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THE IMPACT OF ADHESION MODIFIERS ON SI PSA PERFORMANCE

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Introduction

The customization of tapes is often required to meet or exceed the individual needs of the tape users or the needs of the market. The art of tape manufacturing and developing customized constructs often rely in the innate ability of the researcher to understand and utilize when and how to modify these formulated systems. The modification of formulated systems can include resin modifiers, chain extenders, functional polymers, additives, stabilizers, pigments, diluents, and a host of other ways to customize a tape for a specific tape user, application, or market need. Some tape manufacturers or PSA manufacturers are also skilled at developing the PSA formulations from their starting monomers, oligomers, and resins, thereby building the organic tape base from scratch, so to speak.

Silicones, also called polysiloxanes, are polymers with the chemical formula $[R_2SiO]_n$, where R may be an organic group, commonly found as methyl, phenyl, alkenyl, or hydrogen. These form long polymer chains with the backbone of the polymer forming a (…Si-O-Si-O-Si-O-Si-O-…) chain. Conventional silicone PSAs are essentially a dispersion of silanol (-OH) or vinyl (H_2-C=C-) functional silicone polymers blended with functional siloxane MQ resin in aromatic solvents. The solvent is most commonly toluene or xylene. Some silicone PSA's are solventless, but have the same basic composition of a silicone polymer and a silicone resin at a given ratio.

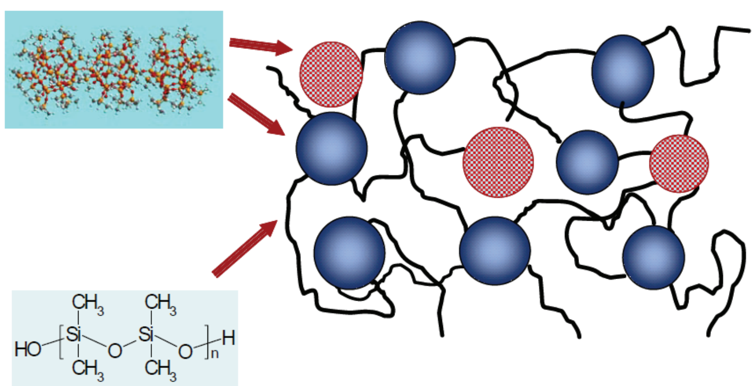


Figure 1. Proposed multi-phase structure for silicone PSAs, based on resin rich, gum rich, and hybrid zones.[1]

When formulating a silicone pressure sensitive adhesive, a number of inputs can be adjusted by the silicone chemist, with a guiding principle being the ratio of resin to polymer. In general, increasing resin content can increase adhesion, with loss of tack, while decreasing the resin content decreases adhesion, and increases tack.

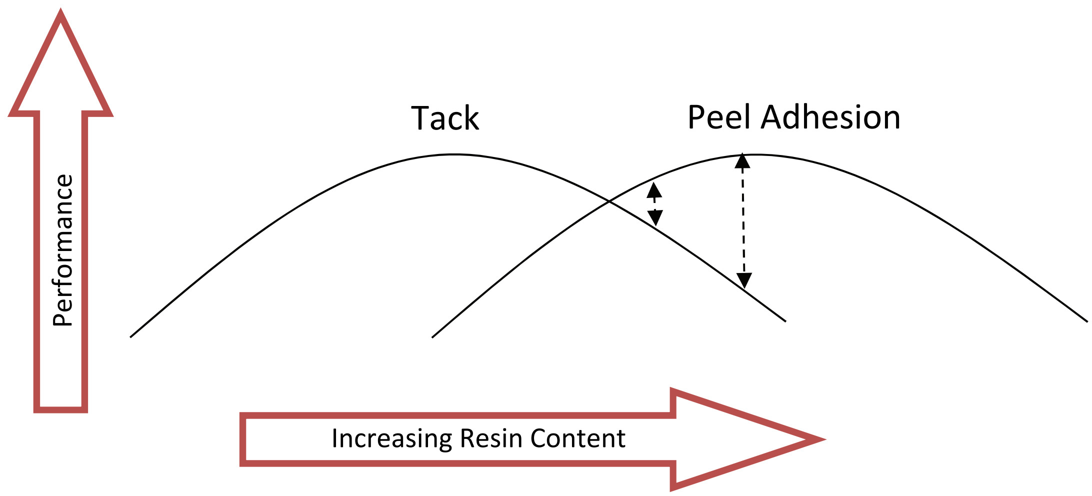


Figure 2. General concept behind silicone PSA formulations.

The customization of silicone PSAs can extend the utility of these systems beyond the pre-formulated base PSAs. Three adhesion modifiers were evaluated to determine the impact based on additive level on the performance of various PSA systems.

<u>Adhesion Modifiers</u>

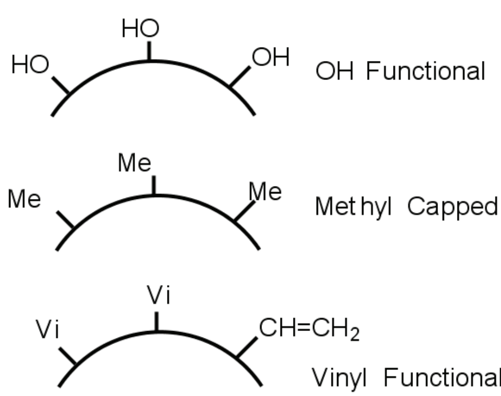


Figure 3. Simplified Adhesion Modifier surface functionality

The adhesion modifiers incorporate various functional groups that are available on the surface, with the intention of interacting with the surrounding environment. The surfaces could interact with the polymer, the resin, the bonding surface, or each other. Each chemical group on the surface, and the underlying $Si\text{-}O_{1/2}$ structure, plays a role in the performance of the tape.

