Silicon Hydride – An Ignored Factor in Release

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Abstract
Silicone network design is crucial in adjusting the release effect of the silicone layer in a PSA laminate. Silicone base polymer, crosslinker, and optionally a silicone resin define the general structure and mesh width of the silicone network. Mesh width and chain mobility are key in mechanistic studies on interfacial slippage, correlating the energy for adhesive slippage on silicone layers with the peel strength.
The surface chemistry of the silicone release layer is defined by silicon hydride. Silicon hydride can interact with the adhesive and increase release force significantly. The contribution of the silicon hydride to peel strength depends on the concentration of hydride groups and the type of adhesive. The concentration of the silicon hydride depends on many factors, i.e. silicone system used, stoichiometric ratio of crosslinker and polymer, cure conditions and liner age.
Despite its importance, but due to its elusive character, the contribution of silicon hydride to release performance and release mechanism has been widely ignored. This paper discusses the individual effects of a silicone system on release performance, emphasizing the importance of silicon hydride on peel strength.

1. Introduction
Peeling a tape is simple. The mechanism of peeling definitely is not.

Generations of scientists spent time and effort on explaining the mechanism of peeling a tape from a substrate.
In the sixties D. H. Kaelble described the influence of surface energy, adhesive rheology, and the peel rate on the debonding mechanism[1, 2, 3].
D. W. Aubrey looked at the crack tip and described the effect of filamentation of the adhesive on the release force[4, 5].
In 1995 Newby and Chaudry introduced the idea of interfacial slippage as a critical factor for the release mechanism[6].
T. Cosgrove proved that silica resin particles significantly reduce chain mobility[7].
A freeze out of interfacial slippage by silicone resins was concluded by G. V. Gordon in 2000[8].
In 2001 Liliane Leger correlated the energy for adhesive slippage in CRA® containing silicone layers with the peel strength[9].

All these researchers contributed to the picture of release mechanism we have today. We see much clearer now, but the puzzle isn't complete yet.

In their quest for truth these scientists ran focused experiments to add still another aspect to the understanding of release mechanism.
In such experiments it is legitimate to limit the number of variables to distill the essential effects, but one shouldn't forget about the limitations applied.

Reading through these articles on release mechanism, it becomes evident that the limitations are mainly in the chemistry employed. Little is usually said about the silicone systems used and the silicone networks created. Even less is said about the surface chemistry of the silicone layer. Can we really understand the mechanism of release without having a closer look on the chemistry employed?

Despite the fact that Fritz Hockemeyer demonstrated the importance of residual Si-H for the CRA®-effect in 1997[10], no effort was made to include this effect into the theories of peel mechanism. On the contrary, one article on the topic of release coating even states that, "it is undesirable to have chemical interactions across the adhesive-silicone interface, i.e. direct silicone hydride-carbonyl bonding". These bonds are there and we have to live with it. In fact, they are necessary for controlled release.

The intention of this paper is a sort of reality check. How do modifications in the chemical composition affect the release properties and how do these effects correlate with the state of the theory on release mechanism. For much of what is in this paper, sufficient explanations in the literature we not readily apparent. The work may even serve as a starting point for those who are more capable in the field of surface science to look for the missing answers.

2. The silicone release layer

The silicone release layer in a typical PSA laminate is the reaction product of

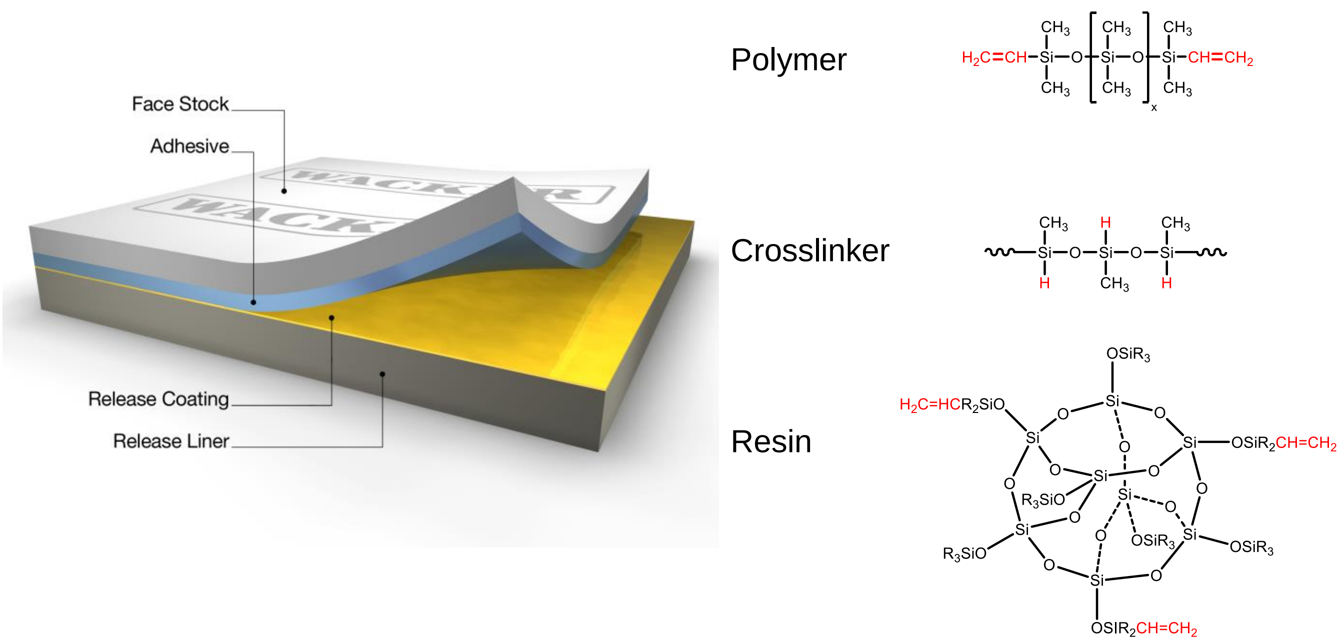


Figure 1: PSA Laminate

1. a silicone polymer with reactive vinyl groups
2. a silicon-hydride functional crosslinkers (Si-H)
3. optionally a silicon resin to adjust the release force

A mixture of these three components together with a platinum catalyst and an inhibitor that provides product bath life is coated and cured on a substrate to form a silicone network.

