points. Survey spectra were collected at a 200 eV pass energy and identified elements from the survey spectra were then analyzed at high resolution with a 20 eV pass energy. Both charge compensation and autoheight were used. The take off angle was 90°. Data were analyzed using Casa 2.3.17 Dev 6 3y software.

### SIMS

SIMS data were acquired using an IonTOF IV SIMS instrument with either a Bi<sup>+</sup> or Bi<sub>3</sub><sup>+</sup> primary ion beam at 25 keV in bunched mode. The area of analysis was 500 x 500 microns with 128 x 128 pixels for 100 frames in a sawtooth pattern with a pulse rate of 120 microseconds. Charge

compensation was used. Data were analyzed using Surface Lab 6.5. Representative data are shown in this paper.

## **Results and Discussion**

### **Contamination Studies**

The adhesive performance of four lots of an acrylic label adhesive was measured on converted samples. These samples were also characterized using XPS and SIMS. For reference, a direct coated material was also examined under similar conditions. The data were interpreted with respect to the peel values so that the most relevant surface chemistry could be identified. First, the surfaces were compared by XPS as shown in Table 1. Peel values are highest for the direct coated material, suggesting that the air interface is different than the transfer coated interface due to differences in the way the adhesive itself dries. However, samples A, B and C all have relatively high Si values as shown in Table 1. The most likely cause of high Si is from polydimethyl siloxane (PDMS), as confirmed in the SIMS data shown in

