

Creating differential release to avoid a sticky situation



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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 the modification of release force by changing Release Control Additives, and methods to create a differential release.

Introduction

Silicone coated release liners are a part of the total label construction and used to transport and hold the label from the raw label manufacturing step through printing and converting to final application. Some applications call for a low release force, some require a high release force, while some applications require a high differential release when creating dual-lined adhesive films or double-sided tapes.

Typically, silicone polymers provide a low release force against many adhesives and have to be modified with Release Control Additives (RCAs), also called Controlled Release Additives (CRA's) in the industry in order to reach a higher level of release force. These RCAs provide higher release force due to variations in the chemical structure, size, efficacy, and reactivity of the underlying silicone resin used in these RCAs.

A silicone resin is made of the same building blocks as silicone polymers, but instead of being a linear chain polymer, a resin is assembled under very controlled conditions to create a 3-dimensional structure, resembling linked balls or cages. (See Figure 1).

When added to a silicone release formulation and coated onto a paper or filmic substrate, a percentage of these resin cages will be on the surface of the silicone, and hence available at the silicone/adhesive interface. These cages then act as locations to which the adhesive is attracted. This attraction creates a higher bond and holds the adhesive to the release liner a little tighter and increases the release force slightly. With higher loadings of this resin in the formulation and at the surface, an increase in release force is observed. One mental image is to imagine these cages as sprinkles of sand onto the surface. The more grains of sand at the surface, the more bonding sites available between the adhesive and the liner.

Due to the variation in the available adhesives and tackified adhesives in the market, hot melt versus emulsion acrylics versus solvent acrylics, different thicknesses and characteristics, it is difficult to pre-determine the impact and attraction level of a specific adhesive to a specific release coating with a specific loading of RCA. Some common trends or behaviors can be used to determine the optimal selection of the RCA for a particular application, but all results should be tested and verified for a given application.

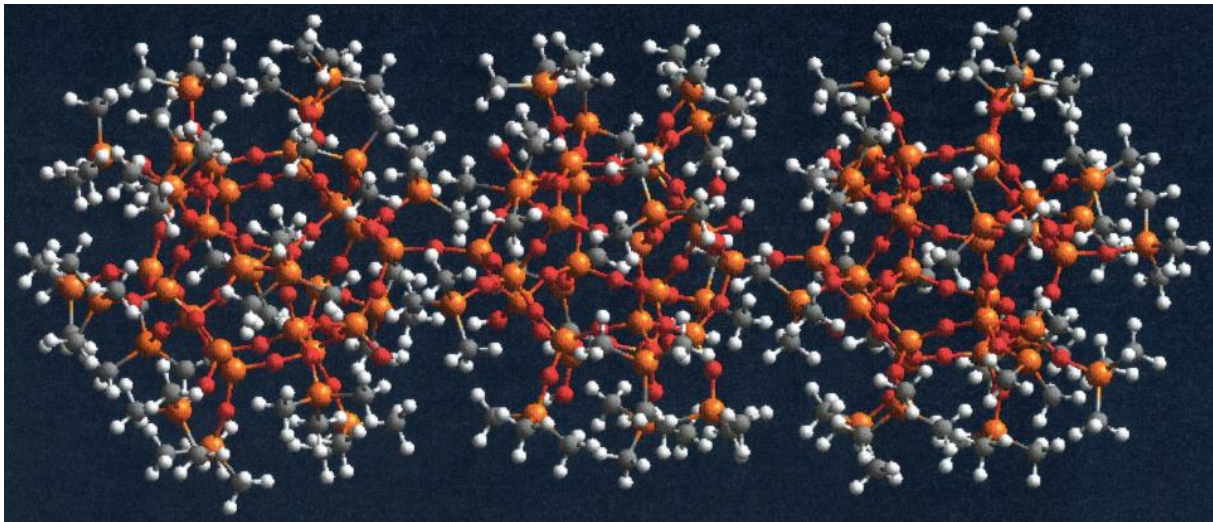


Figure 1. Computer Model of a theoretical structure of a MQ siloxane resin structure (Lin, Durfee, Knott 2009)

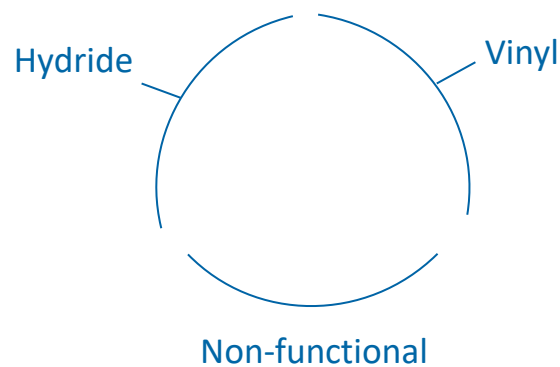


Figure 2. Variations of resins by functionality. Vinyl reactivity on the surface of the resin is the most common configuration, and helps to tie into the silicone crosslinking network.

Resins used in RCAs come in different variations, with different functionality, such as vinyl groups embedded into the structure's surface, but some versions exist with hydride functionality or have no functionality. This difference in functionality, as well as differences in the size of the cage, can lead to different attraction states at the interface.

