LASER DIRECTED INFRARED ANALYSIS (LDIR): *A new IR imaging technology to study functional group spatial relationships in PSA adhesive surfaces*

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Abstract

Sixty years ago, Hock (1) and Wetzel (2) analyzed pressure sensitive adhesive (PSA) surfaces by scanning electron microscopy (SEM) to answer the question '*how is tack lost?*' Their interest was the role of *physical* microstructure on the PSA adhesive surface. Hock and Wetzel proposed a theory of *aggregate accumulation* of PSA components at the PSA surface comprising a microstructure that was essential for tack. In 1957 the SEM was a novel analytical tool in PSA research. Novel state-of-the-art tools have shifted many paradigms in science. In 2001, Gabriele, et al (3) revisited the work of Hock and Wetzel combining the new analytical tools atomic force microscopy (AFM) and the emerging FT-IR microscopic imaging to evaluate the surface microstructure of a PSA and ask the question, '*will new tools give us new information on what comprises the chemical microstructure of a PSA?*' The present study revisited the 2001 work of Gabriele, et al., again evaluating the chemical microstructure of a similar model PSA, this time introducing the new use of laser directed IR imaging technology (LDIR) to a similar model PSA to compare the 2001 conclusions. LDIR analysis of the current model PSA supported the 2001 conclusion, but because of the larger LDIR analytical visualization of the sample format, (5.0 mm X 5.0 mm, for the LDIR *vs.* 400µ X 400µ for the traditional FT-IR microscopic imaging) the expanded visualization of spatially resolved chemical domains offered a new framework for studying PSA material interaction and suggests a new use of PSA controlled release concepts using one of the model compounds poly (glycerol-sebacate) or PGS.

Background

New Eyes: Sixty years ago, Hock (1) and Wetzel (2) analyzed PSA adhesive surfaces by scanning electron microscopy (SEM) to answer the question '*how is tack lost?*' Their interest was in the physical microstructure of PSA adhesive surfaces. In 2001, Gabriele (3) revisited the Hock and Wetzel work to see if new analytical techniques like FT-IR microscopic imaging coupled with atomic force microscopy (AFM) supported Hock and Wetzel's original conclusion with the simple research motivation of asking the question, '*will new tools and 'eyes' give us new perspectives on seminal work?*' The 2001 work did support the original Hock and Wetzel microstructure contention, but with a different 'picture' of what comprised microstructure.

The current authors once again repeated the idea of revisiting past work with a new IR imaging technology called laser directed infrared (LDIR) imaging. This study used LDIR on a model PSA similar to that used in 2001 to specifically compare conclusions with the original FT-IR microscope imaging results.

Hock and Wetzel concluded that PSA adhesion was the physical consequence of the *aggregate accumulation* of functionally active microstructure on the adhesive surface that leads to tack. The aggregate accumulation was the result of a precise mass ratio of ester-to-elastomer solids in the bulk PSA composition. They described changes in this aggregate accumulation on the film surface by changing the ester-to-elastomer mass ratio that resulted in changes in the PSA surface topography. Loss of the aggregate microstructure resulted in loss of tack. Nevertheless, they did not chemically identify the character of the microstructure.

Figure 1 shows the graphic likeness of Hock's original theory showing that maximum tack in a PSA system results from an ideal ester-to-elastomer mass ratio. This 'system-specific' ratio develops the optimal phase-aggregate accumulation of ester and elastomer. Deviation from this ideal phase-aggregate accumulation results in a sharp fall in the property of tack. In any PSA the system-specific "whale" profile remains but the position of the maximum tack "hump," shifts left or right because of material chemistry.

