

ADHESIVE CHEMICAL REACTIVITY INFLUENCES ON SILICONE RELEASE FORCE

By: Kyle Rhodes, Business Development Manager,
Elkem Silicones, York, SC

Abstract

The interface between silicone release coatings and the adhesives applied onto them can be influenced by a number of factors. Some of these factors include physical properties of the release liner and silicone surface, the chemical nature of the interfacial surfaces, and the relaxation state of the silicone at the time of adhesive coating. This paper will explore some of the chemical factors and the influences that these have on release force values.

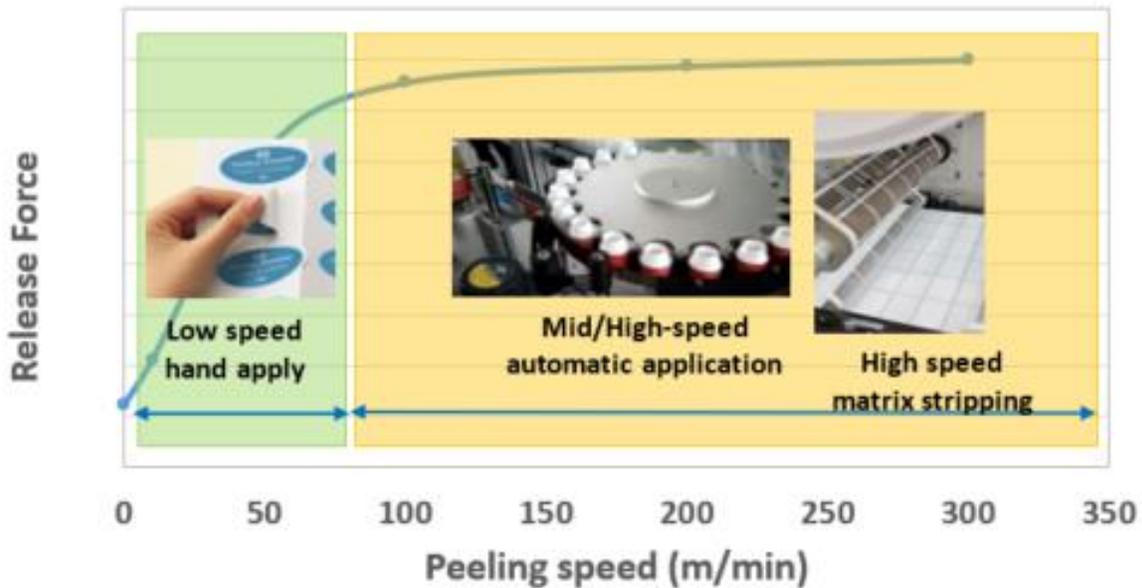
Background

PSTC Method 4 defines the release force as the measure of the force required to separate a unit width of pressure sensitive tape (or label) from a release liner at a controlled angle and speed. The contributing factors that influence the release force can vary greatly. The list of factors is wide and varied, and numerous attempts have been made in previous studies across the industry to help understand each of these variables. Table 1 lists just a few of the factors that are commonly evaluated in the development of a tape or label type construct.

Table 1. Common variables that influence release force

Silicone	Adhesive
Polymer Type Formulation Silicone/Organic Character Viscosity Coating Quality Cure Speed Cure Quality	Type (HM, Emulsion, Solvent) Thickness Performance Needs (Removable, Repositionable, or Permanent) Chemical Interactions
Liner	Process
Type (SCK, CCK, PCK, Glassine, MF, PET) Basis Weight Caliper Surface Roughness Hold out coating Moisture Content Layflat ability	Temperature Line Speed Coating Process Air Temp Web Temp Cure Profile Airflow

Different applications have different release profile needs, ranging from low to high release at low speed, and from low to high release at high speed, and everything in between. High speed automated labeling applications may require a low or medium release at high speed, converters may want the highest speed to strip the matrix, while a hand apply label or tape may want a higher release force.



Graph 1: Release force vs Peel Speed based on application need

The silicone system that is chosen will play a role in the release profile, as will the selection of the adhesive system that is desired for a given application. This particular study evaluated various silicone chemistries against the variation of hot melt formulas, so that the impact of such variations could be understood.