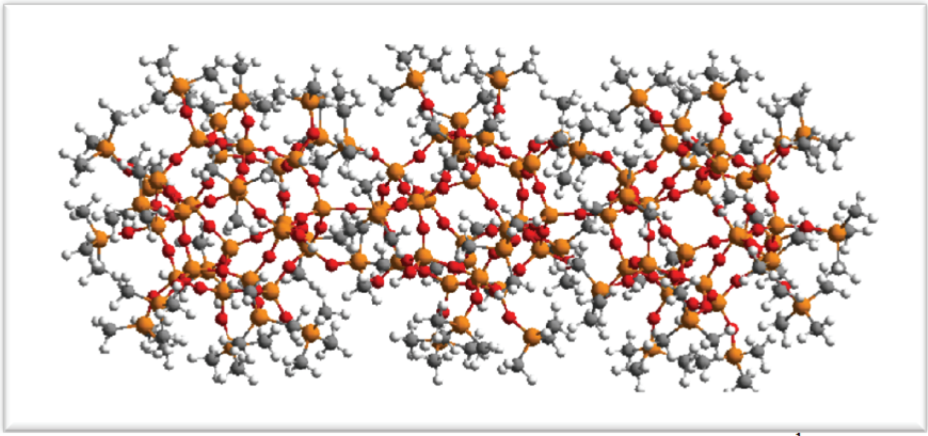


Figure 4. Silicone adhesion modifier proposed structure[1]

This study evaluated the incorporation of these adhesion modifiers into the most common silicone PSA systems, peroxide cured PSAs and Pt catalyzed addition cured PSAs. Silicone PSA's are generally cured either by a peroxide free radical mechanism, or a platinum catalyst induced addition cure mechanism.

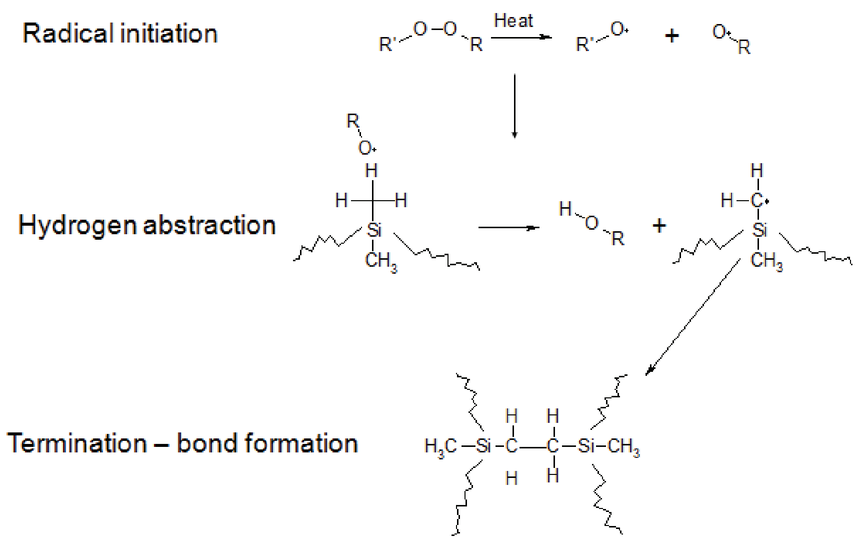


Figure 5. Peroxide induced free radical crosslinking of silicones[1]

Catalysts such as benzoyl peroxide (BPO) can be added at levels of 0.5-4 wt%, depending on the application requirements.

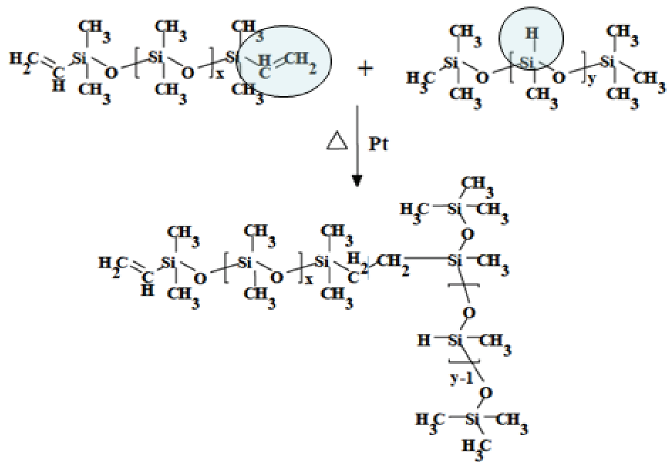


Figure 6. Platinum catalyst induced crosslinking of silicones[1]

Adhesives preparation and characterization

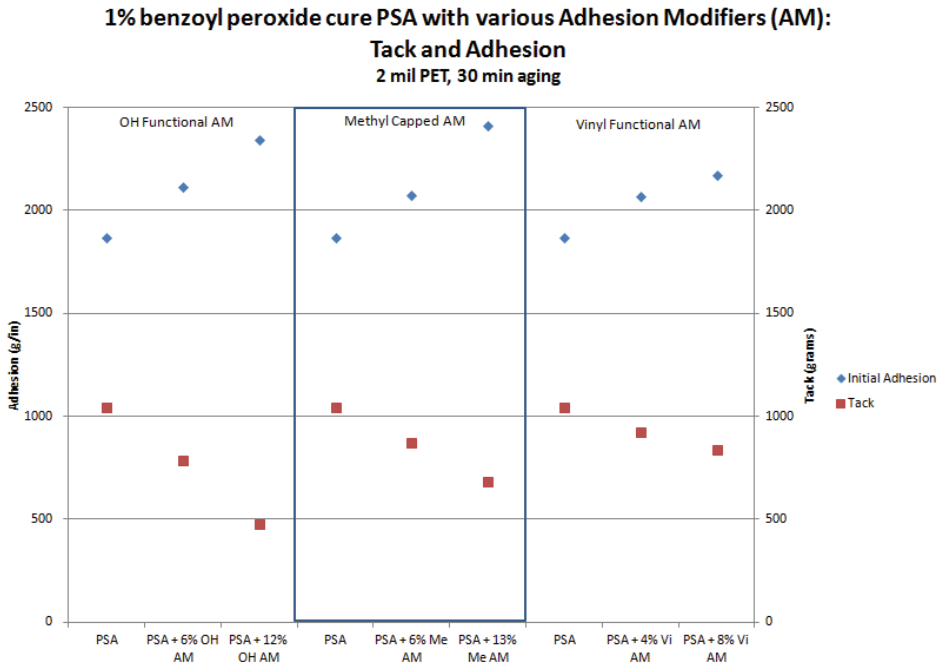
The adhesives evaluated were generally processed in a similar fashion. A solvent solution of BPO was added to a base formulation to yield 1% BPO per silicone solids, and diluted to reach 50% solids with additional xylene or toluene. A bird bar applicator was used to apply a coating onto the specified substrate to yield a 1.5-2.0 mil dry coat weight. PET samples were cured in a static oven at 80^{o}C for 2 minutes to remove the solvent, followed by 180^{o}C for 2 minutes to crosslink the system. Addition cure PSAs were evaluated at 0.4% platinum catalyst levels. Adhesives were characterized by 180^{o} peel adhesion per PSTC-101, probe tack, and rheometry.