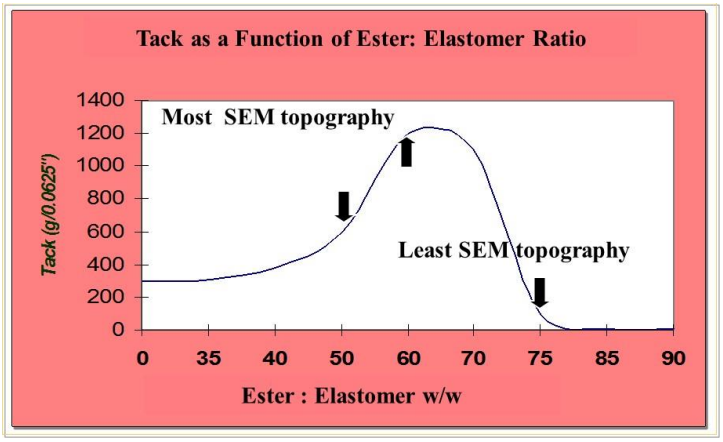

Figure 1 shows the classic 'whale' curve of Hock and Wetzel. Tack was the result of the system specific optimal ratio of ester to elastomer in the composition. Any deviation from this optimal ratio and tack is lost. The optimal ratio is governed by the functional group interaction of formulation components.

SEM imaging is purely a physical still-shadow picture of the surface features without any functional group chemical identity. The same is true for AFM. Nevertheless, the question for the 2001 study was what chemically comprised the 'aggregate accumulation?' Pavia et al. (4) used AFM to study PSA surfaces, but again the information was physical and not chemical. A more rigorous review of FT-IR microscope surface imaging can be found in Snively and Koenig (5), but little existed in PSA research. The point of combining AFM with FT-IR microscope imaging was to identify the functional chemistry of the aggregate features.

Figure 2 from the 2001 study is a composite of scanning electron micrographs (9000X) and the associated AFM micrographs of three different PSA surfaces differing in weight ratios of ester-to-elastomer. The results clearly illustrate that the 60: 40 w/w sample showed the most topography in both the SEM and AFM micrographs. Note the 60:40 films have the greatest surface aggregation of

microstructures just as Hock and Wetzel suggested. As well, the 60:40 PSA had the highest tack. However, the question remained, 'what was the chemistry of this aggregate?'

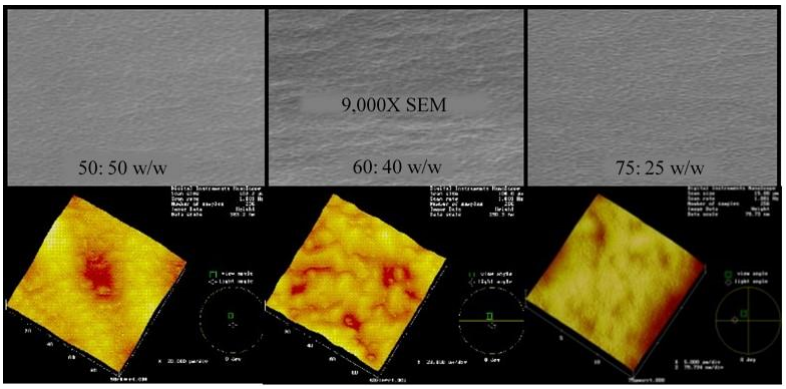

Figure 2 shows the original SEM and AFM comparison of three different w/w PSA compositions of ester: elastomer (3). Note both the SEM and AFM micrographs of the 60:40 sample show the most surface topography.

Figure 3 below is a composite panel of FT-IR microscope images from the 2001 work. Unlike a traditional FT-IR spectrum, the data is a spatially resolved image of functional group distribution and intensity on the PSA surface displayed graphically as a single wavenumber (frequency) focal plane (picture) in a "false" color absorbance scheme. The focal plane detector (FPD) allows for the simultaneous acquisition of spatially resolved spectra as each pixel in the detector provides an independent infrared spectrum of the target surface conceptualized as a grid-plane over the target. Consequently, the FPD acquires independent spectra within each pixel that is then software processed into a graphic presentation. Software processing then allows the researcher to view the focal plane as a graphic spatially resolved functional group image in false color absorbance.