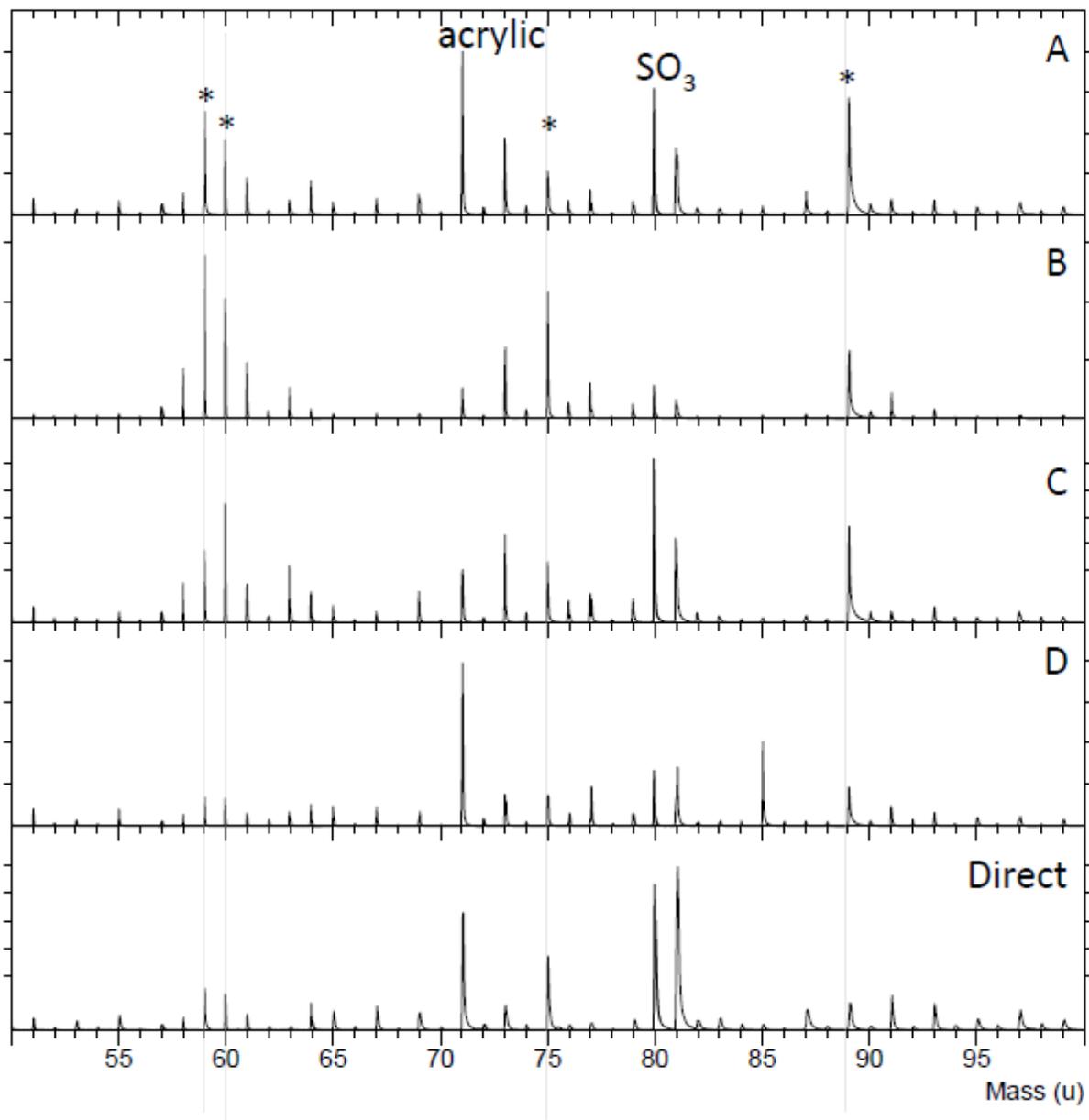


Figure 1. There are two potential sources of this silicone; from the adhesive formulation (such as a defoamer) and/or from the release liner. In this case the adhesives are reported to have the same formulation, making defoamer migration a less likely cause for reduced peel. Transfer of silicone from the release liner from incomplete cure of the silicone or from low molecular weight nonreactive silicones are more likely causes of reduced performance in this case.

Close examination of the silicone signal in the SIMS spectra show additional differences between the adhesives in addition to the concentration differences highlighted by XPS. An ion at  $m/z$  75 ( $\text{SiO}(\text{CH}_3)_2\text{H}$ ) forms from fragmentation of the main chain of the silicone polymer while a fragment at  $m/z$  89 ( $\text{SiO}(\text{CH}_3)_3$ ) is from the end group of the polymer. Typically more end group signal relative to main chain signal indicates a lower molecular weight polymer since the

ratio of end group to main chain groups increases as molecular weight decreases. Lower molecular weight polymers tend to migrate more than higher molecular weight species and are more commonly found at a surface. The presence of silicone at the surface of an adhesive can lower peel. Comparison of the direct coated material, where the only silicone source is the defoamer, and the transfer coated materials, which are also exposed to release liner, shows that the molecular weight of the silicone is generally lower on the transfer coated samples. Using this comparison, the surface of sample A has the lowest MW silicone at the surface while the direct coated sample has the highest.

Table 1. XPS atomic concentrations of species detected from the surface of various lots of adhesive. Low levels (0.2% or less) of F and N were seen on some samples but the values are removed from the table for clarity. – indicates analysis was performed but the element was not detected. Si binding energies are consistent with silicone and S binding energies are consistent with SO<sub>x</sub>. Peel values were from stainless steel (SS) surfaces.

		C	Na	O	S	Si	peel SS 20 min oz/in
<b>A</b>	Average	77.2	0.1	17.0	0.3	5.1	6.7
	StdDev	0.8	0.0	0.3	0.1	0.6	
<b>B</b>	Average	74.3	-	16.3	0.2	8.9	9.6
	StdDev	3.3		1.4	0.1	2.0	
<b>C</b>	Average	77.6	0.1	17.0	0.4	4.5	10.8
	StdDev	0.3	0.0	0.2	0.1	0.6	
<b>D</b>	Average	79.5	0.2	16.5	1.0	2.6	4.0
	StdDev	0.7	0.1	0.2	0.5	0.2	
<b>Direct</b>	Average	79.4	0.3	17.7	0.4	1.8	22.8
	StdDev	1.6	0.1	1.0	0.0	0.5	