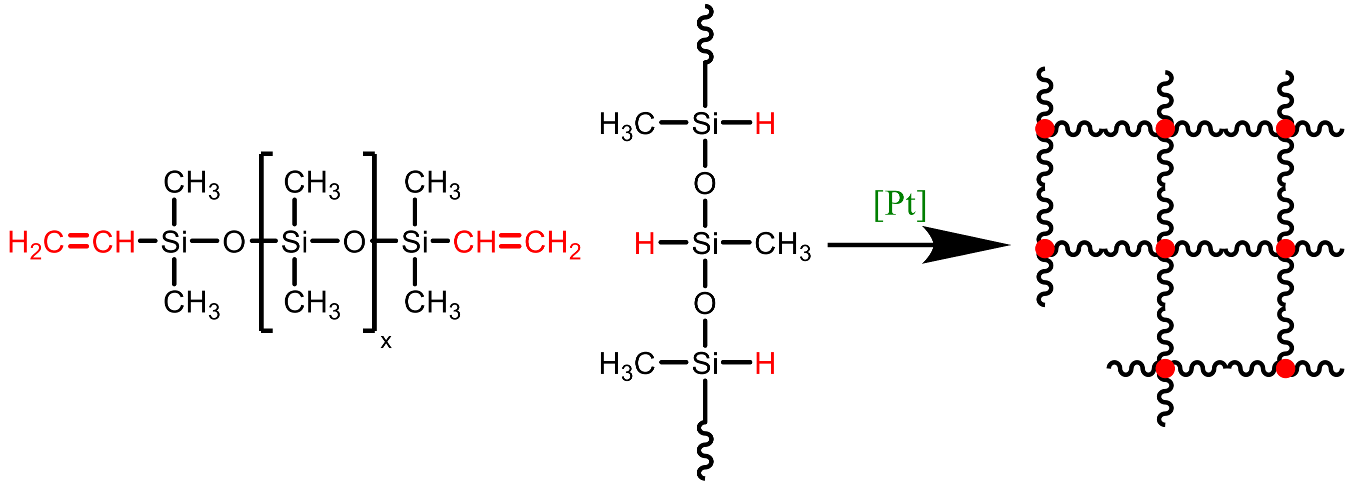


Figure 2: Addition Cure Mechanism

The components affecting the silicone network structure are the silicone polymer, the silicone-hydride functional crosslinkers, and the silicon resin. Platinum catalyst and inhibitor are considered auxiliaries and are more important for the kinetics of the crosslinking reaction than the network structure.

3. Base Polymer

Solvent free silicone release coating polymers have viscosities in the 100-500 cPs range.
This translates into a polymer chain length of roughly 70 to 150 repeating units.
These base polymers carry reactive groups on the end of the chain or at the end of branches off of the chain.

Chain length, structure and number of reactive groups have a significant influence on the mesh width of the silicone network.

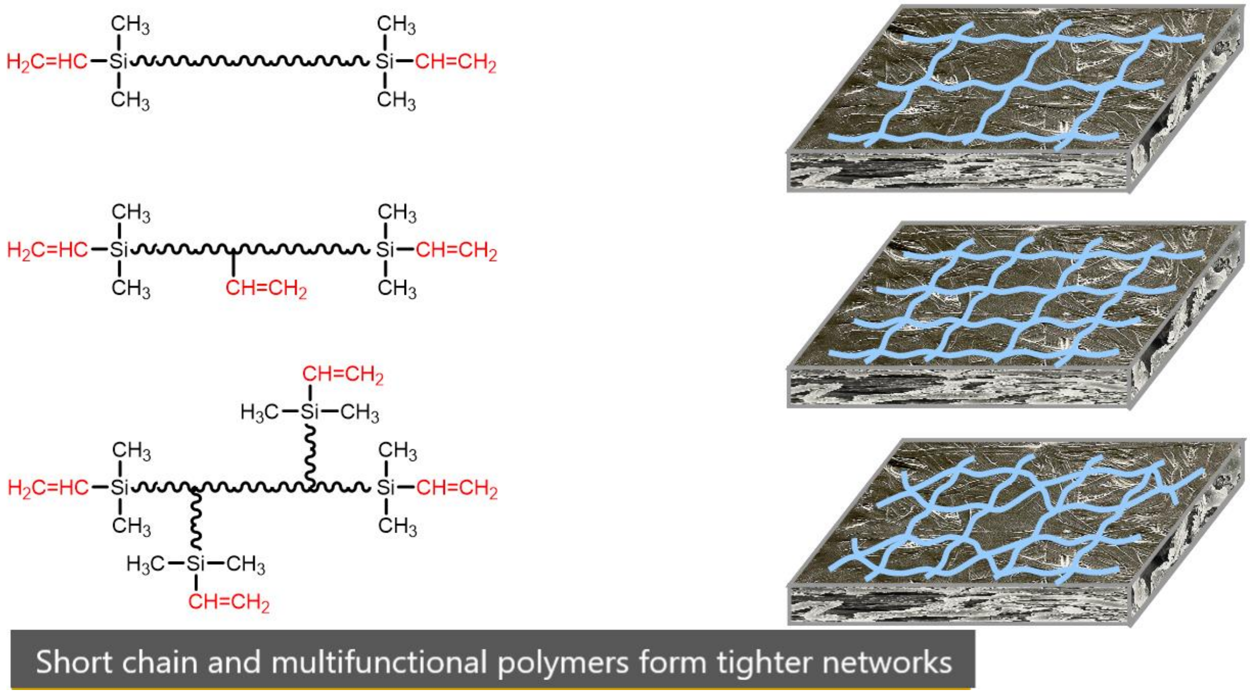


Figure 3: Polymer Structure and Silicone Network

4. Crosslinker Type

The structure of silicon-hydride functional crosslinkers used in solvent free silicone release coating does not vary to the extent of the base polymer. In general, linear crosslinkers are used having 20 to 50 repeating units, whereof 70 – 100% of the repeating units are SiH groups and the remaining part consists of dimethylsiloxy units. There may be other crosslinker designs in the market, but I will focus here on the one used most.