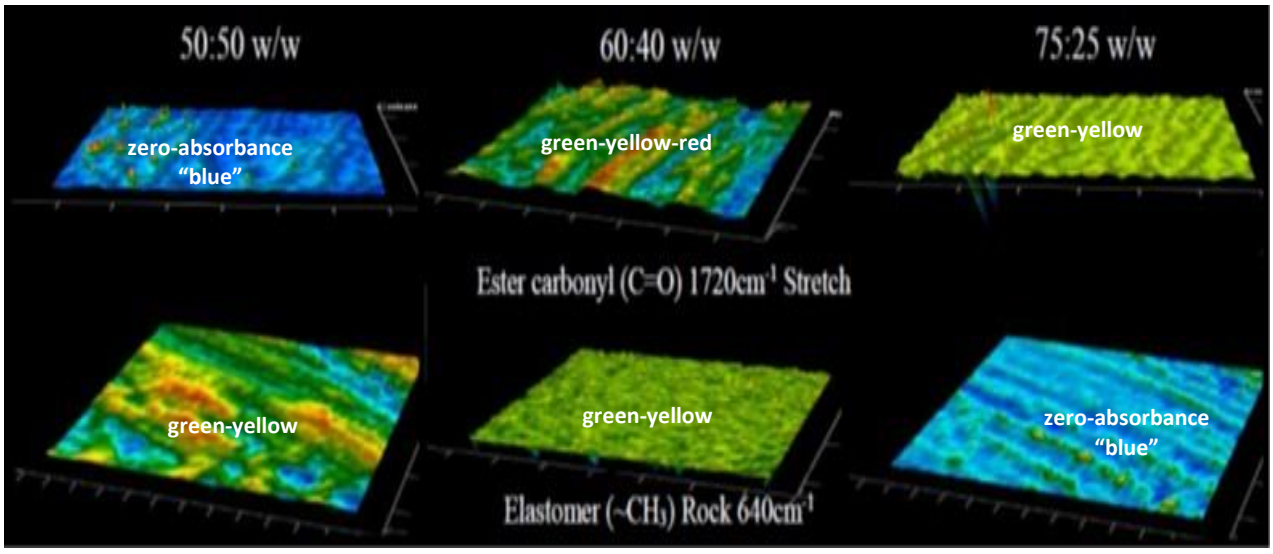

Figure 3 is a full panel comparison of focal plane functional group graphics. Focal plane functional group absorbance data is in false color. Note the zero absorbance focal planes (blue graphic) for the 50:50 ester focal plane and the 75:25 elastomer focal plane. In these samples the component phases have flipped or inverted: no ester resin is present at the 50: 50 PSA surface and no elastomer resin is at the 75:25 PSA surface indicating a component "phase inversion." Only in the 60:40 PSA focal plane surfaces are both the ester and the elastomer simultaneously present as an accumulated aggregate of components. The 60:40 PSA surface had the highest tack. Tack was lost to the disruption of the aggregate distribution resulting from phase inversion. Today's imaging technology allows us to simultaneously observe both focal planes.

For instance, the *false color* scheme assigns the color "blue" to a zero-absorbance intensity; "green" to medium absorbance intensity; and red to the highest absorbance intensity. One must be careful not to interpret the focal plane images as physical topography, but rather as chemical "topology." Today, unlike in 2001, we might describe the focal plane images of the PSA surface as a 'virtual lawn' of functional group chemistry. In 2001, the technology only allowed us to observe a single frequency in the focal plane graphic. Today, hardware and software advances allow us to spatially resolve multiple functional groups within a single focal plane.

The 'Hump:' Figure 1 suggests that optimal tack is 'on the hump.' The FT-IR images in figure 3 suggested that the optimal blend of ester-to-elastomer created a mixed phase or optimal phase-coexistence of ester-to-elastomer. In contrast, blends off the "hump," where tack was lost shows a *phase inversion* of the components at the PSA surface. As an example, figure 3 shows a 50:50 w/w blend where the elastomer dominated the surface (because the ester focal plane is "blue" i.e. zero absorbance); whereas in the 75:25 w/w the ester dominated the surface (here the elastomer focal plane is blue). Only in the 60:40 w/w did both components exist at the surface. Component ratios off the hump disrupt the optimal aggregate accumulation leading to a phase inversion of one component or the other at the PSA surface. Consequently, Gabriele et al. suggested that the roughening or 'aggregate accumulation' was in fact, the specific spatially resolved domains of the ester to the elastomer functional group chemistry. But the nagging question in the 2001 work was, 'is this real or a lucky artifact?'