It is also observed that there is a minimum loading effect before larger release force impacts are observed. Based on the formulation and resin selected, the efficiency of the resin can have a large impact. As the resin loading increases, the effect follows an exponential or polynomial increase curve. One common theory is that these resins form a network of domains across the surface of the release coating, and depending on delivery method, process, and resin type/formulation, additional resin can either increase the size of the domain as they agglomerate into larger bundles, or they stay separated as discrete smaller bundles of resin, but there are more of them sprinkled across the surface.

RCA's are used across multiple release coating chemistries and delivery options, from solventless thermal (i.e. Platinum catalyzed addition cure), emulsion, solvent, and UV curable technologies.

RCA's used in Emulsion-delivered Platinum catalyzed release coatings have the extra step of emulsification. To make these emulsion-based products, the silicone polymers and resins are encapsulated with surfactants and modifiers to allow for suspension within the water base. The process is targeted to deliver the silicone release coating as a layer of different particle sizes, which mix together at the coating process and deposit onto the substrate surface. The coating becomes homogeneous and uniform after the heating step which removes the water and cures the formulation.

Release Control Additives	Functionality	System
RCA Type A	Low Functionality , α -olefin diluent	Solventless Thermal
RCA Type B	Med Functionality Content	Solventless Thermal
RCA Type C	Very Low Functionality Content, Non-Vi	Solventless Thermal
RCA Type D	Low Functionality Content	Emulsion
RCA Type E	Low/Medium Functionality Content	Emulsion
RCA Type F	Low Functionality Content, High efficiency	Emulsion

Table 1. Release Control Additives

Selecting an RCA to meet a desired release target will require some evaluation to determine the optimal loading of the release modifier into the formulation. Below are some helpful graphs as a starting point to selecting the optimal additive and loading for your formulation. Please note that this data was collected based on TESA test tapes (dry tape, and not wet cast adhesive), so results will vary depending on chemistry, process, and application.

Data

The lab data collected in the following graphs were prepared by mixing the ingredients to have a set formulation with a combination of silicone polymers, crosslinkers, platinum catalysts, and Release control additives. Samples were then coated onto a SCK paper and cured on a pilot coater with thermal ovens to reach a cure state identified as <5% extractables as is common in the industry.

Analysis

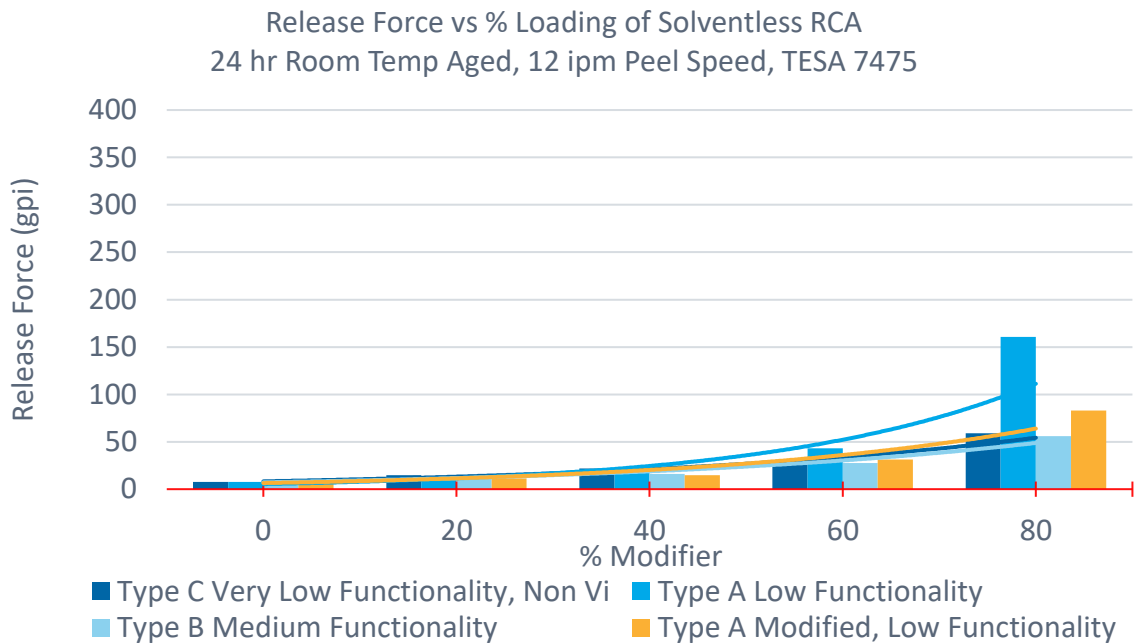


Figure 3. Evaluation of various solventless RCA modifiers with a Vinyl end stopped linear silicone polymer, formulated at 1.75 SiH:Vi ratio. -Tested with TESA 7475 test tape. At only 24 hours, the full interaction between the adhesive tape and RCA has not yet formed.