Sample D has the lowest peel value, as shown in Table 1, yet the Si level is not particularly high in comparison to other samples with low peel values (A and B). In addition to Si, S is also detected from the surfaces of all samples examined. Based on the average value, sample D has

the highest relative amount of S, which may be due to the presence of a surfactant. Surfactant levels are also often associated with changes in peel and tack. SIMS molecular ion images in Figure 2 of the surface of sample D show a nonuniform distribution of only one of the S containing surfactants, dodecylbenzyl sulfonate ( $C_{18}H_{29}SO_3$ ). Most adhesives have uniform distributions of species at the surface, which gives consistent performance. Here the distribution of one surfactant is nonuniform, so in some areas the concentration of the surfactant is locally high. These surfactant-rich areas would be predicted to have low peel. Areas of low surfactant concentration such as the middle and lower right would likely have high peel. The peel measurement would likely have many of these high and low peel areas simultaneously tested across the inch width, which would result in a compromised peel. The high surfactant areas may be even more detrimental than the same amount of surfactant (on average) if uniformly distributed as there are abrupt regions at the peel front with low adhesion, which most likely stops any stretching of the adhesive at the interface.

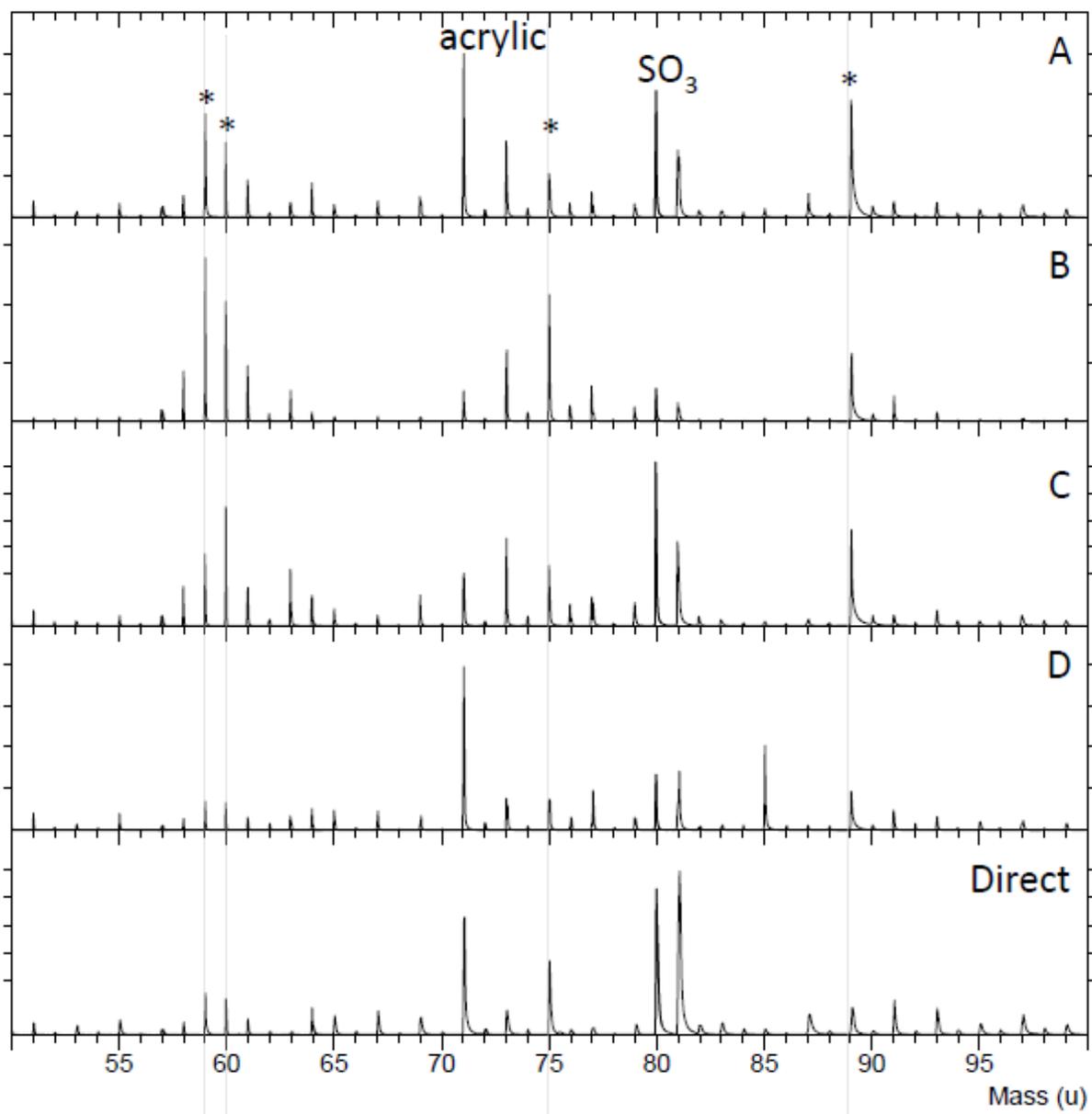


Figure 1. Negative ion SIMS spectra from the surface of five adhesive lots. \* and faint grey lines mark polydimethyl siloxane signal.