LDIR: Size Counts: The analytical limitation of the traditional FT-IR imaging of the 2001 work was the format size or field of view. Each focal plane described in figure 3 is only 400µ X 400µ. Making sense out of the bigger picture of spatial resolution of component domains was like trying to view a piece of artwork through a keyhole. The spot may be interesting, but irrelevant to your study if it failed to represent the true landscape of the surface. Exciting as the results were, the question was, "is it really representative of the entire PSA surface?" In 2001, the technical reason for such a limited physical format was the result of the physical limitation of total energy throughput in the imaging process. In 2001, FT-IR energy sources constrained the 'bigger pictures,' but this was the state-of-the-art at the time.

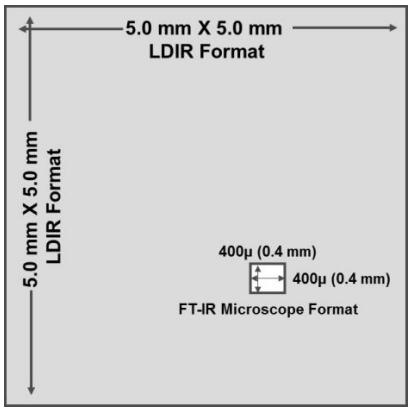

Figure 4 shows the relative format size difference between the LDIR 5.0 mm X 5.0 mm area to the FT-IR Imaging Microscope format area of 0.4mm X 0.4mm (400µ X 400µ). This is roughly a ~160X increase in the viewing format.

LDIR provided this current study with a ~160X expanded field of view offering additionally expanded domain features. LDIR analysis of the current model PSA supported the 2001 conclusion, but because of the larger LDIR analytical visualization format of the sample, (5.0 mm X 5.0 mm, for the LDIR vs. 400µ X 400µ for the traditional FT-IR images) the broader spatially resolved chemical domains offered a new

context for studying material interaction. Figure 4 shows a relative size relationship of LDIR to the traditional FT-IR Microscope imaging formats.

Quantum Cascade Laser: Traditional IR spectrometer light sources depended on the incandescent Globar® thermal source that emitted a blackbody profile in the IR. Although the Globar® source emitted all wavelengths of light and appeared bright to the human eye, emission in the spectral range of IR radiation needed for high resolution IR spectroscopy was relatively weak. In 1994 Bell Labs developed a semiconductor device called the quantum cascade laser (QCL).

QCLs are constructed of multiple layers of alternating semiconductor materials. This construct forms energy wells that confine electrons to particular energy states determined by the thickness of the layers, as well as the materials of construction. In the presence of an external electric field, an electron passes through the QCL by repeatedly transitioning between the energy states defined by the 'stacked' materials. At each transition, a photon whose wavelength is determined by the energy difference between energy levels may be emitted. Since the properties of these layers is engineered, QCL's can be designed to emit light at any arbitrary wavelength from the mid-IR to the THz region of the spectrum. This is in contrast to a traditional semiconductor laser diode, in which the wavelength of the emitted light must be chosen from a discrete set of bandgap energies. In addition, a QCL may contain many "sub-stacks" each of which is designed to operate a different wavelength. This property allows for the design of broadband emitting devices capable of emission with over an octave of wavelength range (7) (11).

The consequence of this device is that the QCL provides nearly a million times more intensity at any single wavenumber (frequency) of interest. The million times factor in intensity enables high resolution imaging over larger sample areas and at speeds previously impossible.