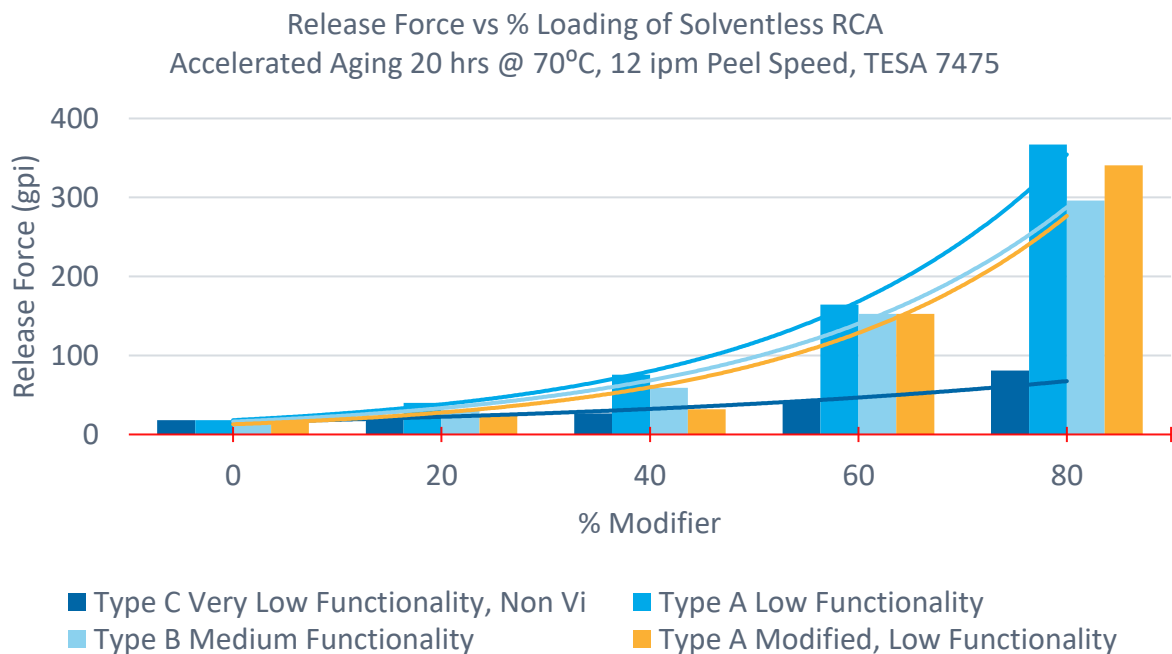


Figure 4. Evaluation of various solventless RCA modifiers with a Vinyl end stopped linear silicone polymer, formulated at 1.75 SiH:Vi ratio. Tested with TESA 7475 test tape. Simulation of room temperature aging to ~1 month through accelerated aging at 70°C shows a stronger response between the adhesive tape and the RCA/silicone blend.

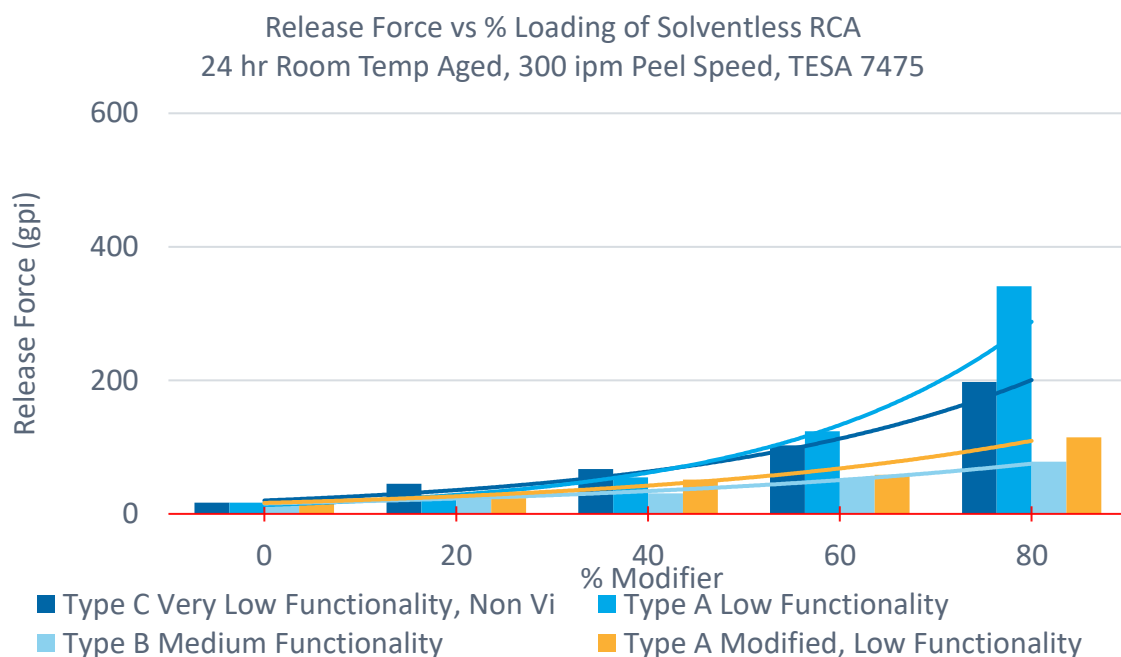


Figure 5. Evaluation of various solventless RCA modifiers with a Vinyl end stopped linear silicone polymer, formulated at 1.75 SiH:Vi ratio. Tested with TESA 7475 test tape. A higher release force pull speed shows a stronger response and interaction compared to low speed pull testing even at only 24 hours aging.