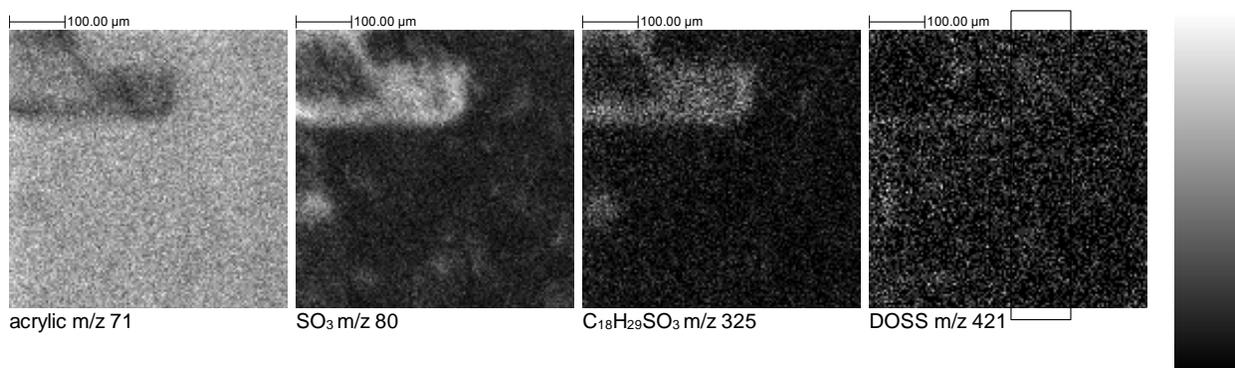


Figure 2. Negative ion images of sample D. Field of view is 500 x 500 μm. The ion imaged is listed below each image. DOSS is dioctyl sulfosuccinate.

### Changes in Process

The distribution of small molecules, such as surfactants, can be influenced by many factors in a water-based latex. This has been extensively studied in simple, predominantly single latex polymer and single surfactant systems<sup>5-22</sup>; however in complex systems like PSAs with multiple surfactant types<sup>2,23</sup> it is not straightforward to predict the influence of composition and coating conditions. Difficult to control external conditions such as exposure to humidity<sup>24</sup> are also known to influence the properties of these systems. A common trend for these studies is to use nonrealistic or excessive amounts of surfactant so that detection is analytically feasible. In a few instances surface sensitive methods are reported in the literature including one reference<sup>25</sup>, which states that SIMS is the most suitable technique for characterizing surfactant desorption. Here, we use highly surface sensitive methods, such as XPS and SIMS, and can therefore analyze materials at the surfactant concentrations used in commercial products. The limited use of surface sensitive instruments in the literature is likely due to availability and cost of these instruments; however more institutions are purchasing these instruments, which may revolutionize our understanding of these systems.