Results and discussion

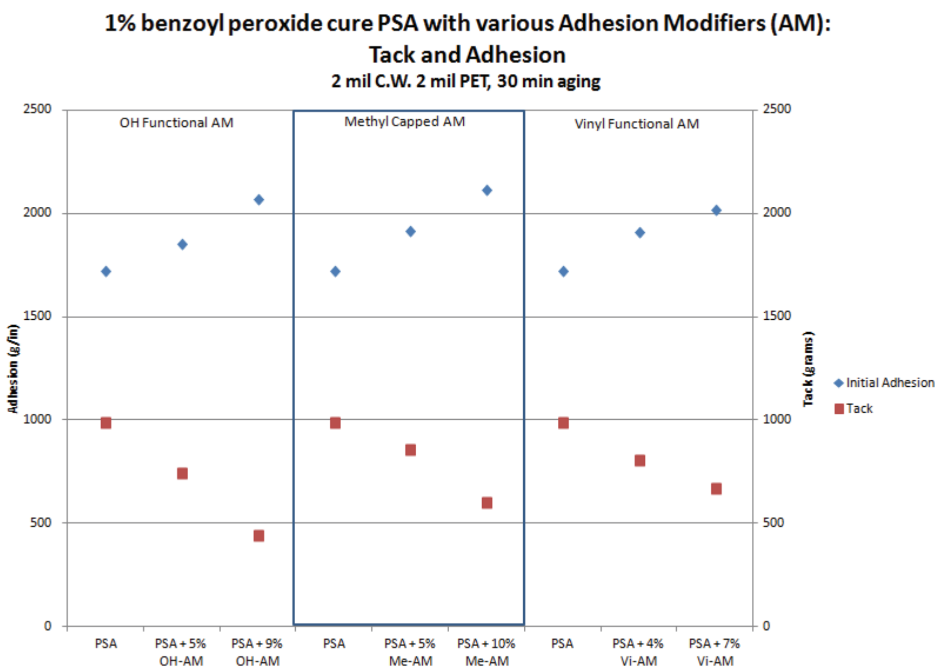
This study looked at a subset of multiple adhesive formulations, and selected two adhesive systems that represented typical results within the data set. Samples of the tape as applied to stainless steel panels were evaluated at both room temperature and accelerated aging conditions. Multiple levels of common adhesion modifiers were evaluated. It should be noted that these adhesion modifiers are dissolved in Xylene at different % solids levels, so some variation in percentages can be expected depending on the formulation. They are useful as guides to understand the effects of adding 3-10% adhesion modifier as delivered.

<u>Peroxide Cure Si PSA</u>

Peroxide cure Silicone PSAs are useful as masking materials, and for their ability to survive high temperatures, and impact ruggedness and durability to the construction. The free radical curing mechanism allows for a more random nature of the crosslink matrix, and a higher level of crosslinking.



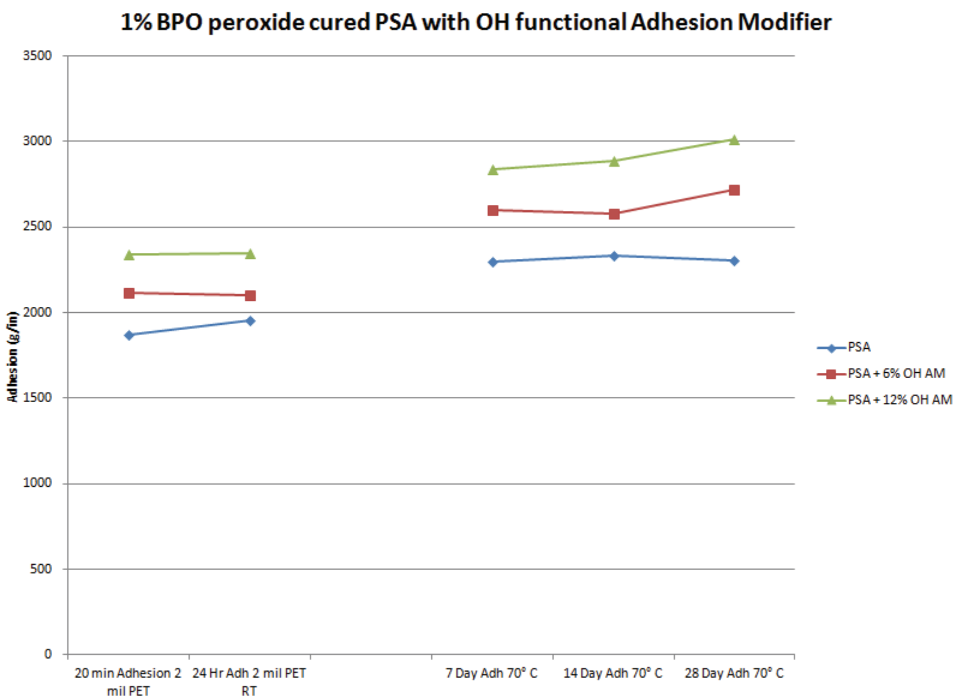
Graph 1. A typical example of a Si PSA was examined, comparing OH, Methyl, and Vinyl functionality on the adhesion modifier surface, and the impact on 180^{o} peel adhesion and tack. The impact of adhesion modifier shows greater differentiation between surface functionality.