Silicone Systems

Silicone polymers can have different functionalities, ranging from vinyl groups, to acrylate groups, or epoxy groups, to name just a few commonly found in release coatings.

Silicone polymers with acrylate functionality, with the acrylate either terminal (end of chain) or pendent (side of chain), can vary in length, and vary in the relative ratio of acrylate groups as compared to the quantity of silicone groups.

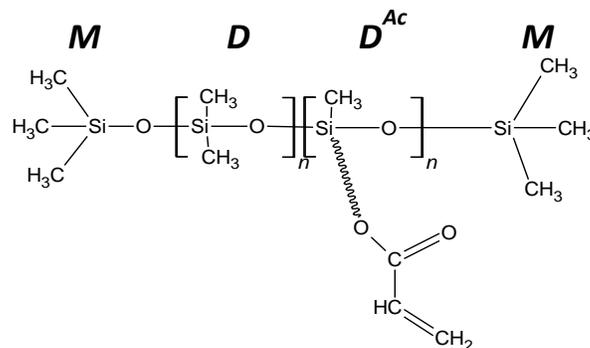


Figure 1. Silicone Polymer with acrylate functionality.

It is common when formulating Silicone acrylate release coatings, to blend various silicone chain lengths with other chain lengths in order to optimize the ratio of silicone character (D units) to acrylate character (D^{Ac} units).

Table 2. Silicone UV Acrylate polymers formulations

UV Acrylate	D Silicone Character Chain Length	D ^{Ac} Acrylate Character Chain Length	Formulation Ratio
Low Release Formulation	Medium	Low	56%
	Low	Low	30%
	High	Low	14%
Medium Release Formulation	Medium	Low	70%
	Low	Low	30%
High Release Formulation	Medium	Low	10%
	Low	Low	90%

Silicone acrylate systems are polymerized by the use of a photoinitiator that forms free radical moieties, which react through the double bonds of the acrylate group to extend the polymer and create crosslinking within the silicone matrix. These systems cure at low temperature with exposure to UV light within a very short cure window when exposed to high intensity UV light. These systems do require an inert atmosphere, with <50 ppm Oxygen at the surface, so as to eliminate oxygen inhibition.

Silicone Epoxy

Silicone polymers with epoxy functionality, with the epoxy either terminal (end of chain) or pendent (side of chain), can also vary in length, and vary in the relative ratio of epoxy groups as compared to the quantity of silicone groups.

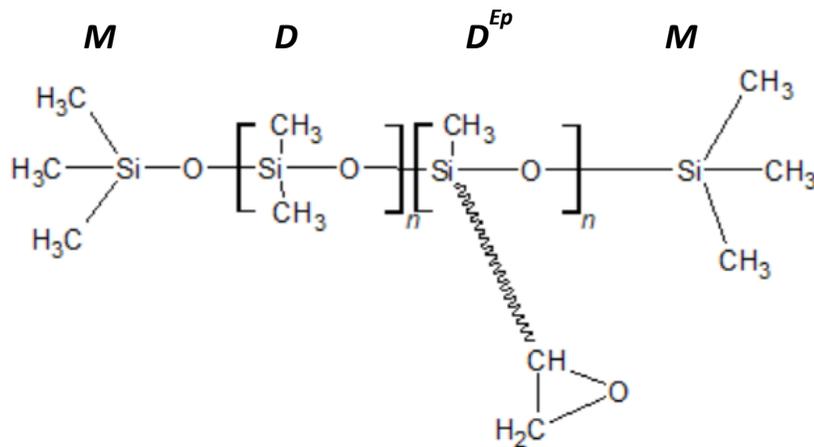


Figure 2. Silicone Polymer with epoxy functionality.

It is common when formulating Silicone epoxy release coatings, to blend various silicone chain lengths with other chain lengths in order to optimize the ratio of silicone character (D units) to epoxy character (D^{Ep} units).