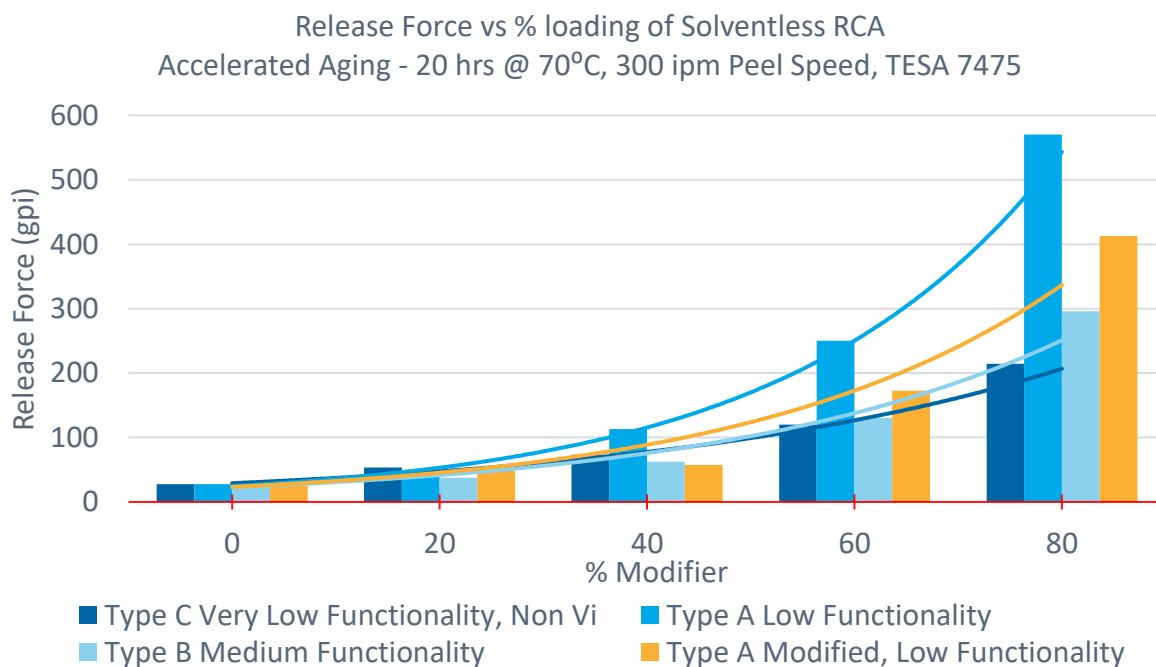


Figure 6. Evaluation of various solventless RCA modifiers with a Vinyl end stopped linear silicone polymer, formulated at 1.75 SiH:Vi ratio. Tested with TESA 7475 test tape. Simulation of room temperature aging to ~1 month through accelerated aging at 70°C shows a much stronger response between the adhesive tape and the RCA/silicone blend and pulled at this higher pull speed. The interaction between this particular acrylic based test tape and the low and medium reactive RCA modifiers has a higher effect compared to other types of adhesives.

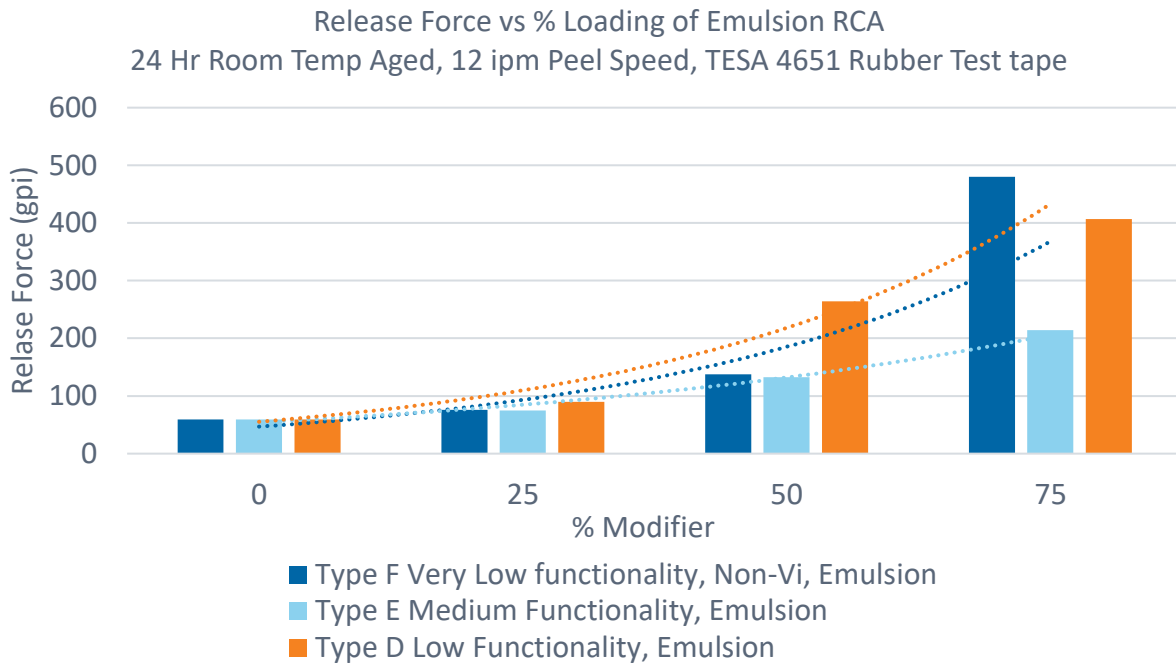


Figure 7. Evaluation of various emulsion RCA modifiers with an emulsion multifunctional silicone polymer, formulated at 1.7 SiH:Vi ratio for Type F and Type E, and 2.0 SiH:Vi ratio for Type D. Testing conducted with TESA 4651. At only 24 hours, the full interaction between the adhesive tape and RCA has not yet formed, but exhibits a higher adhesive/RCA interaction compared to the TESA 7475 acrylic test tape. There is more interaction with the vinyl content along the backbone of a multifunctional polymer with 0% RCA loading compared to a VES release coating system with this particular rubber adhesive based test tape.