As there is always a large number of crosslinking points on one crosslinker chain and hardly any spacer in between, the effect on mesh width of different crosslinkers is marginal.

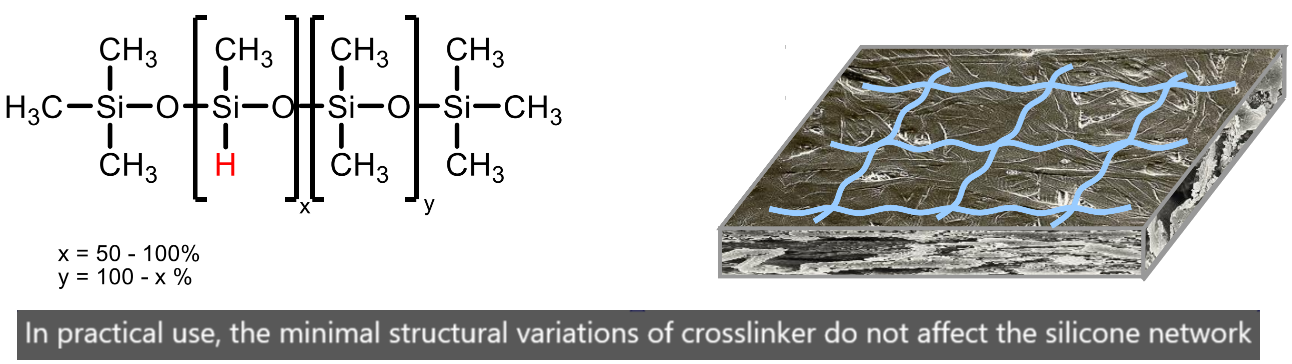


Figure 4: Crosslinker Structure and Silicone Network

5. Stoichiometry

Addition cure systems are typically formulated with a molar excess of crosslinker. This ratio of crosslinker to polymer in a system is generally expressed in the industry as the SiH/Vinyl ratio. Common ratios used to formulate can range from 1.2 to 3.0 or higher.

This means there is always an excess of silicon hydrogen left on the surface. In the case of a 1.5:1 SiH:SiVi ratio there is one SiH group per every other crosslinking point.

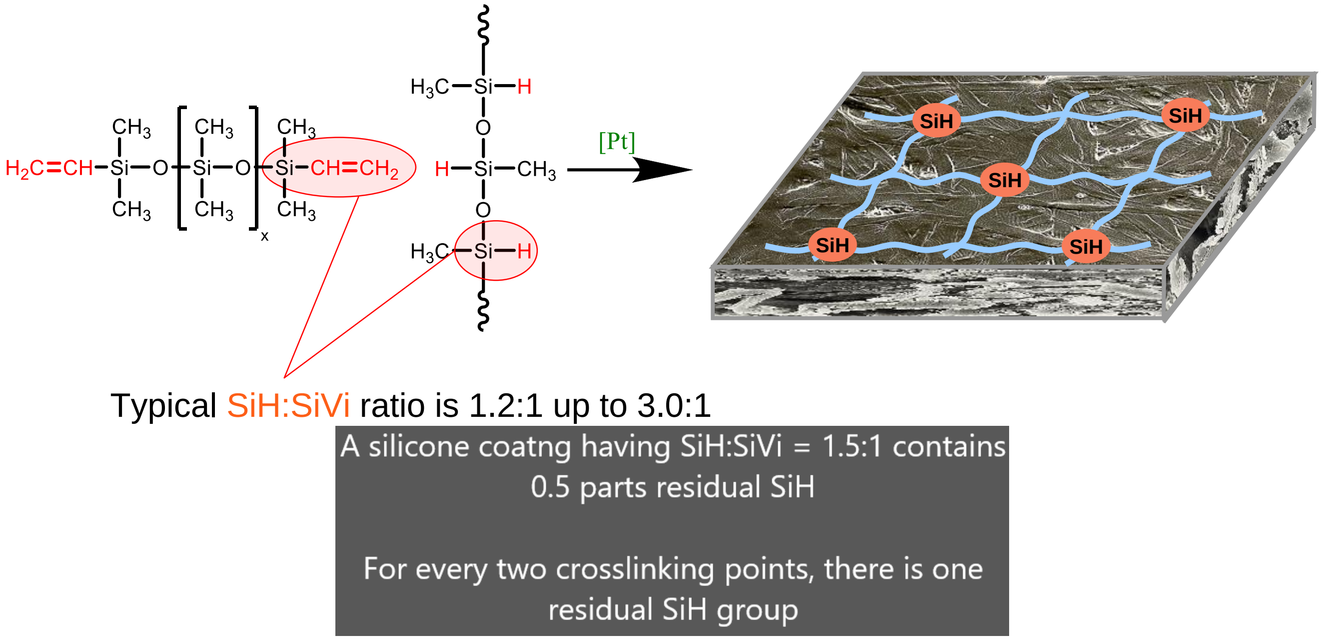


Figure 5: Stoichiometry and Surface Chemistry

6. SiH Effect on Release

Glassine paper was coated with a reactive silicone system containing a 200 cst. linear polymer and crosslinker using stoichiometric ratios of SiH:SiVi of 1.4:1, 1.7:1, and 2.2:1. The silicone coatings were fully cured. After cure the theoretical surface concentration of the 2.2:1 coating was three times the SiH surface concentration of the 1.4:1 formulation, assuming no SiH being consumed in side reactions.

Coated papers were laminated with two different PSA tapes: the tesa® 7475 with an acrylic-based adhesive and PVC substrate, and the tesa® 7476 with a rubber-based adhesive and cloth substrate. At a low peel rate, release force increased with SiH concentration for both tapes. At high peel rates, release force did not change significantly with increasing SiH concentration for both tapes.