Table 3. Silicone UV Epoxy polymers formulations

UV Epoxy	D Silicone Character Chain Length	D ^{Ep} Epoxy Character Chain Length	Formulation Ratio
Low Release Formulation	Medium Very High	Low Low	95% 5%
Medium Release Formulation	Medium	Low	100%
High Release Formulation	Medium	Mid	100%

Silicone epoxy systems are polymerized by the use of a special photoinitiator that forms a super acid moieties, which react through the ring structure of the epoxy group, to extend the polymer and create crosslinking within the silicone matrix. These systems cure at low temperature with exposure to UV light within a very short cure window when exposed to high intensity UV light. These systems do not require an inert atmosphere during cure.

Silicones with vinyl groups

Silicones with vinyl groups at the end of the chain, i.e. end blocked, or pendent groups on the side of the chain have been studied throughout the years quite extensively by various researchers. It is well known that these polymers can be varied in chain length, vinyl content, vinyl location, varied in crosslink density by varying the associated hydride crosslinker type, and length, as well as utilizing the addition of a controlled release additive (CRA) to modify the release profile at various peel speeds. The low release formulation, without CRA, was used as a reference point for comparison.

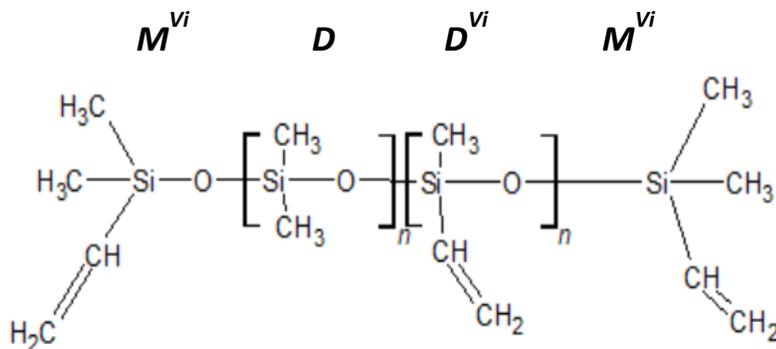


Figure 3. Silicone Polymer with vinyl functionality

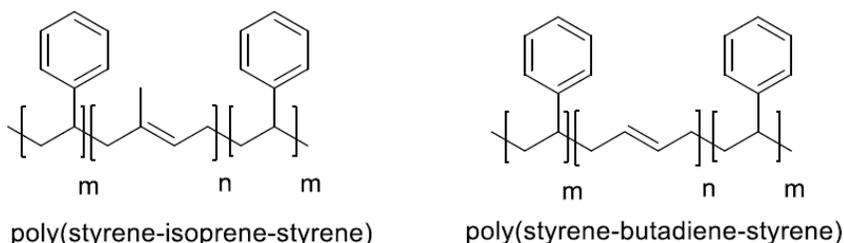
Table 4. Silicone w/ vinyl polymers formulations

Addition Cure, Pt Catalyst	D Silicone Character Chain Length	D ^{Vi} Vinyl Character Chain Length	Formulation Ratio
Low Release Formulation	Very High Mid	Low (EB and/or Pendent) Hydride: Low	98% 2%

Silicone polymers with vinyl functionality cure with heat in the presence of a platinum catalyst. This particular system was formulated to have a SiH:Vinyl ratio of 1.8, and a platinum catalyst level of 50 ppm Pt. This particular silicone polymer was a VEB (vinyl end blocked) polymer, with no reactive vinyl pendent along the chain.

Hot Melt formulations

Labels and tapes may utilize hot melt pressure sensitive adhesives in order to meet specific end application needs, cost, and performance. Common starting blocks for hot melt systems are poly(styrene-isoprene-styrene) or poly(styrene-butadiene-styrene), as shown below in figure 4.



polystyrene : SP : 9.2 - Tg : 100°C
 polyisoprene : SP : 8.2 - Tg : -65°C
 polybutadiene : SP : 8.5 - Tg : -106°C

Figure 4. SIS and SBS hot melt starting components

The SIS and SBS hot melt systems can be adjusted by adjusting the ratio of styrene to isoprene or butadiene to modify the Tg of the combined system.

Resins can be used to modify the hot melt system. It can be common to utilize a rosin tackifier, or to utilize a derivative of C5 aliphatic or C9 aromatic starting materials to create a new resin system. In this study, some combinations of these materials were used to study the effects on silicone release. Simple hot melt formulas were used for the study, at a set formulation level. These were not commercially available hot melts, but rather for research purposes only.