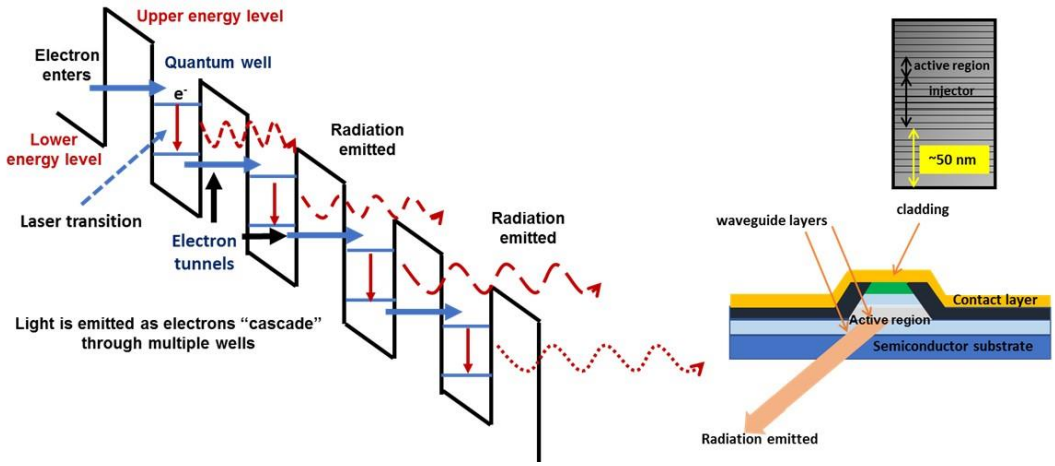

Figure 5 shows a typical QCL emission scheme with multiple active regions through which electrons cascade. Note the multi-layer package construct on the right. As the electron drops through each well radiation is emitted. The gray laminate shows the layer formation in the active region of the semiconductor package (6). (Note: graphic is author's version)

Clinical significance in PSA performance: There was no original commercial interest in this LDIR study, only an analytical curiosity and interest in the new LDIR technology. However, the large format analysis presented a focused opportunity to study a new bioresorbable glycerol-ester resin poly (glycerol-sebacate) or PGS (8) as a PSA component earmarked for chronic wound care dressings.

PGS is known to have inherent antimicrobial and non-immunogenic features in tissue engineering. PGS interest in wound dressing technology is clear. It is well known that patients suffering from chronic wounds like diabetic ulcers have compromised immune systems and often present an allergic reaction to PSA's commonly found in wound care dressings that can further damage the fragile skin of older patients leading to infection and other complications.

The LDIR allowed us to evaluate a specially formulated PSA containing PGS as an atraumatic 'release agent'. Material A was designed to reverse adhesion on-demand to painlessly remove the PSA from the skin. The LDIR results showed us how the release mechanism worked.

This study suggests that reexamination of classic seminal work with emerging state-of-the-art technology may offer new perspectives within the same research themes, shifting paradigms without bruising the basic premise, while allowing historic results to remain important to the foundation of science and technology

Materials & Methods

Ester: Elastomer Model PSA: Simple PSA formulation hand sheets were prepared using poly (glycerol-sebacate) (PGS) (8, 9) formulated with a polyisobutylene resin. The PSA was prepared in varying elastomer (PIB): ester (PGS) ratios of 25:75; 50:50; and 75:25 in d-limonene solvent.

IR Imaging Spectrometers: Samples were imaged by Agilent Technologies LDIR Microscope as well as on a traditional FT-IR imaging microscope & spectrometer, a Perkin-Elmer Starlight® imaging microscope and DigiLab Stingray.

Material A: A second sample of a proprietary PGS modified acrylic PSA wound care adhesive was imaged by LDIR to see if the release mechanism could be visualized. LDIR sample target format surfaces were 7.5mm by 7.5 mm whereas the original 2001 FT-IR imaged target format surfaces were 400µ X 400µ.

Results

A. Ester-Elastomer Model PSA

LDIR shows a much more detailed example of phase inversion in both the 25:75 and 75:25 samples mimicking the phase inversion of the 2001 study. Note that pink spheres are ester functional domains and the green sea is elastomer functional domain.