Release Force vs % Loading of Emulsion RCA in a Multifunctional silicone polymer
Accelerated Aging 24 hr @ 50-70°F, 12 ipm Peel Speed, TESA 4651

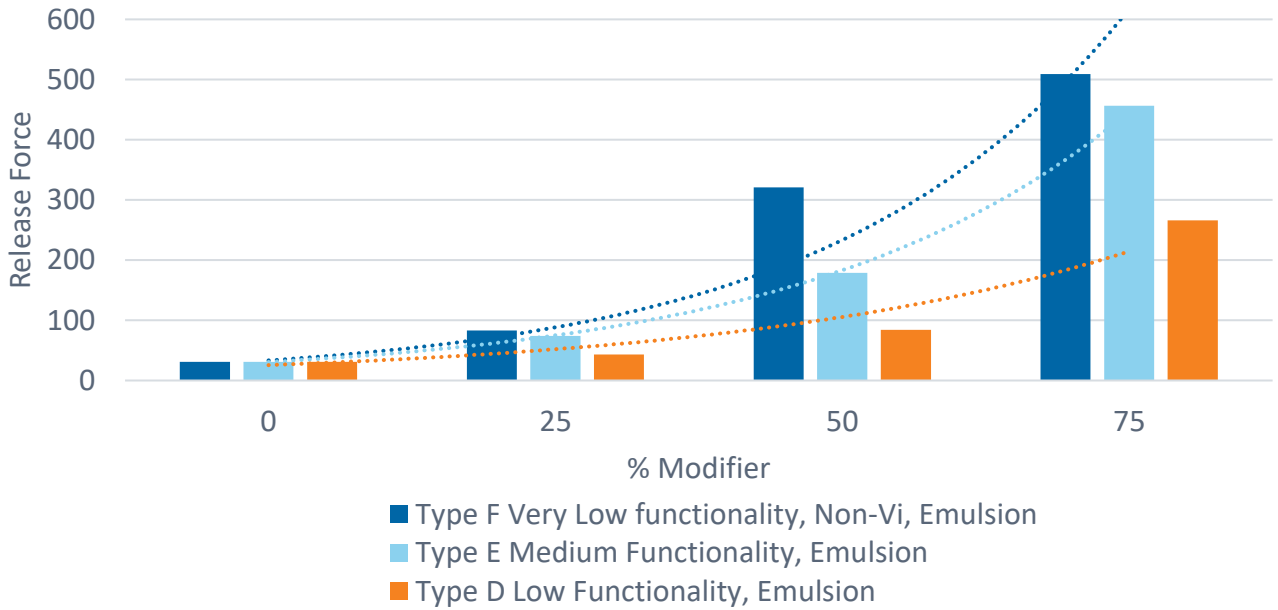
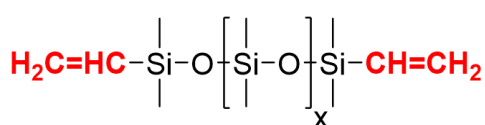
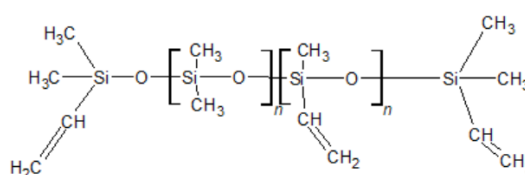


Figure 8. Evaluation of various emulsion RCA modifiers with an emulsion multifunctional silicone polymer, formulated at 1.7 SiH:Vi ratio for Type F and Type E, and 2.0 SiH:Vi ratio for Type D. Type F and Type E were aged at 50°F while Type D was aged at 70°F. Simulation of room temperature aging to ~1 month through accelerated aging at 50/70°C shows a much stronger response between the adhesive tape and the RCA/silicone blend even at this low pull speed. The interaction between this particular rubber based test tape and the medium reactive RCA modifiers and non-vinyl RCA modifiers has the strongest effect. The interactions at the highest loadings show the strongest response, but may start to exceed the paper strength. The aggressiveness of the adhesive, the adhesive thickness, and a high RCA loading may lead to lock up with aging, so proper release coating selection is critical.

The evaluation of these release control additives also included looking at the impact of short versus long chain linear silicone polymers, sometimes called Vinyl End Blocked (VEB) or Vinyl End Stopped (VES) (depending on the researcher), and the impact of a ramped release speed analysis. VEB silicone polymers only have reactive vinyl groups at the end, or terminal position, of the silicone chain. Included in this study were multifunctional (MF) polymers, which are silicone polymers with reactive vinyl groups at the end of the chain, as well as on the side of the chain. This evaluation is intended to provide an understanding of the impacts of polymer chain length and functionality while utilizing one low functionality resin, RCA Type A.

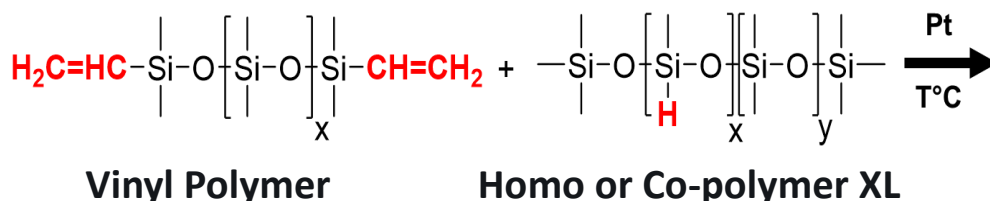


VEB Vinyl Polymer



Multifunctional Vinyl Polymer

Figure 9. Chemical structure comparisons of a vinyl end blocked silicone polymer and a multifunctional vinyl silicone polymer.