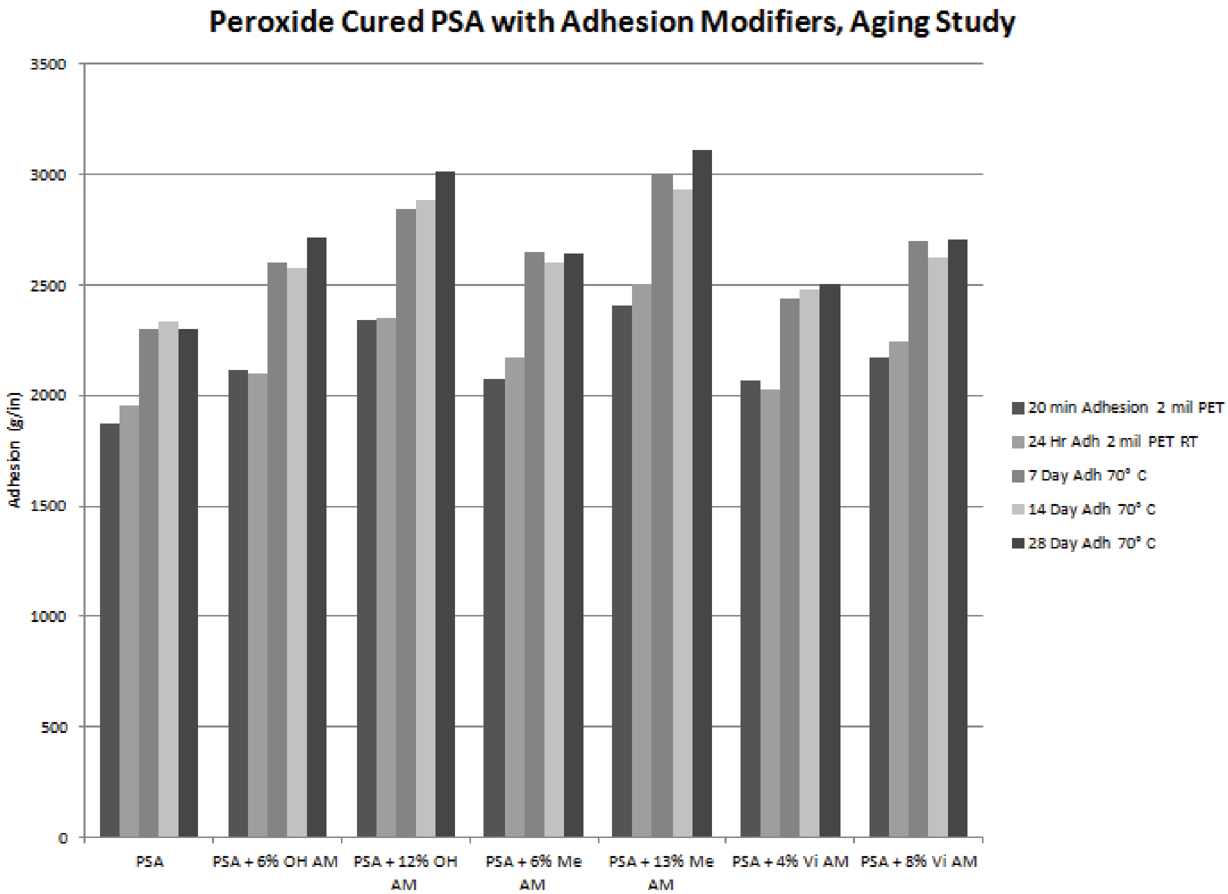
Graph 2. Typical Example of a 2nd benzoyl peroxide cured Si PSA, comparing OH, Methyl, and Vinyl functionality on the Adhesion Modifier surface, and the impact on 180^{o} peel adhesion and tack. This particular example showed that all three adhesion modifiers had a more subtle

difference between the effects. The effects are dependent on the formulation of the PSAs, and should be evaluated for application suitability.

This particular example above of a benzoyl peroxide cured PSA has similar behavior for initial values of peel and tack when using 5-10% of either an OH functional or methyl capped adhesion modifier package. The vinyl functional surface showed a slightly less increase in adhesion, with a slightly less drop in tack values. The trends among multiple peroxide cure PSAs that were examined show some variation from formulation to formulation, but overall remain consistent. It was also noticed that individual adhesives could be tailored specifically to meet the application requirements.



Graph 3. Back to the adhesive examined in Graph 1, this graph shows a comparison between initial and 1 day, as well as 70 ^{o}C aging for 7, 14, and 28 day show the expected increase due to the resin/polymer ratio change. The increase in adhesion when exposed to 70 ^{o}C is likely due to increased crosslinking, increasing cohesive strength.



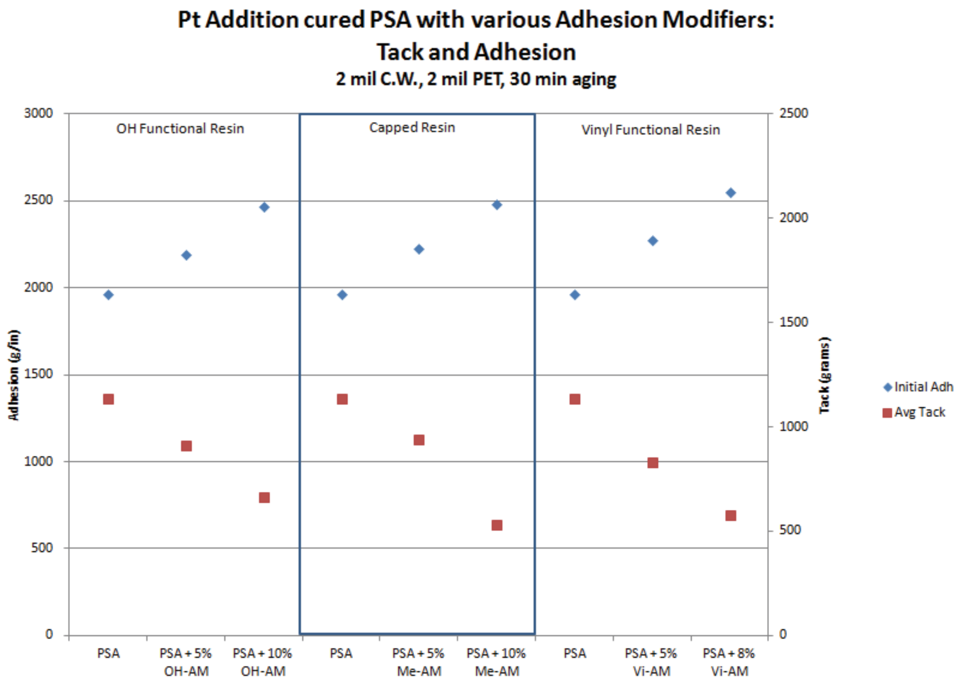
Graph 4. Comparison of the peroxide cured PSA, with different aging effects due to the various functional adhesion modifiers. These examples consistently showed the samples maintaining a higher adhesion level even after accelerated aging. OH AM = OH functional Adhesion Modifier; ME AM = methyl capped Adhesion Modifier; Vi AM = Vinyl functional Adhesion Modifier.