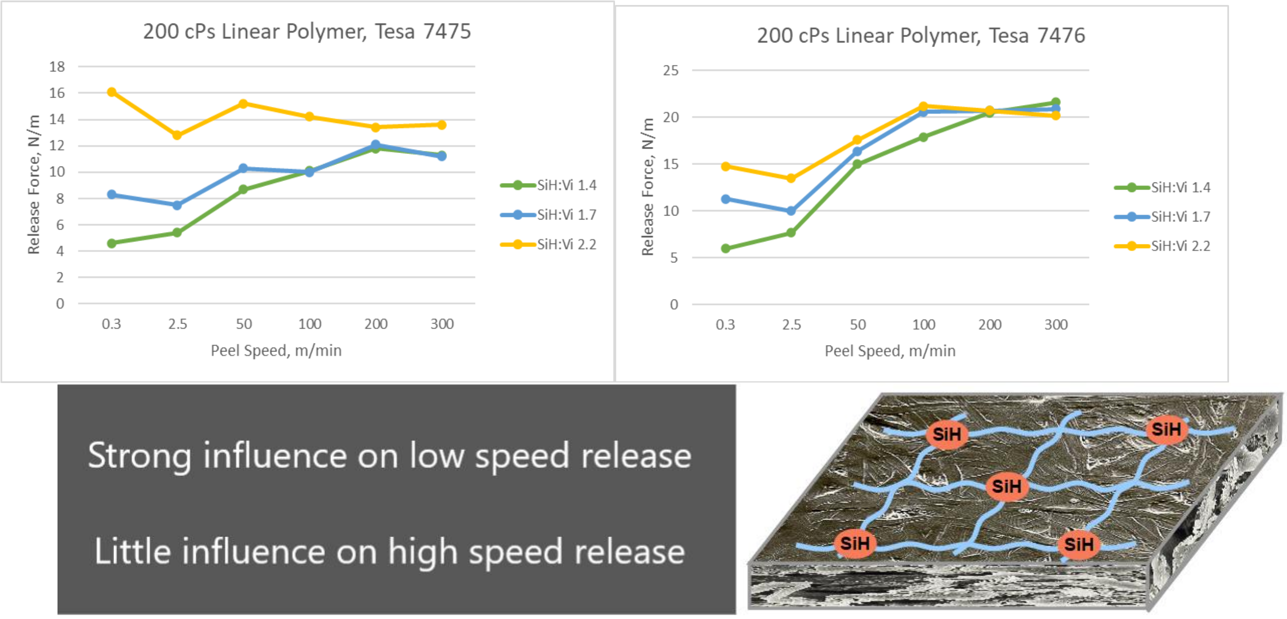


Figure 6: Effect of SiH Concentration on Release

7. SiH Effect on Release After Aging

SCK paper was coated at four different SiV:SiVi levels. In this case, initial cure was kept around 10-15% extractables (85-90% affixed) to emphasize aging effects. Within 60 minutes of silicone coating, acrylic adhesive was wet-cast onto the liner and dried using an automated lab sheet coater.

Despite the intentionally poor initial cure, age up wasn't too pronounced. It was only really an issue at low speed. At medium and high speed, age-up was minimal. In fact, in the case of the high speed 1.6:1 sample, it even dropped a little, which is often seen in well-cured systems in their first weeks of aging. The value of the ubiquitous 0.3 m/min (12"/min) low speed test is often called into question, and this only adds to that discussion.

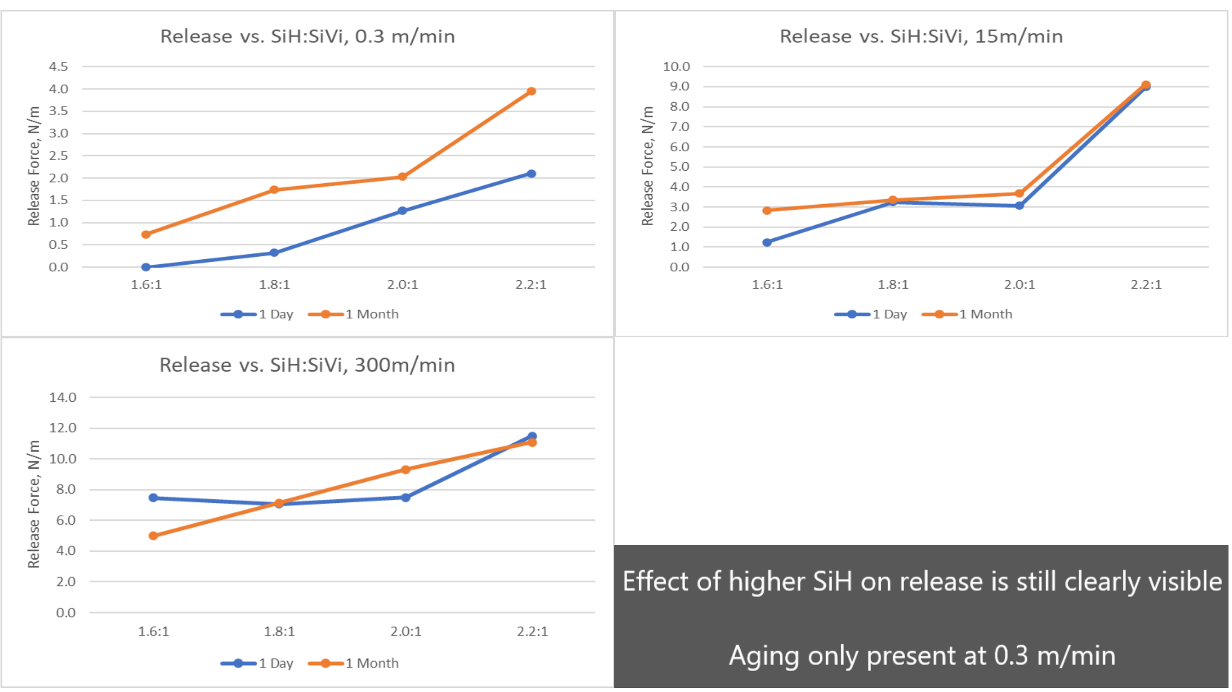


Figure 7: Release Effect of SiH and Peel Speed vs. Aging

8. Silicone structure and surface chemistry

Shorter polymer chains or multifunctional polymers form tighter networks having more crosslinking points. Additionally, they have more residual SiH groups when formulated with the same stoichiometric ratio.