Vinyl Polymer

Homo or Co-polymer XL

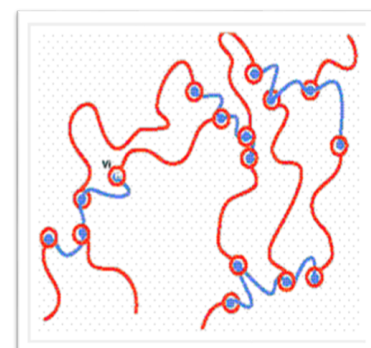


Figure 10. The platinum addition cure mechanism showing the vinyl groups reacting with the hydride groups of the crosslinker, in the presence of a platinum catalyst and heat, to form a 3-dimensional crosslinked network. The release control additives can tie into this network, depending on the structure and functionality.

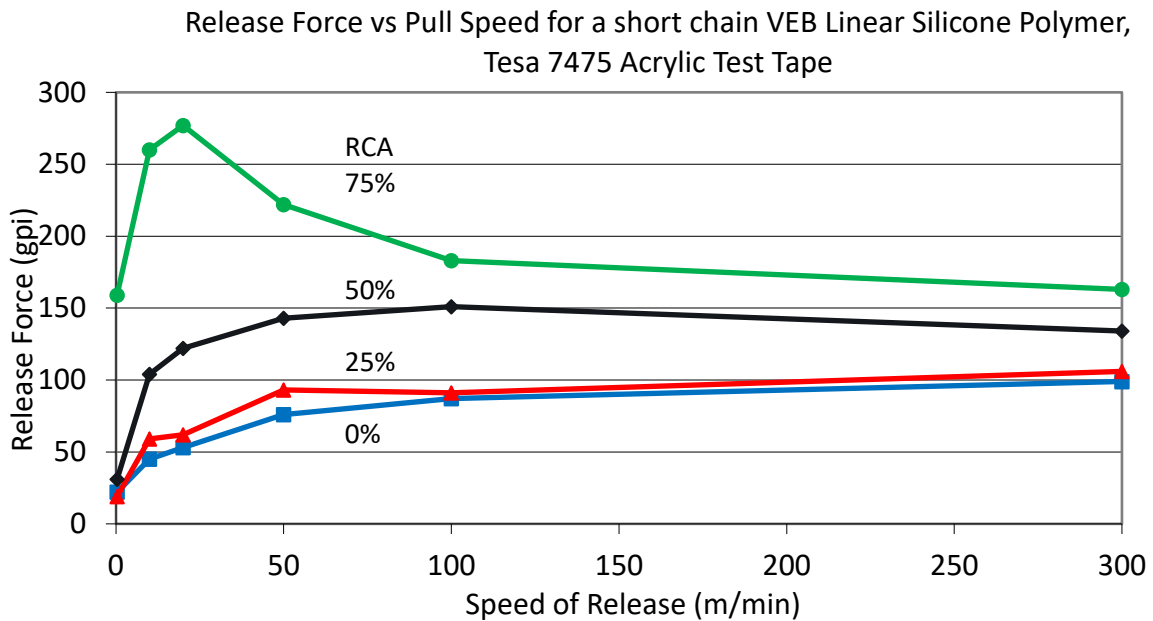


Figure 11. Effects of a Vinyl reactive RCA Type A upon a short linear polymer with a copolymer crosslinker over a range of speeds. This combination exhibits a high crosslink density due to the short chain effects, and exhibits a high impact on low pull speeds at high loadings of RCA, but as the speed increases, the impact may be reduced for the higher RCA loadings.