The composition of the peroxide curable systems does have an impact on which adhesion modifier should be selected, and the adhesion modifiers may give different initial and accelerated aging performance accordingly. Full evaluation of the different functional modifiers should be encouraged to understand the impact within a given system.

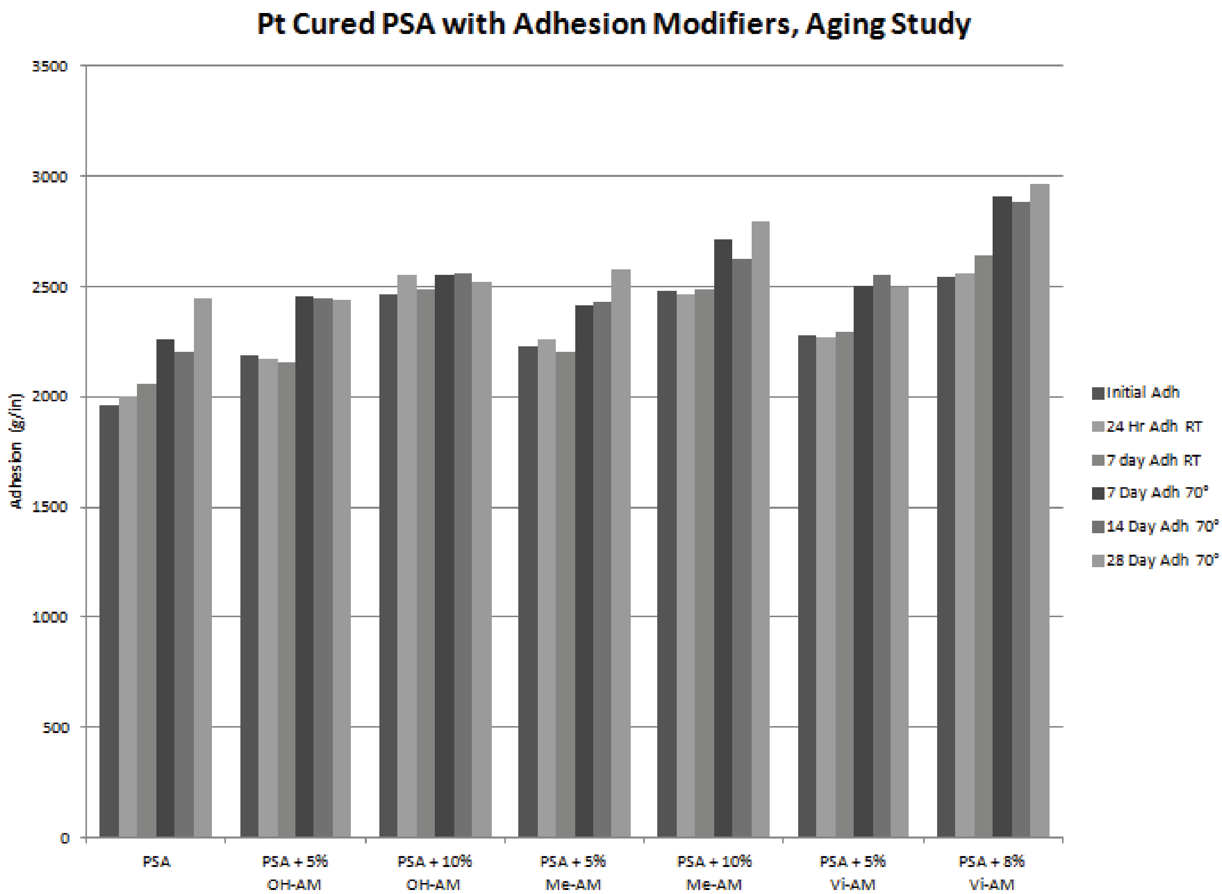
Platinum Addition Cure Si PSA

Platinum catalyzed addition cure silicone PSAs offer the ability to cure at lower temperatures, making them desirable for temperature sensitive substrates. The ability to modify the peel adhesion and tack for platinum cured PSAs is examined below.

The various functional surfaces of the adhesion modifiers did not have significant differentiation on this particular platinum catalyzed addition cure PSA selected for this study, and any of the three can yield similar additional peel adhesion.



Graph 5. Typical Example of a platinum addition cured Si PSA, comparing OH, Methyl, and Vinyl functionality on the Adhesion Modifier Surface, and the impact on 180° peel adhesion and tack.



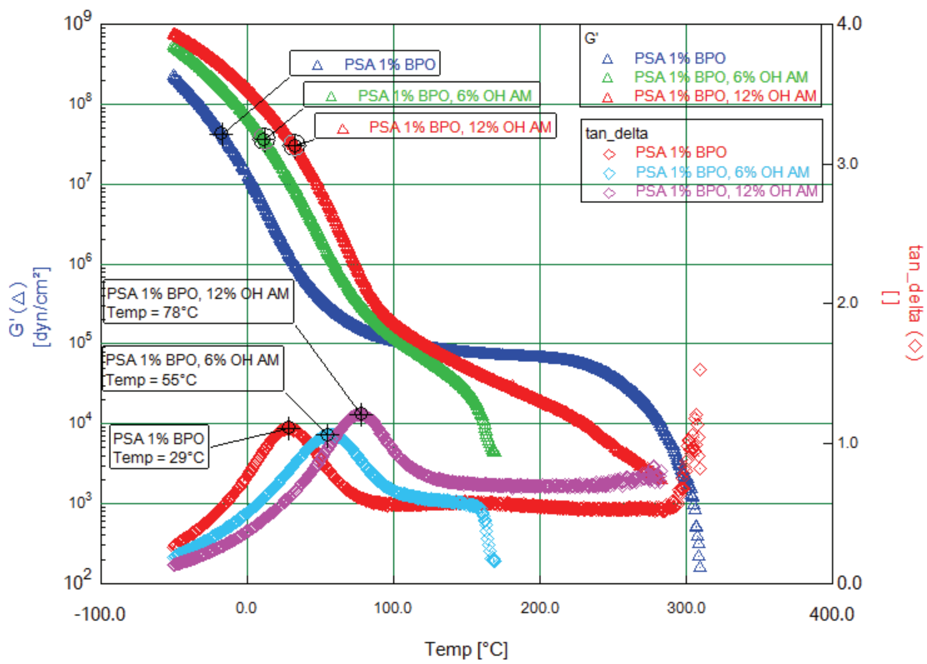
Graph 6. Comparison of a Platinum cured PSA, with different aging effects due to the various functional adhesion modifiers. These examples consistently showed the samples maintaining a higher adhesion level even after accelerated aging.