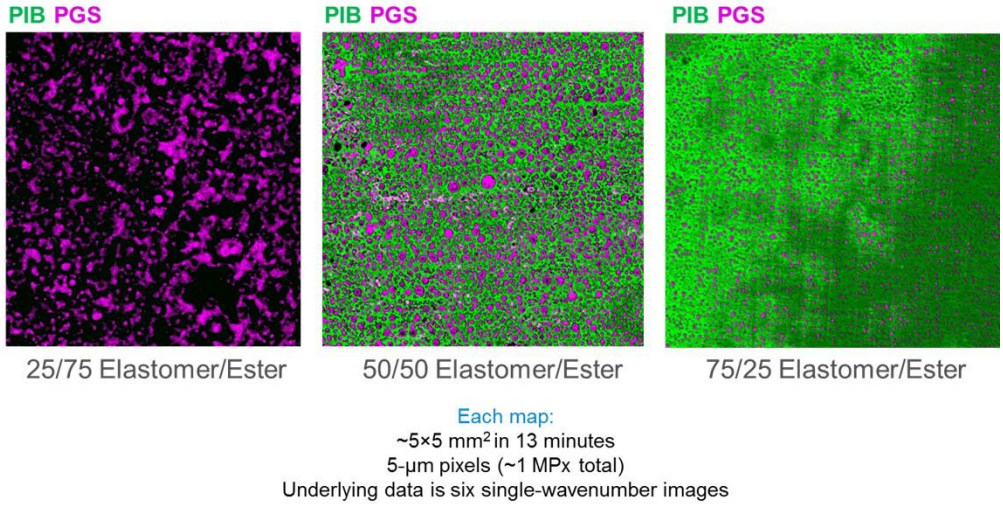

Figure 5. The LDIR format, in contrast to the FT-IR imaging format of 2001 (DigiLab Stingray) is 5.0 mm X 5.0 mm vs 400µ X 400µ. The PGS ester domains appear as (pink) geometric circles in these graphics. These circles appear to vary in diameter as a function of the mass ratio of resin to elastomer. The PSA appears as a matrix sea of elastomer (green) with ester islands (pink) composed of PGS. Note the phase inversions in both the 25/75 elastomer-to-ester and 75/25 elastomer-to-ester blends. Only the 50:50 shows what is an aggregate of both components and had the highest tack.

B. Acrylic | PGS Material A

Example of release mechanism: The release of the PSA adhesion from the skin is facilitated through the design of the PSA carrier film (12). Micropore through-holes in the PSA carrier film provides an open vertical conduit to the bulk adhesive from the dressing top-side. To remove the PSA the wound care attendant simply swabs isopropyl alcohol (IPA) over the perforated carrier. IPA wicks down through the micropores holes to penetrate the bulk film. LDIR results show that the IPA perfuses the bulk film laterally partitioning the aggregate contact with the skin to facilitate painless release. The lateral partitioning forms a 'coffee ring' void of the ester from the aggregate.

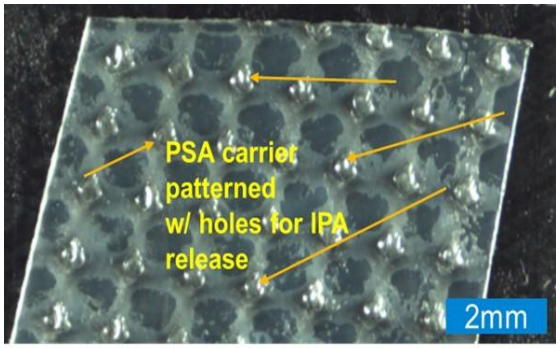

Figure 6 shows the Material A perforations on the PSA carrier film. These are through-holes that allow the isopropyl alcohol (IPA) swipe to percolate solvent through the bulk PSA film to the skin-adhesive interface.