We have seen that the number of residual SiH groups on the release layer has a big impact on release. If we want to see the effect of the silicone network on release, the SiH effect has to be eliminated.

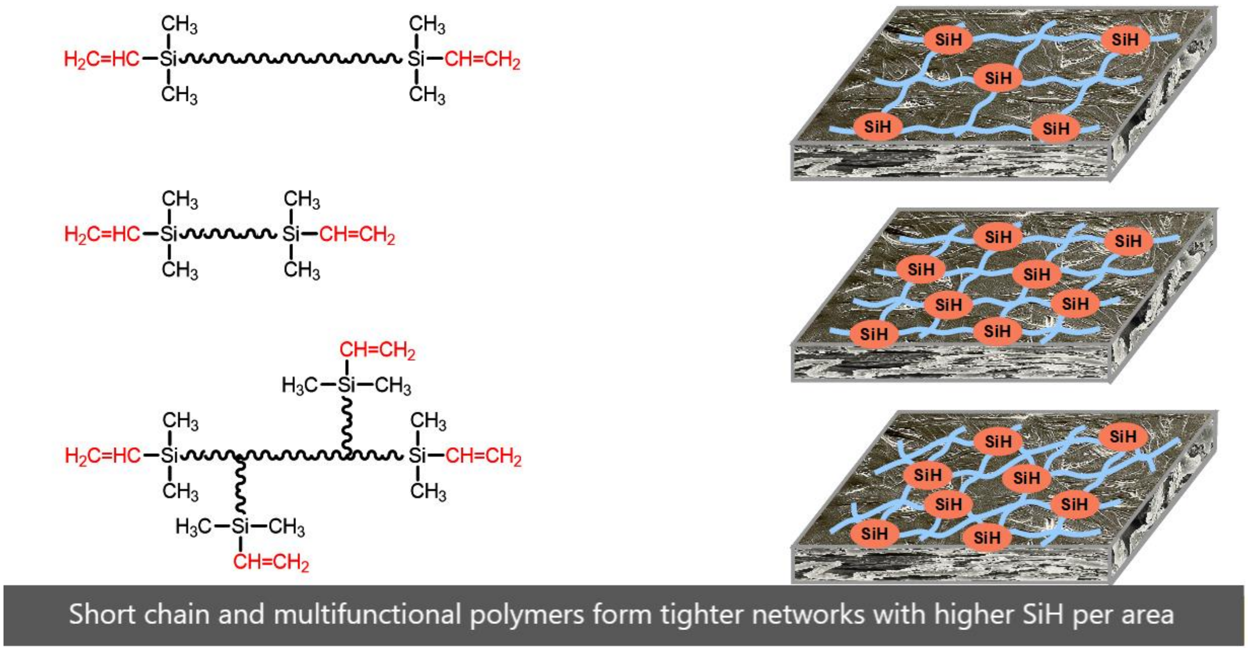


Figure 8: Effect of Silicone Structure on Surface Chemistry

9. Silicone network and release

Three different polymers were compared to identify the effect of the silicone network on release.

A short chain linear polymer having a viscosity of 200 cPs, a long chain polymer having 500 cPs, and a branched multifunctional polymer were used.

All three polymers were formulated with a crosslinker in such a stoichiometric ratio that the same absolute amount of residual SiH was left after completion of cure.

Having the same absolute amount SiH on the surface, all effects can be attributed solely to the different silicone networks created.

At low peel rates there is hardly any difference amongst the three polymers in release. This is true for tesa® 7475 with an acrylic-based adhesive and tesa® 7476 with a rubber-based adhesive.

At high peel rates the network formed from the 500 cPs polymer has the highest release and the tight network formed from the branched polymer has the lowest release.

When increasing the surface SiH concentration from 100 ppm to 175 ppm, release force at low peel speed increases, but release at high peel speed remains pretty much unchanged.

Figure 9: Effect of Silicone Network on Release

10. Release additives and network structure

Additives used to increase the release force for silicone systems usually contain reactive silicone resins.
In 1995 Newby and Chaudry introduced the idea of interfacial slippage as critical for the release mechanism. T. Cosgrove proved that silica resin particles significantly reduce chain mobility.
The freeze out of interfacial slippage by silicone resins was postulated by G. V. Gordon in 2000.
In 2001 Liliane Leger correlated the energy for adhesive slippage in CRA® containing silicone layers with the peel strength.
So, it is today's common understanding that silicone resins attract the silicone chains and reduce their mobility.