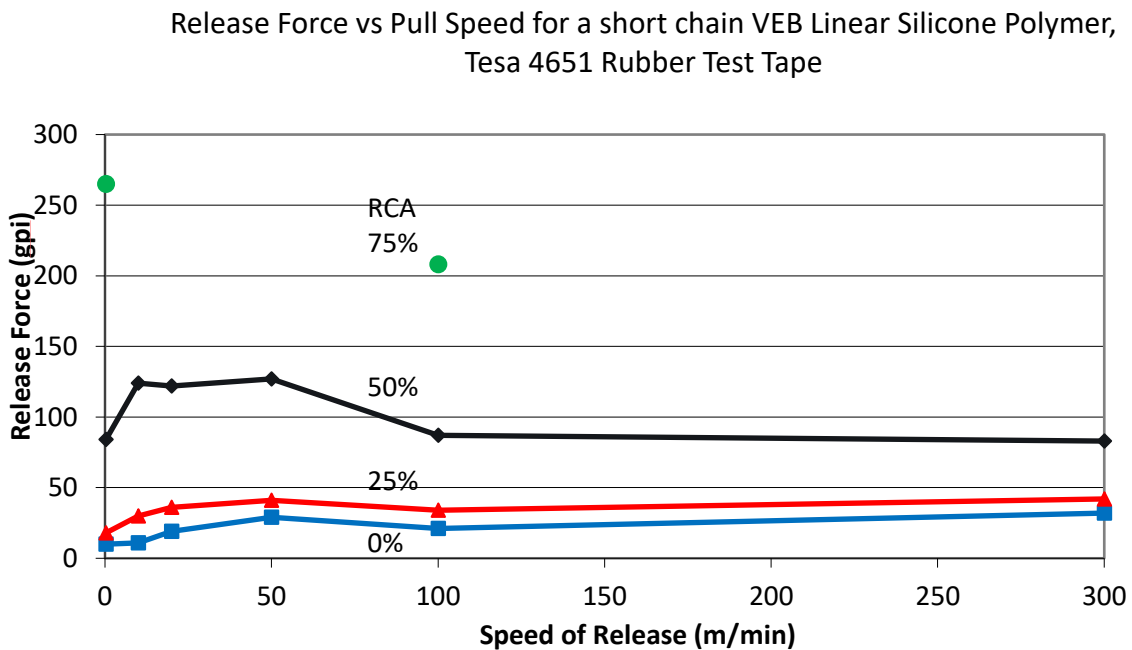


Figure 12. Effects of a Vinyl reactive RCA Type A upon a short linear polymer chain system over a range of speeds. This combination exhibits a high crosslink density due to the short chain effects, and exhibits a high impact on low pull speeds at high loadings of RCA, but as the speed increases, the impact may be reduced for the higher RCA loadings.

Release Force vs Pull Speed for a longer chain VEB Linear Silicone Polymer
Tesa 7475 Acrylic Test Tape

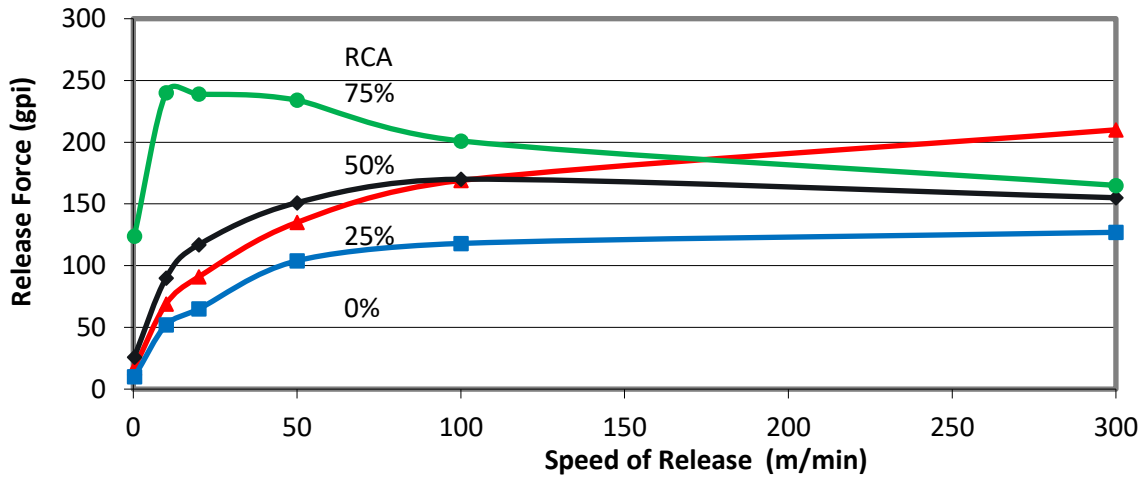


Figure 13. Effects of a Vinyl reactive RCA Type A upon a longer linear polymer chain system over a range of speeds. The elongation of the silicone chain due to the less crosslinked nature of the release coating, combined with the adhesive/RCA interactions at the surface give a higher response at both low and high pull speeds.

Release Force vs Pull Speed for a longer chain VEB Linear Silicone Polymer,
Tesa 4651 Rubber Test Tape

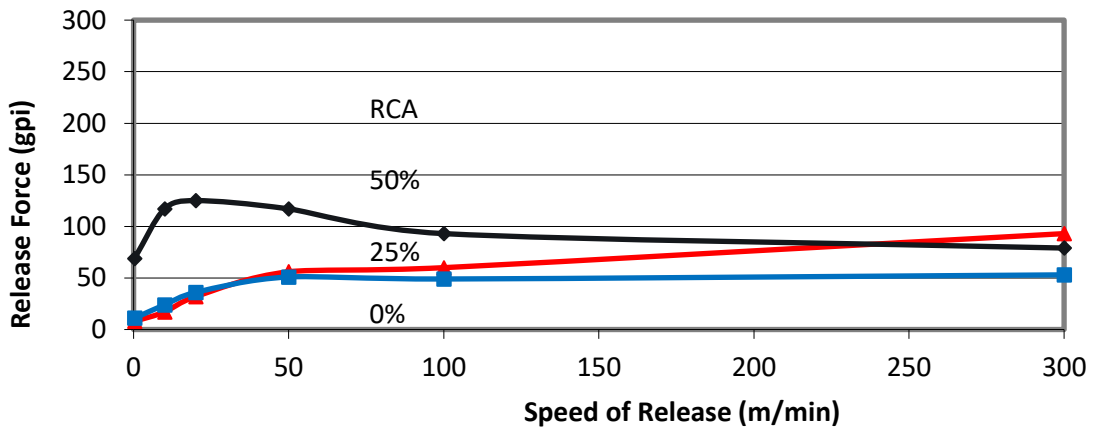


Figure 14. Effects of a Vinyl reactive RCA Type A upon a longer linear polymer chain system over a range of speeds. The change in adhesive type can have a large impact on the interactions between the adhesive and the RCA on the surface, combined with the crosslink density and flexibility of the silicone layer itself.