<u>Rheometry</u>

The study of the modulus as a function of adhesion modifier concentration was useful to examine the relative impact a given additive can have on the system over a temperature range. While many commercial examples of a silicone tape can utilize 1- 4% benzoyl peroxide, with better temperature performance usually stemming from higher levels of peroxide, a lower peroxide concentration was selected to amplify effects from the adhesion modifier. Additional levels of peroxide may be able to offset any negative impacts on the final system.

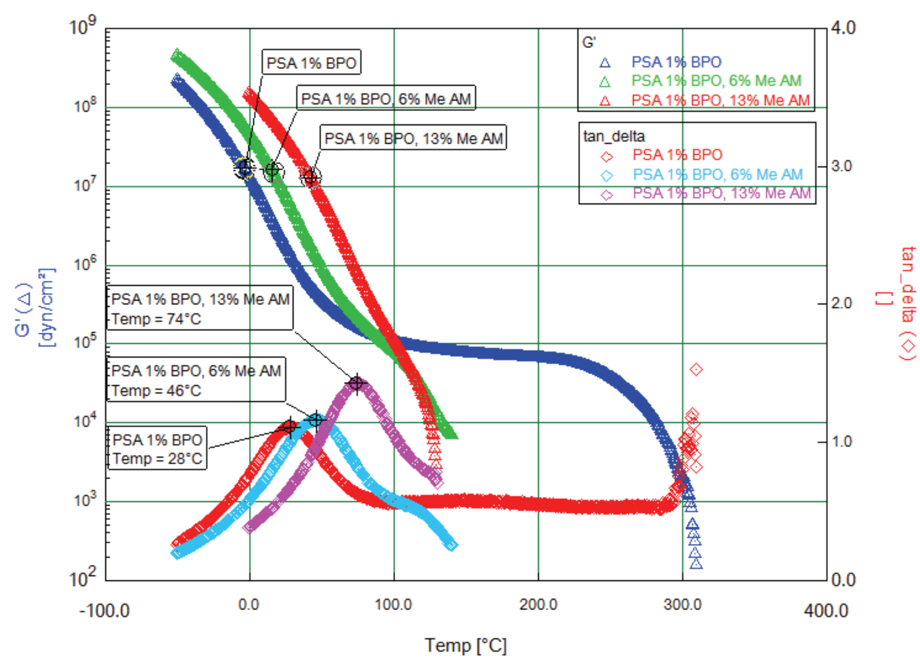
Of particular interest was the examination of the modulus at room temperature, and the shift of the glass transition (Tg) temperature by the incorporation of the higher Tg adhesion modifiers as a component of the formulation.

Peroxide cured PSA Temperature Sweep with OH functional Adhesion Modifiers

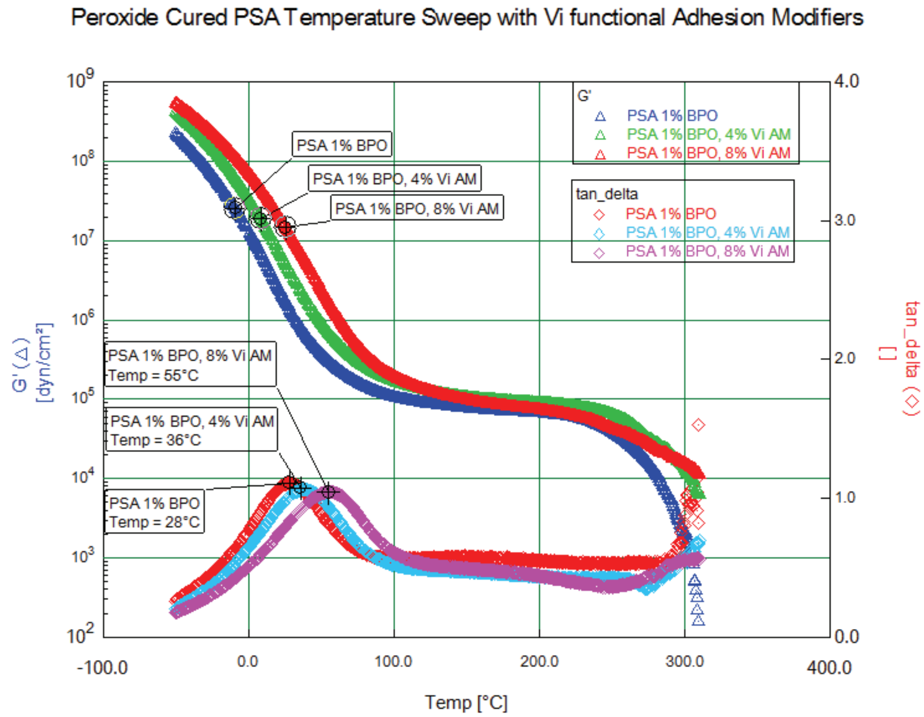


Graph 7. The addition of OH functional adhesion modifier into this particular peroxide cure PSA shifted the tan-delta inflection point from somewhere close to room temperature to a point around 75°C at the highest addition level. The resulting shift in modulus at room temperature is mirrored by the drop in tack values, as seen in Graph 1.