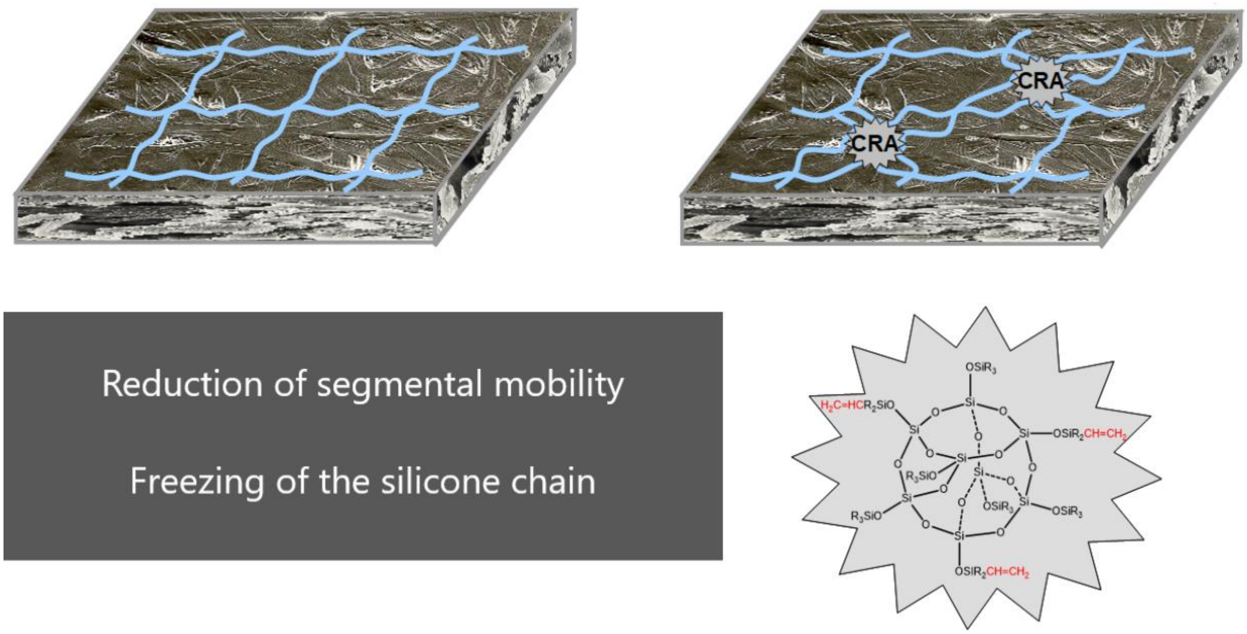


Figure 10: Release Additives and Network Structure

11. Effect of silicone resins on release

It is well known that silicone resins increase the release level, but it is much less known what contributes to this effect.
Liliane Leger correlated the energy for adhesive slippage in CRA® containing silicone layers with the peel strength, but no information was given on the effect of the surface chemistry of the silicone release layer.
Modifying a silicone release layer with a reactive silicone resin usually goes along with an increase in network density and a change in surface chemistry, meaning residual SiH concentration. Network density and SiH both have a significant impact on release, as demonstrated earlier.
To single out the contribution of network density to a controlled release system, we used a reactive silicone resin and a non-reactive resin and took care to maintain a constant residual SiH-concentration for the release layers tested.
Acrylic Tesa® 7475 and rubber-based Tesa® 7476 both respond to a 20% addition of a reactive silicone resin and a non-reactive resin. The level of increase in release force strongly depends on the peel speed applied. The response of the rubber-based adhesive being much stronger than that of acrylic tape A 7475.
It is noteworthy that no difference between the reactive and the non-reactive resin is seen with the rubber-based adhesive in release increase. This tells us that an increase in network density due to the crosslinking reaction of the reactive silicone resin does not contribute significantly to the controlled release effect.
It is also important to note that the increased efficacy of the non-reactive resin does not mean that it is recommended over a reactive one. This particular study does not assess stability upon aging. Stability of non-affixed resins is generally much worse than that of reactive resins.

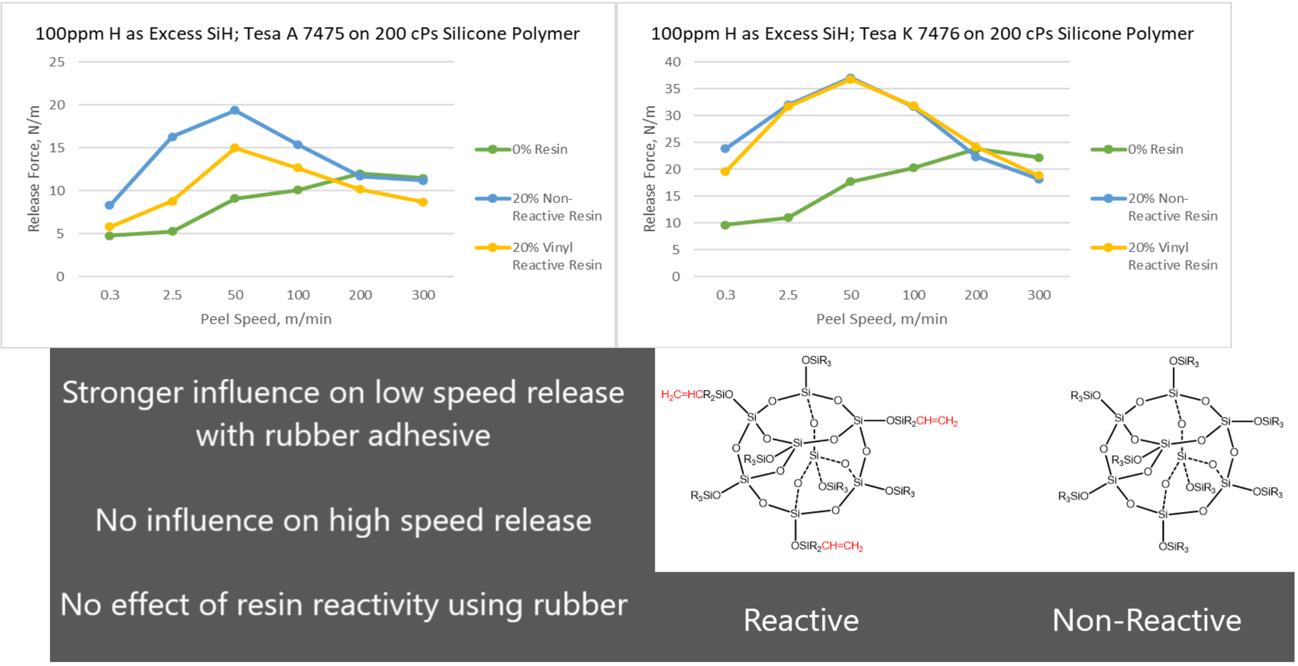


Figure 11: Effect of Silicone Resins on Release

12. Chemical instability of the silicone interface

Before discussing potential SiH effects on controlled release we'll have a short excursion into silicone surface chemistry to get us back from an ideal world to the real world.
Residual SiH groups are not stable!
They can react with moisture to form Si-OH groups, and these again can crosslink with other SiH groups to form chemically inert Si-O-Si bonds. They don't react instantaneously, but they react in real time. This reaction happens both during silicone cure and during aging of the silicone release liner.
Only SiH bonds and SiOH bonds can significantly interact with chemical reactive groups in the adhesive, Si-O-Si bonds can not.
This is one of the root causes for release variations.
SiH in a silicone layer can be measured by FMIR (Frustrated-Multiple-Internal-Reflection). The SiH vibration peak 2160 cm^{-1} is set in relation to the Si-Me peak at 1445 cm^{-1}. This ratio is called relative extinction and is an indicator for the amount of SiH on the silicone layer. With this method we can follow how SiH is lost during liner aging.