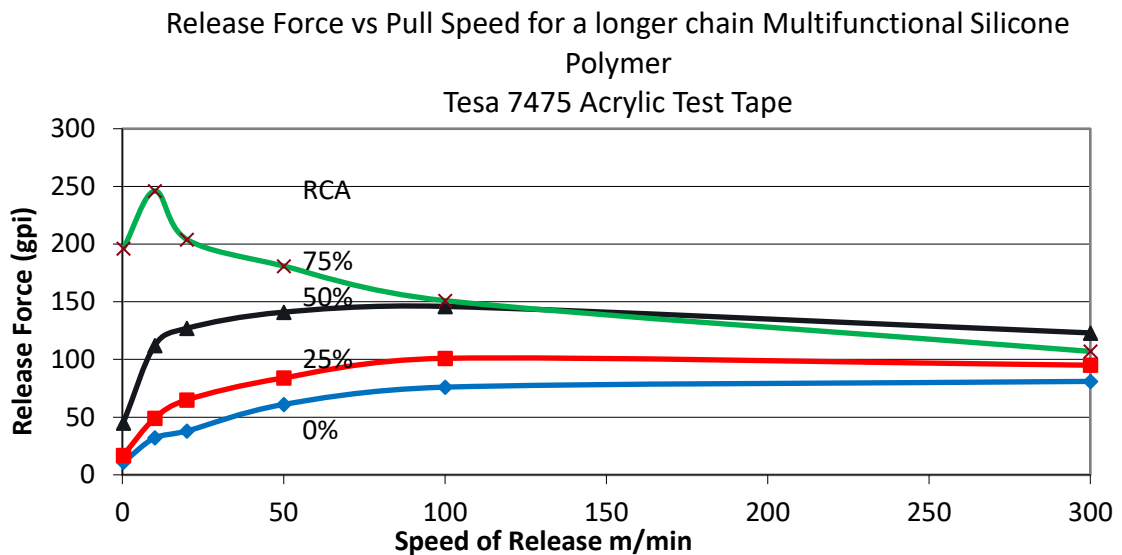


Figure 15. Effects of a Vinyl reactive RCA Type A upon a long multifunctional polymer chain system over a range of speeds versus the TESA 7475 Acrylic test tape. This again demonstrates that the combination of adhesive type, silicone type, and RCA tape all need to be considered for an application as a function of pull speed.

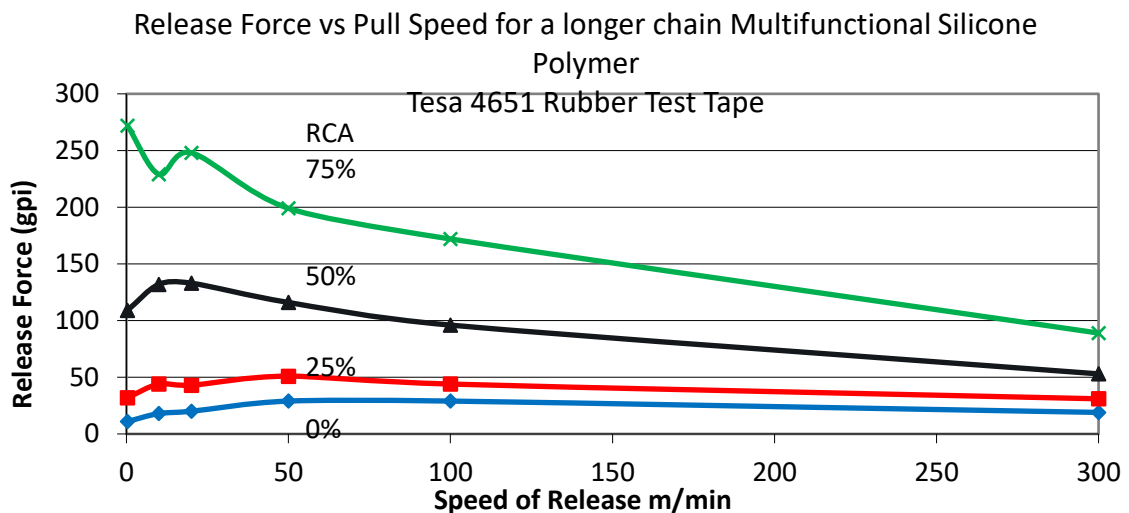


Figure 16. Effects of a Vinyl reactive RCA upon a long multifunctional polymer chain system over a range of speeds versus the TESA 4651 Rubber based test tape.

Conclusion

As seen in the previous graphs, the interaction between the polymer chain length and chemistry can have an impact at different RCA loadings, as well as with different adhesive systems, in contact with the silicone surface. The evaluation of each system will be uniquely tailored to each application.

Silicone Release Control Additives can play a critical role in the application in order to target a given release value. In some cases, they can be substituted by evaluating the efficacy and efficiency between the available RCA options, but may require slightly more or slightly less to achieve the same desired release force.

Creating a differential for double sided tape products or a tight release label application, where a differential of 2-4x is desirable to avoid release liner confusion, can be done in a multitude of different ways. Direct casting the adhesive onto a silicone coating versus laminating an adhesive coating that is already cured onto a pre-siliconized liner will have an impact as well. Understanding the interactions is important in order to control these interactions and materials choices.