C5 aliphatic / C9 Aromatic resin starting points

Rosin tackifier (variations not shown)

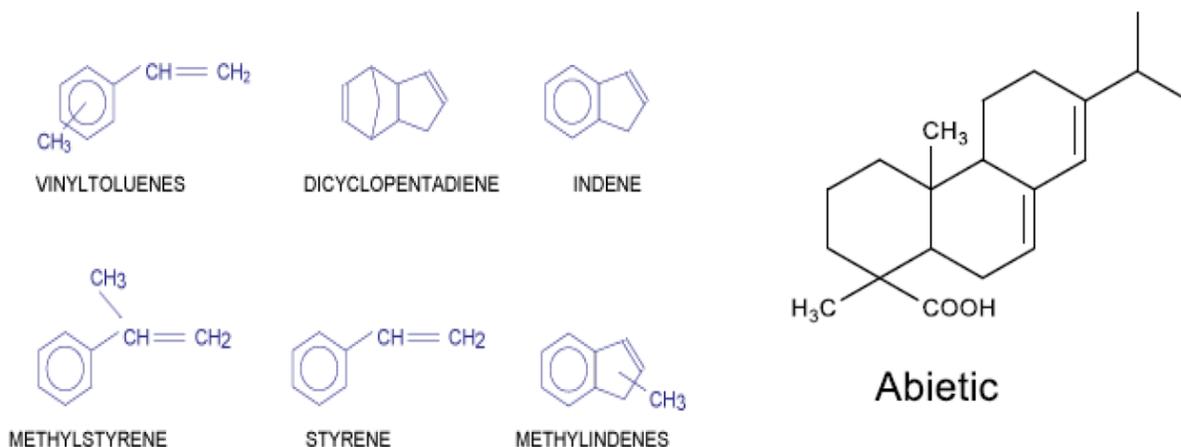
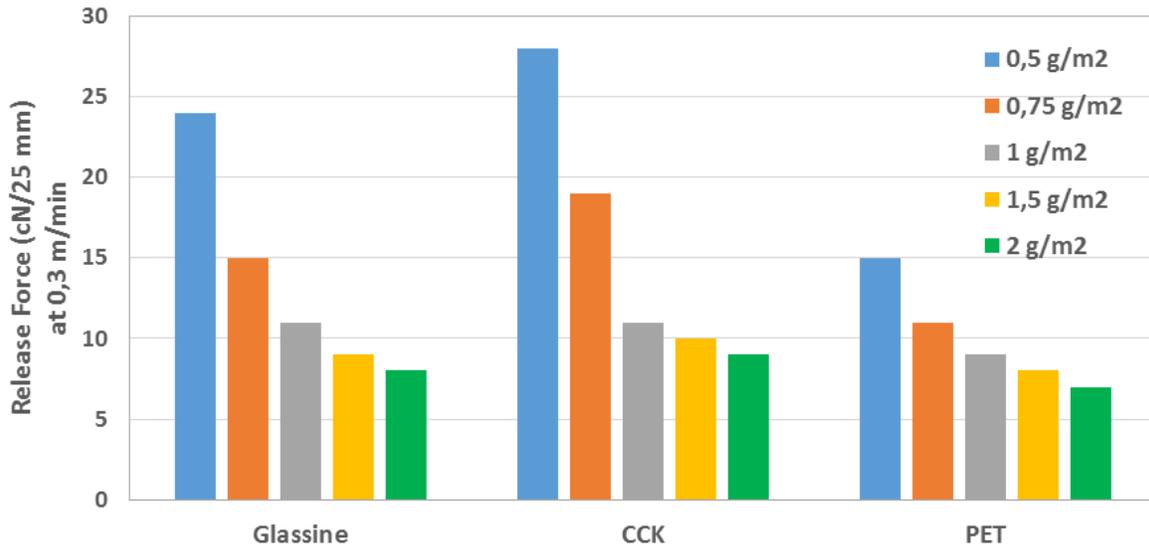