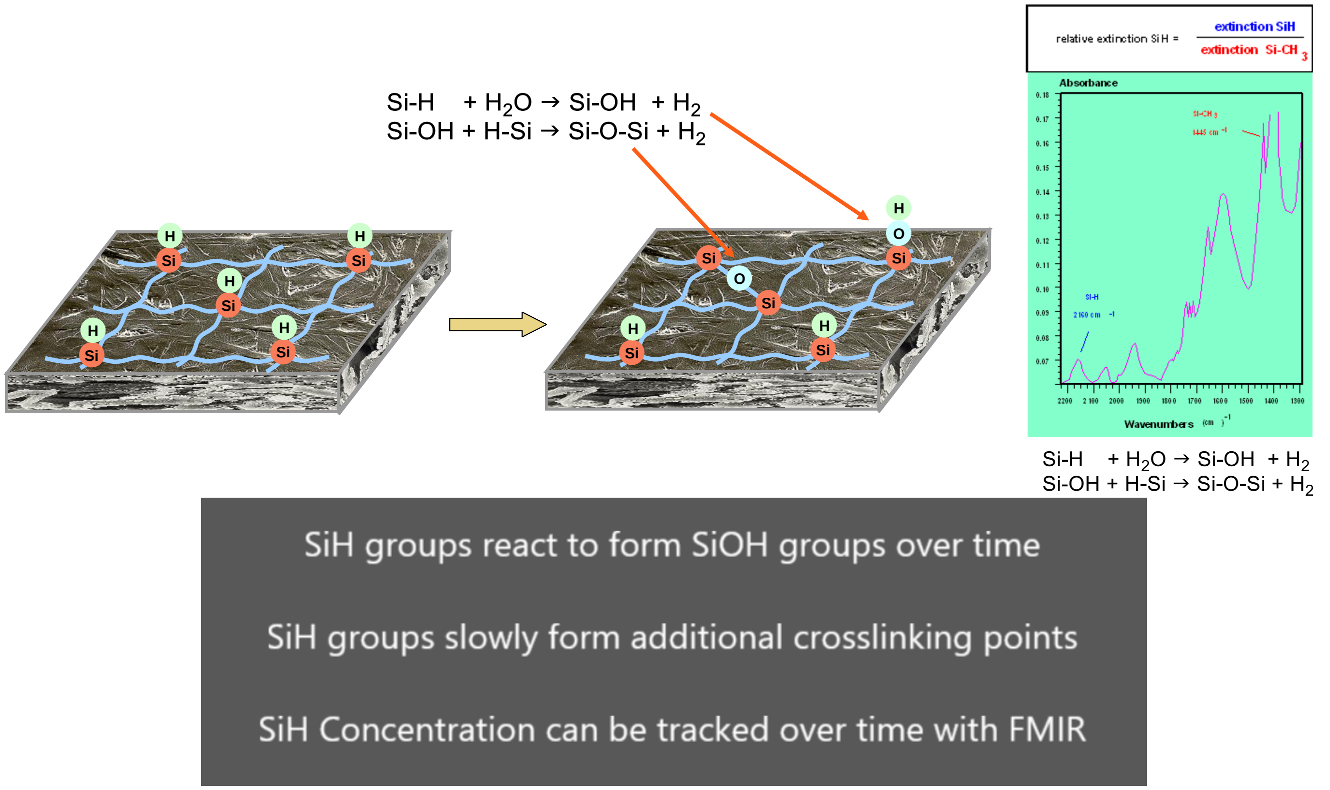
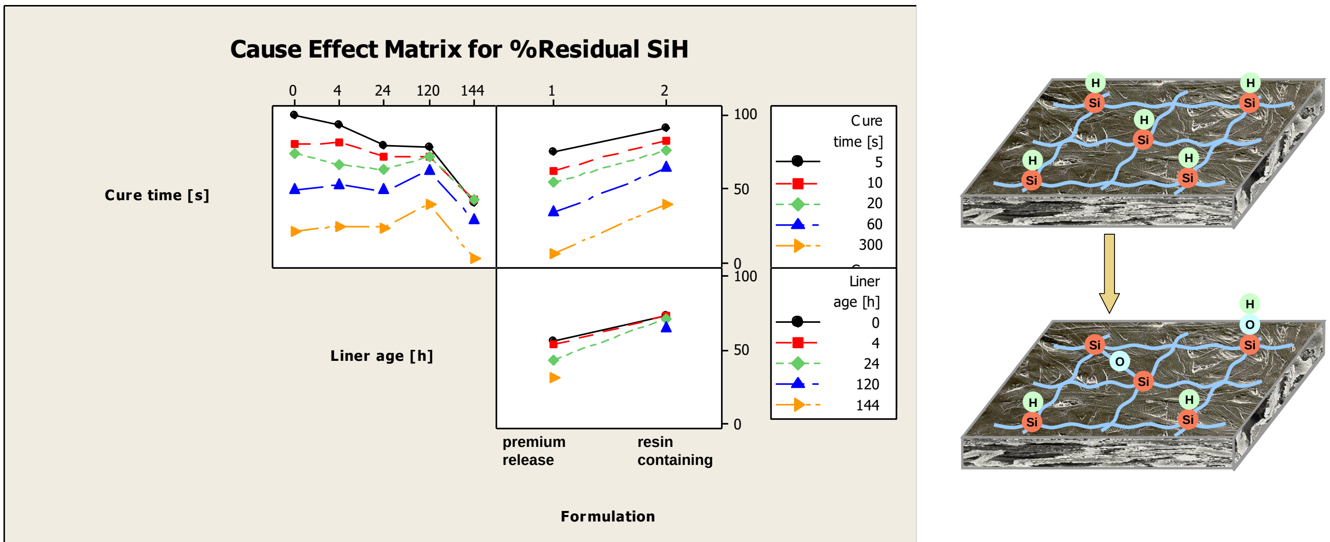


Figure 12: Chemical Instability of the Silicone Interface

13. Stability of the SiH group:

The SiH concentration on a silicone surface was measured by FTIR. The relative reduction of the residual SiH was correlated with the time used for cure and with the age of the siliconized release liner. A premium release formulation and a resin containing formulation were tested.