Small changes in polymerization processes can have large influences on adhesion properties. While there are many variables that can influence adhesion, such as cross-linking influencing shear, we focused on the influence of surface chemistry on peel. In Table 2 XPS data are shown for the same polymer composition produced using three closely related processes. The peel data indicate that process 1 produces a polymer with significantly different adhesive properties compared to process 2 and 3, with about double the peel and a failure mode of adhesion failure to backing. When surface data are analyzed, it is immediately apparent that process 1 results in a film with much lower Na and S levels than the other adhesives. SIMS data from the same surfaces confirms this observation by indicating a relatively lower level of surfactant (SO<sub>3</sub>) relative to acrylic polymer from process 1 compared to process 2 or 3 (Figure 3). When the level of surfactant is very low, adhesion between the steel panel and the adhesive becomes stronger than the adhesion between the adhesive and backing, switching the failure mode to the opposite

side of the adhesive. Process 2 and 3 show similar peel values, which would usually be considered equivalent with the error of peel testing. For processes 2 and 3, the XPS data indicate small but significant differences in between the systems in the level of S. Depending on the use of the adhesive, differences in performance might be seen between process 2 and process 3. Understanding the surface composition in the context of peel data provides insight into the process used to produce polymers of identical polymer compositions and highlights the importance of process consistency.

Table 2. XPS results in mol% from the surfaces of adhesives from different processes. The peel data and failure mode are also shown. A is adhesive and AFB is adhesive failure to backing. Peel values were measured on stainless steel (SS) panels.

		<b>C</b>	<b>Na</b>	<b>O</b>	<b>S</b>	<b>Si</b>	<b>180° PEEL, SS, 20 MIN DWELL (oz/in)</b>	<b>Failure Mode</b>
<b>Process 1</b>	Average	77.5	0.2	21.5	0.42	0.3	80.2	A/AFB
	StdDev	0.3	0.1	0.1	0.05	0.2		
<b>Process 2</b>	Average	76.4	0.7	21.5	0.81	0.6	41.7	A
	StdDev	0.5	0.2	0.1	0.03	0.3		
<b>Process 3</b>	Average	75.2	1.2	21.9	1.07	0.6	40.0	A
	StdDev	0.6	0.2	0.2	0.06	0.3		
<b>Process 3</b>	Average	74.3	1.2	22.5	1.16	0.9	40.0	A
	StdDev	0.2	0.2	0.1	0.03	0.2		