Figure 5. Common hot melt resins and tackifiers

Table 5: Hot Melt Formulations

Trial	Polymer	Tackifier	Aliphatic/Aromatic hydrocarbon
SIS-R-O1	Styrene-Isoprene-Styrene	Rosin	Oil 1
SIS-R-O2	SIS	Rosin	Oil 2
SIS-C-O1	SIS	C5/C9	Oil 1
SIS-C-O2	SIS	C5/C9	Oil 2
SBS-R-O1	Styrene-Butadiene-Styrene	Rosin	Oil 1
SBS-R-O2	SBS	Rosin	Oil 2

When building the parameters of this study, it was important to utilize a common silicone coat weight on the 1.5 mil PET that was used. When coating paper liners, the basis weight of the paper, the surface roughness, and the use of a hold out coating (clay or starch) can have an influence on how much silicone will sit on the surface of the paper versus how much will wick into the paper, leaving less silicone on the surface. If a silicone does not provide adequate coverage of the paper fibers, then the adhesive may see some of these fibers, and yield a high release.



Graph 2. Influence of silicone coat weight on common liner materials

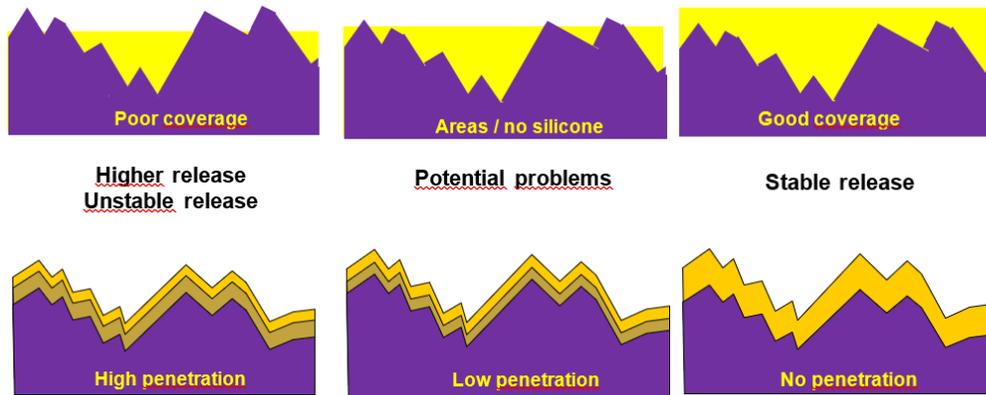
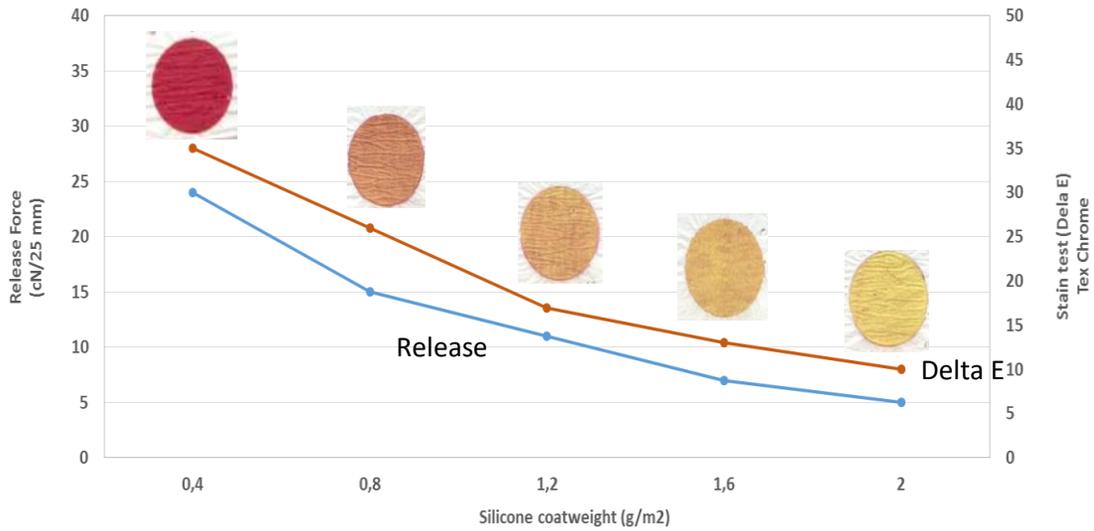


Figure 6. Influence of silicone coat weight

The amount of coverage can often be measured by staining the fibers of the paper with some common dyes, like Shirlastain or Malachite green, and reporting colorimetry readings as Delta E values.