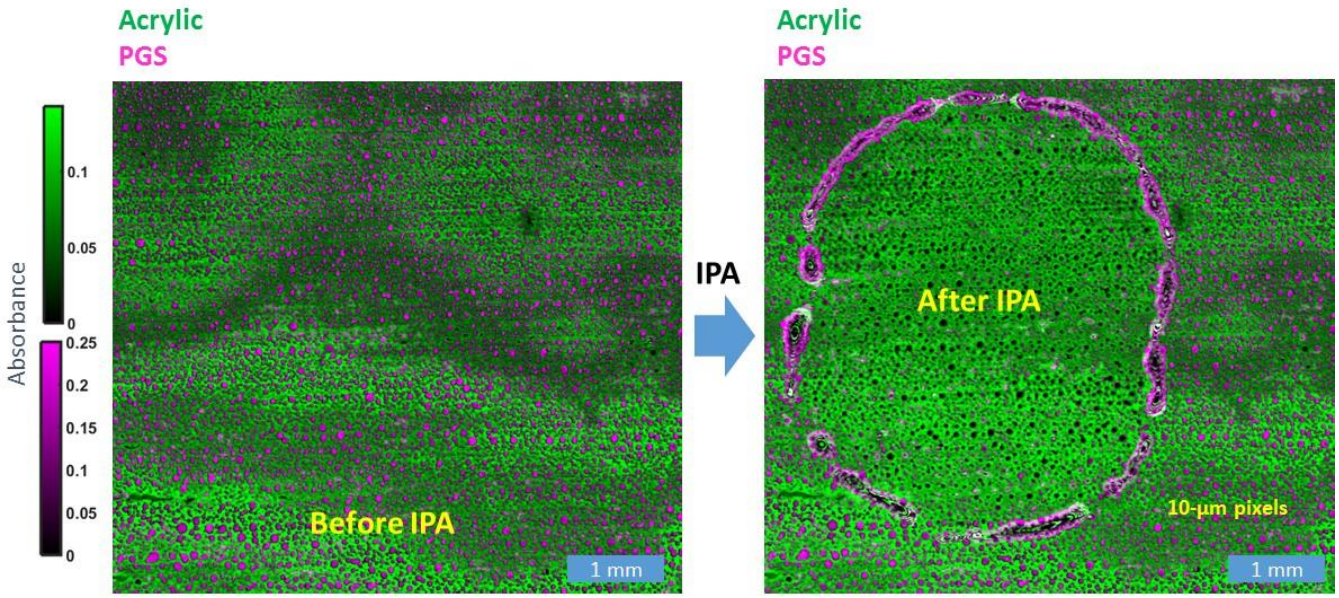

Figure 7 shows the Material A mechanism. The acrylic PSA is formulated with the PGS ester to be safely removed from skin using a simple IPA swipe to the topside of the PSA carrier. IPA travels through the bulk film to force a 'coffee-ring' effect that breaks the tack at the skin-PSA interface. IPA solvation of PGS at the PSA skin interface destroys on-demand the tack associated with the aggregate accumulation of components at the PSA surface.

Discussion & Conclusion

While it was exciting at the time, looking back at the 2001 imaging results and comparing performance with LDIR it was clear we were only seeing a fraction of the chemical picture**.** Advances in energy throughput, software and hardware have expanded the capabilities of IR imaging. In this study, the LDIR spectrometer, using a broadly tunable QCL radiant source with improved spectral radiance provided more energy and efficient optical coupling to sample target areas providing a big picture advantage to surface analysis. This feature allowed the LDIR analysis to expand the visualization of microstructure and the expanded format provides a more reasonable picture as to how material interplay manifests itself (10).

It was stated that the formulations varied slightly in mass ratio for maximum tack between the 2001 and present study. In the 2001 study, it was a 60/40 blend with the highest tack. In this study, it was the 50:50 blend that showed the highest tack. This is the result of polymer chemistry in both physical and functional group variation between materials. Nevertheless, what was consistent between this study and the 2001 study was the flip-flop or phase inversion of the components of composition that destroyed the aggregate features of the PSA surface (SEMs of the present surfaces not shown).