It can be seen that with longer cure time, the residual SiH is greatly reduced with the premium release formulation and a resin containing formulation. This means that SiH stability is low at high temperatures with both systems. At ambient conditions we observed a certain loss in SiH with the premium release formulation but a constant amount of SiH with the resin containing formulation. This indicates a SiH stabilizing effect for the silicone resin.

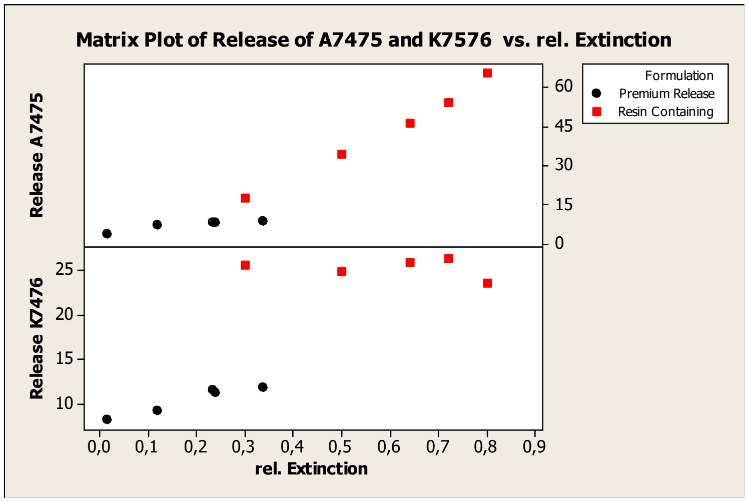


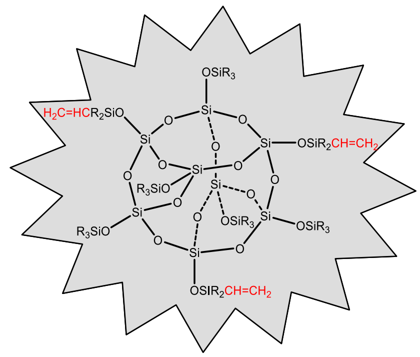
Low stability of SiH at high temperature exposure (long cure time)

Resins stabilize SiH

Figure 13. Effects on the Stability of the SiH Groups

14. Correlation of SiH concentration with release effects:
It’s amazing how differently acrylate and rubber-based adhesives A7475 and K7476 respond to surface SiH in premium release coatings and resin containing coatings.
The premium release coatings of both adhesives respond to increasing SiH levels with an increase in release. Absolutely contrasting is the response to increasing SiH levels of the corresponding 40% resin loaded release coatings.
While the resin loaded release coating provides a high release against the rubber based adhesive undisturbed by any change in surface SiH, the acrylic adhesive A7476 reacts with great sensitivity to any change in SiH concentration.
At low SiH levels there is hardly any high release effect of the resin.





SiH is essential for resin effect with acrylate adhesive

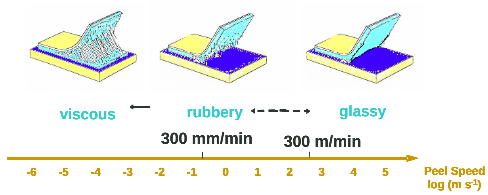
SiH is not essential for resin effect with rubber adhesive

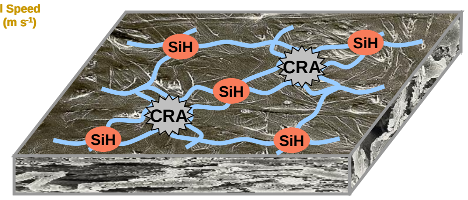
Figure 14. Effects of the SiH groups on Release Effects

15. Release effects and release mechanism from a chemist's perspective
We have seen that release effects depend significantly on the peel speed applied. D. H. Kaelble’s and D. W. Aubrey’s findings on the change of adhesive properties with peel speed and consequently a change in failure mechanism helped us to understand this effect.
The idea of interfacial slippage visualized the effect of the crack tip of the adhesive sliding over the silicone surface with its highly mobile chain segments. A reduction of segmental mobility or even freezing the silicone chain by adding silicone resin corresponds very well with our experience of tighter networks providing higher release values and resins pushing release even higher. We can associate this effect with the adhesive struggling over a surface with high slip resistance.
But what has residual SiH got to do with it?
We’ve seen that acrylic-based tesa® 7475 and rubber-based tesa® K7476 both respond to the concentration of SiH in resin free silicone release coatings. So, there has to be interaction between the adhesives and the SiH-group.
But why does SiH have no effect in resin containing release coatings with rubber-based tesa® K7476, while it is essential for the resin effect with Acrylic tesa® 7475? This is a difficult question to answer, but a study on the SiH mechanism would greatly contribute to our understanding of the mechanism of peeling.

Figure 15. Release Effects and Release Mechanism

✓CHANGE OF ADHESIVE PROPERTIES AND MECHANISM WITH PEEL SPEED



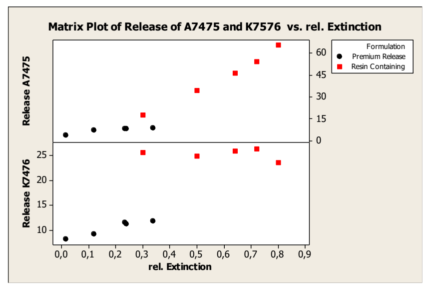


✓INTERFACIAL SLIPPAGE

✓REDUCTION OF SEGMENTAL MOBILITY

✓FREEZING THE SILICONE CHAIN BY RESINS

?SiH-EFFECT AND ADHESIVE-TYPE?



16. Conclusion

Peeling a tape is simple. The mechanism of peeling definitely is not.

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