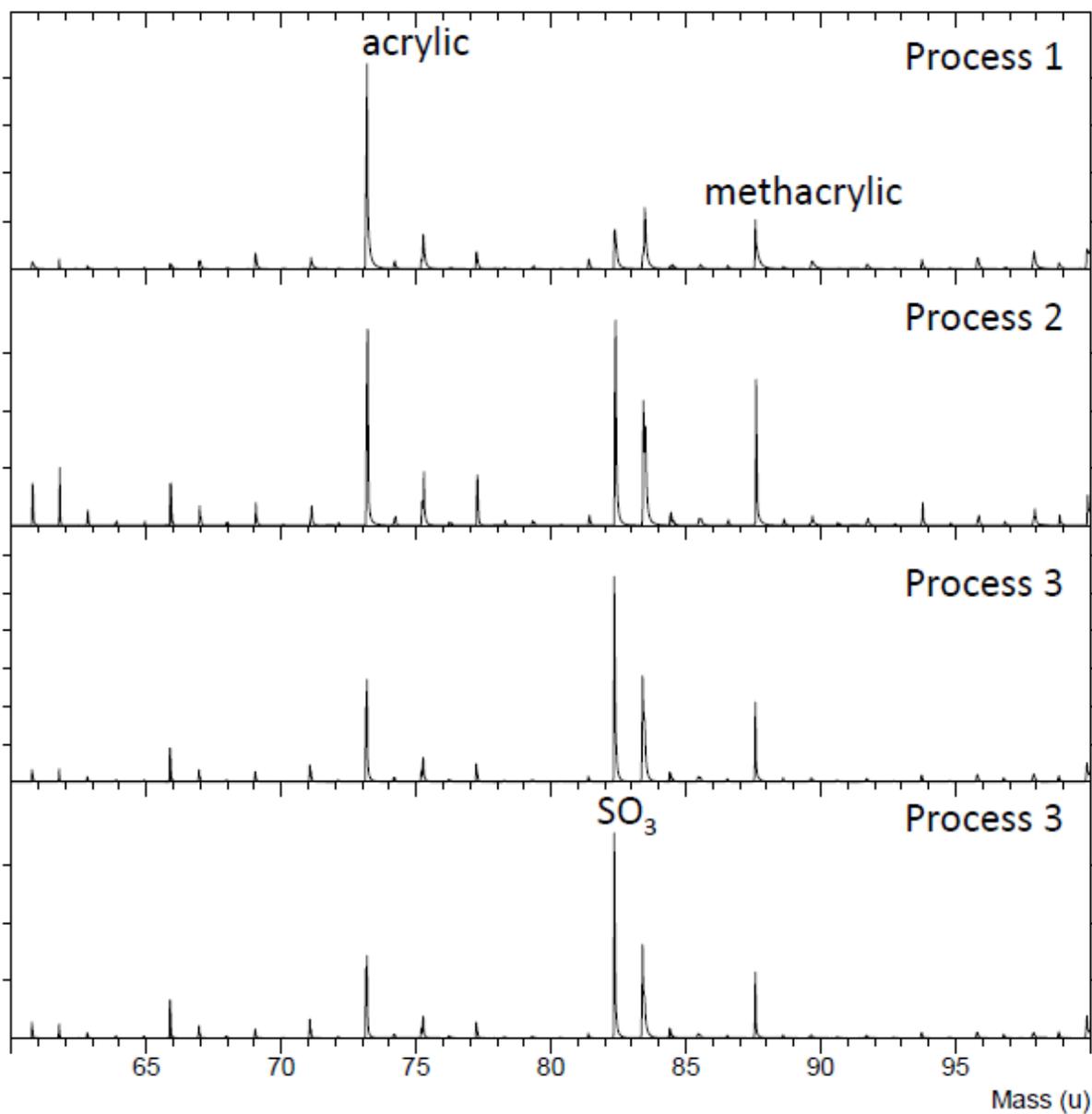


Figure 3. Negative ion SIMS spectra from the surfaces of adhesives from m/z 60-100.

Surface analysis can also be used to evaluate process consistency as it is sensitive to mobile and small molecules in an adhesive. In Table 2 the XPS data for two replicate batches from process 3 are indistinguishable within the certainty of the method. The SIMS data shown in Figure 4 further support this consistency. SIMS has higher detection limits and more surface sensitivity than XPS and the spectra are indistinguishable. The highlighted portion of the spectra showcases the ability of SIMS to detect each surfactant based on a unique molecular ion. Both alkyl benzyl sulfonate and dioctyl sulfosuccinate fragment into the  $\text{SO}_3$  ion highlighted in Figure 3. Based on

these SIMS spectra one would expect identical adhesive performance if there are no bulk changes to the polymer chemistry.