Graph 3. Influence of silicone coat weight

In this study, to remove the influence of fibers and silicone coat weight, a silicone coat weight of 1.0 gsm on a smooth PET liner was selected.

Experimental Results

Hot melt formulations were coated onto various siliconized liners, and evaluated for probe tack, loop tack, peel, and shear on stainless steel panels, as well as release performance under Finat 10-3 slow speed release testing.

Table 6. Experimental results for hot melt performance

Trial	Polymer	Tackifier	Oil	Probe Tack g/cm ²	Peel g/in	Shear (h), 1 in	Release g/in
SIS-R-O1	SIS	Rosin	Oil 1	3873	1910	181	6.0
SIS-R-O2	SIS	Rosin	Oil 2	2951	1120	166	4.8
SIS-C-O1	SIS	C5/C9	Oil 1	4073	2390	75	3.2
SIS-C-O2	SIS	C5/C9	Oil 2	3514	2050	29	3.5
SBS-R-O1	SBS	Rosin	Oil 1	5059	2080	288	1.6
SBS-R-O2	SBS	Rosin	Oil 2	4877	1630	288	1.7

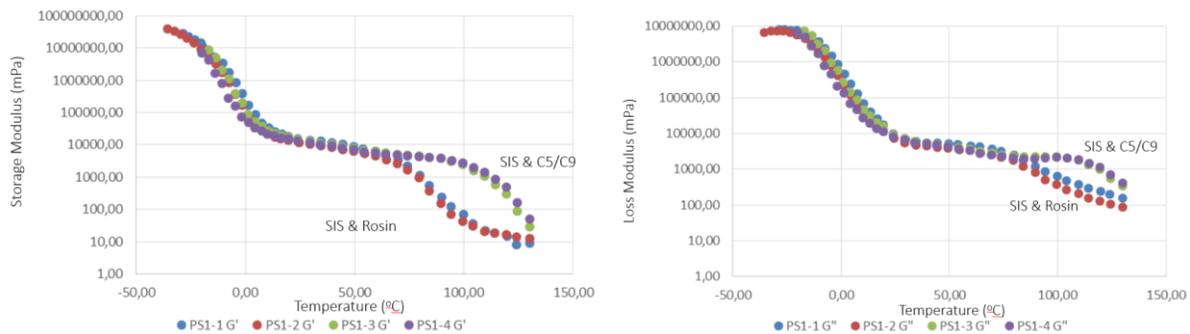
The rosin tackifier in SBS HM gave superior performance in probe tack and shear results, with moderate peel performance against stainless steel panels, and yielded the lowest release force.

The same rosin tackifier in SIS gave moderate probe tack, the lowest peel force, moderate shear results, but the highest release force.

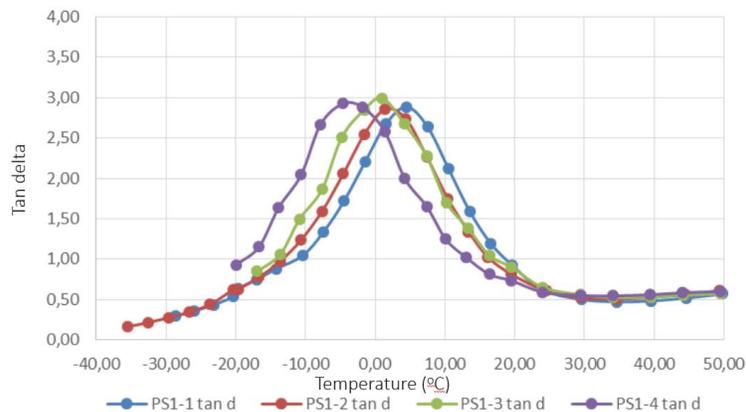
The SIS utilizing the C5/C9 tackifier gave good probe tack results, the highest peel force, moderate release force, but the lowest shear results.