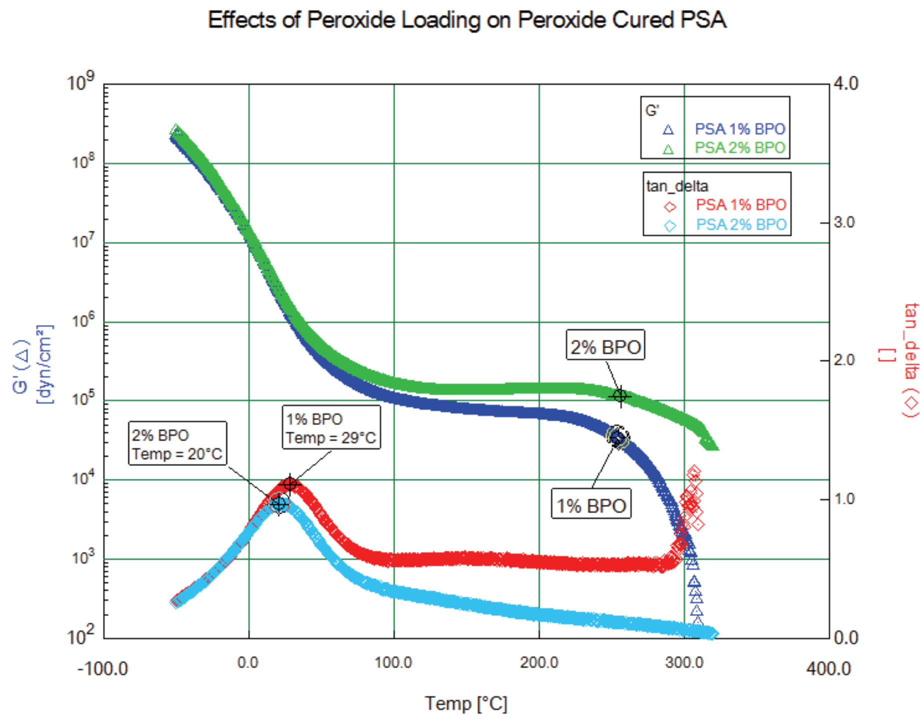
Peroxide Cured PSA Temperature Sweep with Me capped Adhesion Modifiers



Graph 8. The incorporation of methyl capped adhesion modifier into the system at similar levels showed a similar increase in the tan_delta inflection point, with the typical shift to higher G' modulus levels.



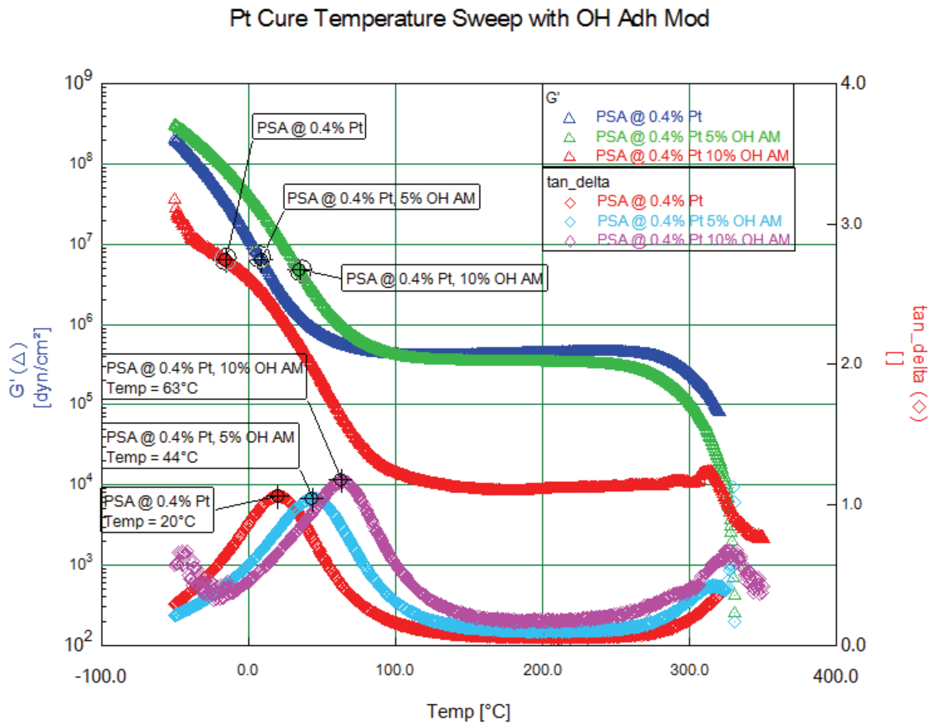
Graph 9. The incorporation of vinyl functional adhesion modifiers into the system, albeit at lower relative levels, indicate a similar trend. The level of adhesion modifiers is lower, so the effects on adhesion are slightly less, yet retain a more stable elastic plateau.



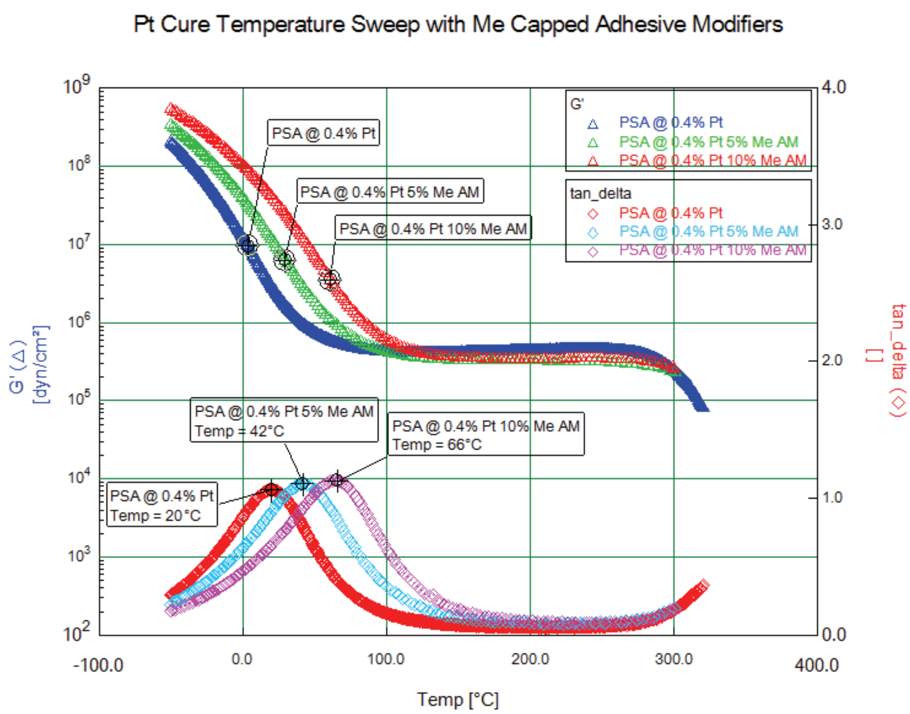
Graph 10. The effect of peroxide loading on a peroxide cured PSA.

While the testing done for this study was conducted at 1% benzoyl peroxide, it has been shown in previous papers that increasing the peroxide level to 2, 3, or even 4% can lower the tan_delta inflection point, and even approach 10^{o}C or 0^{o}C for a given system. This can sometimes shift the modulus at room temperature, or stabilize the elastic plateau to survive higher temperatures. Higher peroxide loading may shift the room temperature G' elastic modulus to lower values, retaining some of the desired tack.