The LDIR results in this study support the 2001 suggestion that the aggregate accumulation described by Hock and Wetzel are a composite of a spatially resolved ester-elastomer derived microstructure. However, LDIR imaging defines the aggregate landscape of ester domains (pink spheres) in the elastomer (green sea) more reliably than the FT-IR imaging in the 2001 study.

Nevertheless, the surface image results in figure 5 fail to identify what exactly "sticks" to the surface: ester or elastomer. In contrast, Material A samples favor the ester as the dominant component of tack because once the aggregate is disrupted (coffee ring) the tack is released. The 2001 work suggested that the optimal surface *aggregate accumulation* leading to PSA *tack* was driven by a functionally distinct

ester-elastomer chemical phase relationship at the PSA surface. This relationship was identified as distinct functional group chemistry by FT-IR imaging rather than the physical description by SEM or AFM. The tack brought on by this *aggregate accumulation* is thus affected by the chemical interaction of the spatially-resolved phase-modulated resinous matter: a balanced aggregate accumulation of the ester and the elastomer supports tack.

Because the optical format of the 2001 images were so small it was a 'fingers crossed' speculation that the surface behaved uniformly. In contrast to the traditional FT-IR imaging format, the larger LDIR format presented a more uniform and broader picture of the chemical domain *aggregate accumulate* relationship of ester and elastomer. Because of LDIR's larger field of view, it was possible to measure the LDIR images with some degree of statistical quality (results not shown) that was not available in the 2001 imaging format.

The real value of LDIR technology is confirmation of the analysis of a "real life" adhesion release or loss of tack behavior in critical skin contact adhesive dressings. Patients with chronic wounds often have fragile skin on the periphery of the wound because of a potential number of comorbid conditions. Often the PSA of a dressing adhesive sparks an inflammatory response that aggravates the skin peripheral to the wound and results in additional trauma on release from the skin. Atraumatic removal of a PSA adhesive from the skin is a benefit to the overall healing process in chronic wound therapy.

In the Material A sample, the LDIR clearly shows that the release mechanism of the PSA is the collapse of the *aggregate accumulation* of the surface structure of the PSA. In our example, you see that the distribution of PGS in Material A before treatment of the adhesive with isopropyl alcohol (IPA). Following IPA treatment, the aggregate accumulation of PGS in the acrylic film spreads away or migrates from the center of the PSA spot (under the micropore perforation) into a "coffee-ring" like structure. This "coffee-ring" migration of PGS destroys the aggregate accumulation to release the PSA with minimal or no trauma to the skin.

The clear benefit of seeing the picture of this chemical graphic of aggregate accumulation in 2-D is what the microstructure means to expanding the development of a PSA. In this case, the simple fact that the PGS domains are visualized as spheres is important to the future development of formulations based on bioresorbable controlled release of actives and biologics delivered to the skin. In microstructures where the PGS acts like a microparticle controlled release structural domain as well as a component to a PSA could mean a different approach to formulating an active PSA rather than considering the component merely as a service component to a wound care PSA adhesive. For instance, it is conceivable that PGS micro-domains can be designed to contain additional APIs for wound care in a controlled release construct and contribute to adhesion of a PSA.

Conclusion

The significance of this work demonstrates the utility of LDIR to surface analysis and the exploration of material mechanisms. It also demonstrates that revisiting classic research with a new set of tools can offer the researcher new viewpoints. It is the picture of the interaction of matter that makes this imaging technique of value to the researcher.

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Acknowledgements: Thank you to Christopher R. Moon, Ph.D. Manager, Imaging Group, Yang Han, Chad Hoke, Alan Rein, Guthrie Partridge, California Research Center, Spectroscopy & Vacuum Solutions Division, Agilent Technologies, Inc., Santa Clara, CA for their generous time and consideration to evaluate this work on their new LDIR technology; Chris Sassoon, US Molecular Spectroscopy Sales Manager Agilent for his help in directing communication; Carissa Smoot, Kayla

Wroblesky, Secant Group R&D for their analytical help in evaluating PSA materials; and Dr. Howard Rosing, MD Ph. D. of Global Biomedical Technology