Differentiating between Oil 1 and Oil 2 showed some impact, but only a minor influence as compared to polymer choice and tackifier choice.

The hot melt formulations were also evaluated by DSC rheometer, with parallel plates, at a frequency of 10 rad/sec, utilizing a temperature sweep from -40 to +130°C.

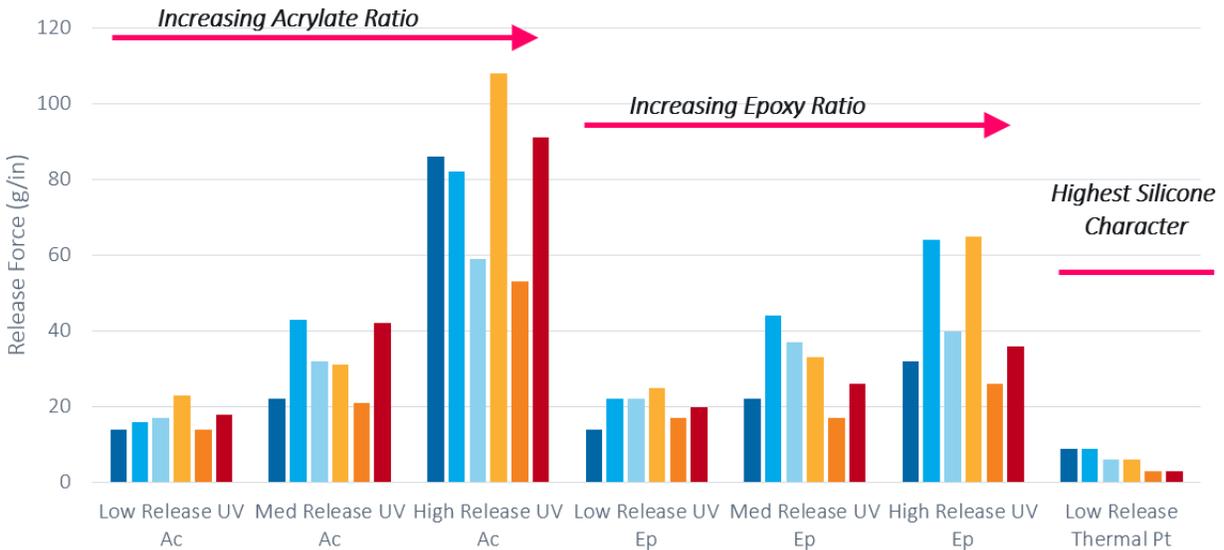


Graph 4. The G' storage modulus and G'' loss modulus of the SIS polymer, showing differences in the rubbery plateau and melt flow zones between rosin and C5/C9 tackifiers.



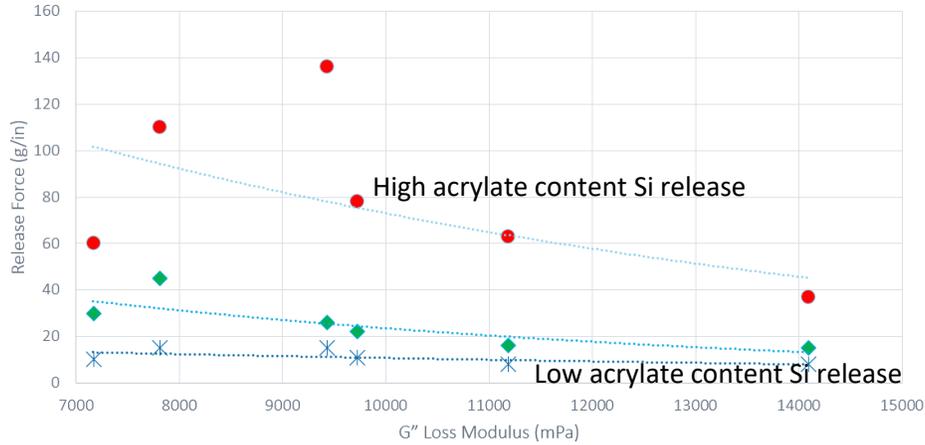
Graph 5. Tan δ of the SIS polymer, showing a change in melt temp, with slight differences depending on rosin/C5-C9 tackifiers and differing oils, and their compatibility between hard and soft domains and aromatic/aliphatic natures.