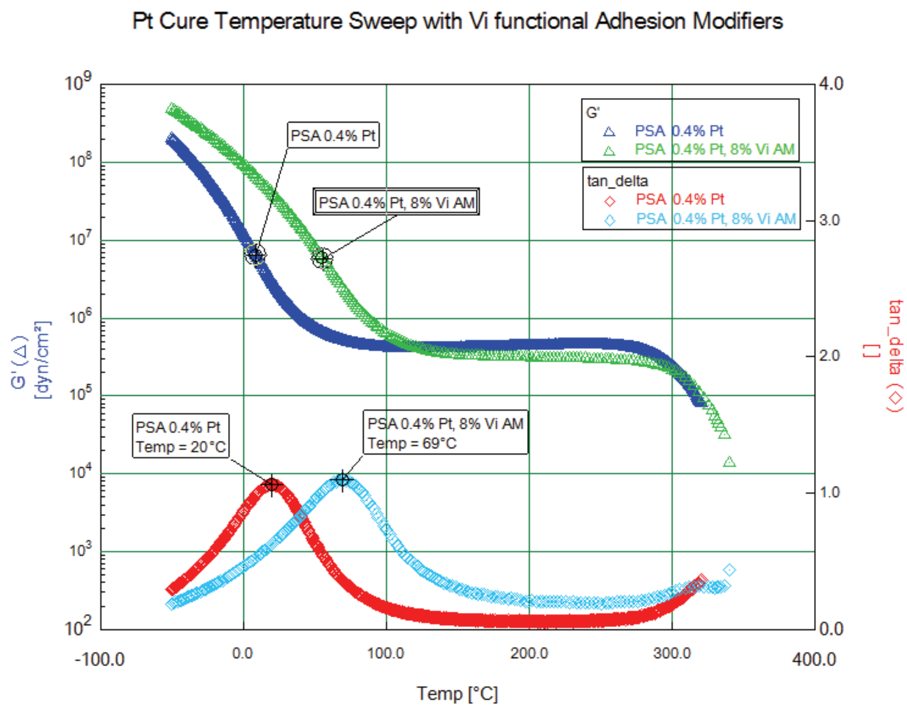
The addition of OH functional adhesion modifiers into the platinum catalyzed additional cure PSA shows a similar shift to higher tan_delta inflection points, reaching above room temperature, with similar shifts in G' modulus values at room temperature. The PSA has stiffened with the incorporation of the adhesion modifier to a higher baseline elastic plateau. The incorporation of the methyl capped and vinyl functional adhesion modifier has similar effects, as seen below.



Graph 11. The incorporation of the OH functional adhesion modifier into the platinum catalyzed addition cure PSA.

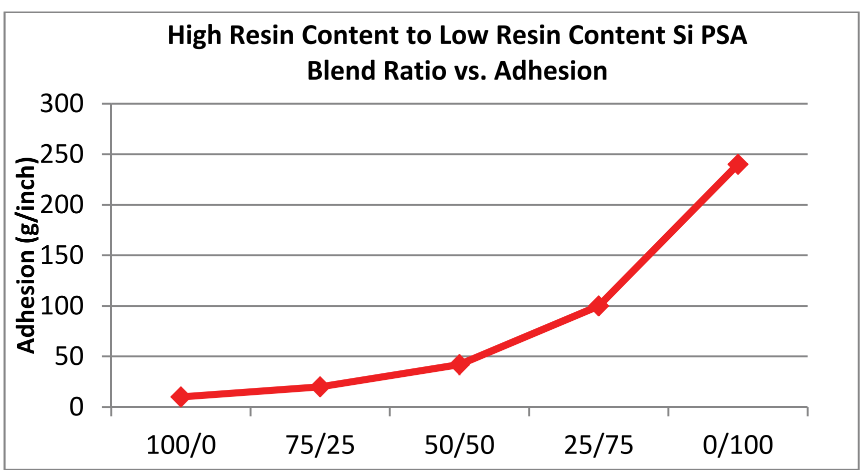


Graph 12. The incorporation of the methyl capped adhesion modifier into the platinum catalyzed addition cure PSA. One difference is the common baseline modulus of the elastic plateau between 100-300 ^{o}C.



Graph 13. The incorporation of the vinyl functional adhesion modifier into the platinum catalyzed addition cure PSA.

The ability to modify the adhesion strictly through the use of modifiers is not the only route to achieve a customizable adhesion level. The blending of two platinum catalyzed addition cured Si PSAs is demonstrated below to highlight the ability to modify the overall adhesion level of a tape sample. The resulting mixture of high resin content PSA with low resin content can achieve a range of adhesion levels.



Graph 14. The ability to blend a high resin content PSA with a low resin content PSA is another way to achieve a customizable adhesion level.

Summary

The utilization of silicone pressure sensitive adhesives for masking, protection, or permanent bonding sometimes requires customized formulations to meet the demands of the application. Many developments come from a direct interaction of the tape manufacturer with researchers at the silicone manufacturer, and can lead to novel and unique polymers and resins, and different fundamental research efforts to create new and exciting formulations to meet unique challenges presented by the industry.

Other developments arise from the ability of the researchers and engineers at the tape manufacturing level to develop new formulations for a particular application, quickly and efficiently. Developing an understanding of the impact of adhesion modifiers on a given silicone PSA formulation under various conditions can lead to improved product offerings and a unique value to offer to customers.

The incorporation of OH functional, methyl capped, and vinyl functional adhesion modifiers had a profound impact on the peel adhesion of both peroxide cured PSA and platinum catalyzed PSAs, leading up to a 40% increase in peel strength. An understanding that the increase in peel strength will come with a resulting decrease in tack value can help to find the right balance of properties to meet the application needs. A study of the adhesion modifiers show that some adhesion modifiers are more effective in certain formulations, and not as effective in other formulations. Evaluating each system on an application by application basis can lead to a better understanding of the entire construction.

REFERENCES

1. Lin, S., Durfee, L., Knott, A., & Schalau, G. (2009). *Silicone Pressure Sensitive Adhesives* (Vol. Technology of Pressure Sensitive Adhesives and Products). (I. Benedek, & M. Feldstein, Eds.) Boca Raton, FL: CRC Press.