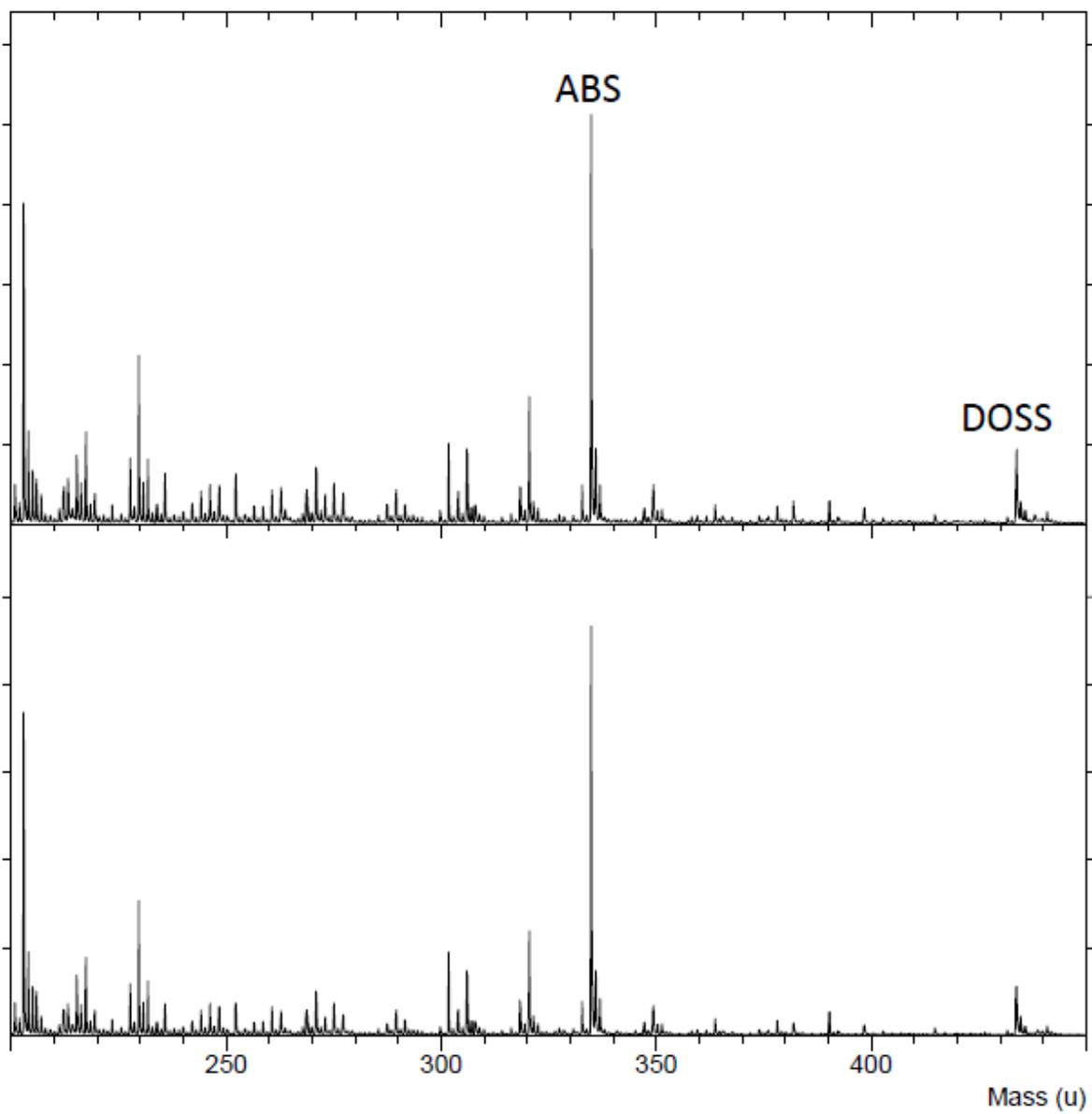


Figure 4. Negative ion SIMS spectra from the surfaces of both adhesives made using process 3 from m/z 200-450. ABS is alkylbenzyl sulfonate and DOSS is dioctyl sulfosuccinate.

## Conclusions

Surface analysis plays a critical role in understanding adhesive performance. Although bulk properties are crucial to pressure sensitive adhesive performance, small amounts of contamination at a surface can have drastic effects on adhesion. In this report two different classes of surface chemistry alterations were shown. In the first, the same adhesive was found to vary due to contamination with silicones. Additionally, a nonuniform distribution of surfactant was shown to have an adverse effect on peel due to regions of high surfactant concentration and poor adhesion. In the second set of examples variations in surface chemistry were shown due to different polymerization processes. Here the surface concentration of surfactant also correlated to peel.

The surface sensitivity of SIMS and XPS are useful in determining the chemical causes of poor adhesion. Other surface sensitive techniques can lack the detection limits and often have deeper information depths and are poorly suited to these studies.

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