The hot melt formulations were coated onto siliconized PET release liner, which had been precoated with different silicone types and formulations as identified in the background information. Samples were allowed to age 7 days, and then pulled at low speed per Finat 10 method.

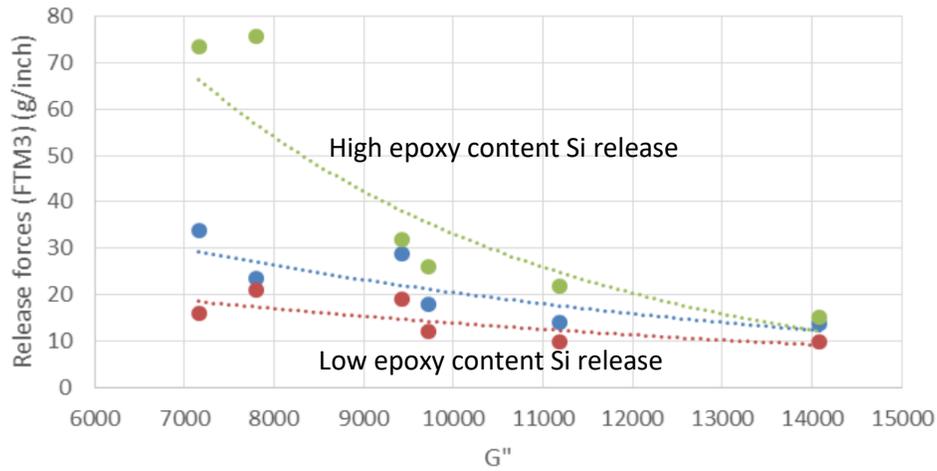


Graph 6. The various hot melt formulations showing release values as grouped by silicone release formulation/type.

Graph 6 above shows minor variations among different hot melt systems when grouped by silicone formulation and type. For example, all hot melt formulations gave similar release profiles between 15-21 g/in release when coated onto a low release UV acrylated silicone. The data set shows a relative increase in release, depending on the acrylate character in the silicone release coating. While there are variations among the hot melts with a wider difference at higher release rates (see High release UV acrylate), this can be utilized to control the release rate for a given application need. It also shows that different tackifiers and oils will have a different effect even among the same release coating system. Similar trends can be seen with the epoxy silicone chemistry.



Graph 7. Release force vs G'' loss modulus for UV silicone acrylate system (SIS/SBS combined).



Graph 8. Release force vs G'' loss modulus for UV silicone epoxy system (SIS/SBS combined)

Plotting release force versus G'' loss modulus shows an inverse relationship at higher organic content (epoxy or acrylate content), whereas lower release seems to give a more linear relationship between release and loss modulus.

Conclusion

The factors that influence release force have a number of inputs that can be either synergistic or antagonistic. Compatibility of the components within variations of hot melt systems can have an effect on the overall performance of the hot melt to meet different application needs, and may work in the favor of achieving a desired release, or may work against achieving a desired release.

Within a given system, when on 1 particular silicone chemistry, the polymer type of SIS or SBS can have a low influence on the release force, but tackifier type and plasticizer/oil type can have a low/medium influence on release. Changes within the combined system and how it affects the

modulus of the material, either loss or storage modulus, have a larger impact on the flow and interaction of the adhesive on the interface with the silicone.

The organic content can be used to have a larger influence on the release force, and allow for the fine tuning of the UV silicone type release coatings to achieve the desired result needed for the application.

References

I.Benedek, “Technology of PSAs and products”, **2009**, Edited by I.Benedek and M.M.Feldestein (CRC Press – Taylor and Francis Group).

I.Benedek, “Pressure Sensitive Adhesives and applications”, **2004** (Marcel Dekker, Inc.).

S.G.Chu, “Dynamic Mechanical Properties of Pressure-Sensitive Adhesives”, **1991**, pg 97-138, *Adhesive Bonding*

Acknowledgements

I would like to thank Sebastien Marrot, Amelie Ribour, and Karine Borecki for their efforts in this study.