Thermally Resistant Methyl-PSA

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1.0 Abstract

Silicones, or polysiloxanes, are polymers with the chemical formula [R2SiO]n, where R may commonly be an organic group such as methyl, phenyl, alkenyl, or hydrogen. Since their inception in the early 1940s, silicones have quickly found a variety of applications due to their unique balance of properties arising from their structure. Silicone pressure sensitive adhesives utilize some of these distinctive characteristics in the development of high temperature tapes.

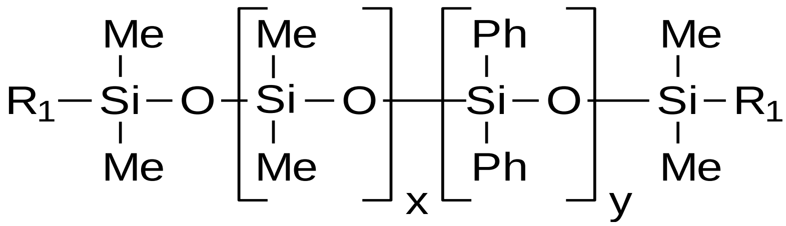
Solvent-based silicone pressure sensitive adhesives cover a significant market volume in applications related to masking and insulation in the electronics, electric and automotive industry. More recently, application demands require special PSAs having high temperature resistance, residue-free removal and excellent high temperature lap shear. Although certain phenyl-based PSAs are able to meet these requirements, their performance to cost balance drives many customers to request similar properties from methyl-based PSAs. In an attempt to address this demand, we embarked on a program to develop a new methyl-based PSA, having excellent high temperature resistance, with a suitable balance of peel & tack performance.

Several technical approaches have been tried in order to achieve this goal, leading to the introduction of a methyl-based, BPO-curable silicone PSA. The material shows good high temperature resistance, with some characteristics such as high temperature lap shear exceeding those of current phenyl based silicone PSAs.

2.0 Introduction

Silicone polymers enjoy some distinct advantages in the pressure sensitive adhesive (PSA) industry. Their advantages include stable performance over a wide temperature range, solvent and chemical resistance as well as ability to adhere to very low surface energy substrates (e.g., fluoropolymers, polyolefins, silicone release coatings).

The chemical make-up of the silicone pressure sensitive adhesive is very mature. The two main components are a high molecular weight methyl or phenyl silicone gum which is physically blended in a solvent (e.g., Toluene, Xylene or the mixture) with a special molecular weight, highly branched silicone resin. For typical BPO-curable silicone PSA, the two components are chemically reacted together through a condensation reaction and supplied in solution to a customer at high solids concentration. Before coating, it is typical to dilute for easy of coating and add a peroxide to the blend and crosslink it at a high temperature after a drying phase for complete cure. Figure 1 shows the high molecular weight methyl or phenyl silicone gum.



R1=OH, vinyl…

Figure 1. Typical Structure of a silicone gum

The silicone resin used in silicone PSAs is normally called an MQ resin. MQ resins are relatively low molecular weight and high Tg silicate resins made from a combination of Q units, SiO_2, and M units, $SiO_{0.5}(CH_3)_3$, as shown in Figure 2.

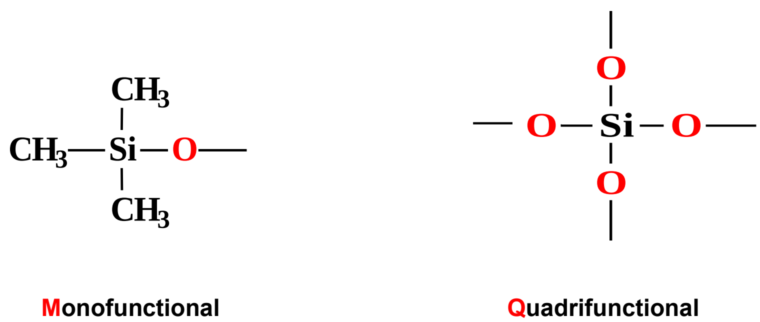


Figure 2. Typical Structure of M unit & Q unit

Typically, the ratio of M/Q units is controlled between 0.7 and 1.2. The MQ resin normally contains residual silanol groups and may contain other functional groups, such as vinyl groups, allowing it to react with the silicone network. The addition of MQ resins to silicones increases the Tg and decreases the plateau modulus of the blend, thereby changing tack and adhesion of a silicone PSA. The MQ resin is a key factor impacting silicone PSA high temperature performance. MQ resin characteristics affect resin viscosity, which in turn depends on several parameters impacting the resin's application performance: molecular weight, molecular structure, and silanol content. The amount of resin, expressed as % solids, is another PSA performance modifier. Figure 3 shows the typical structure of a MQ resin.

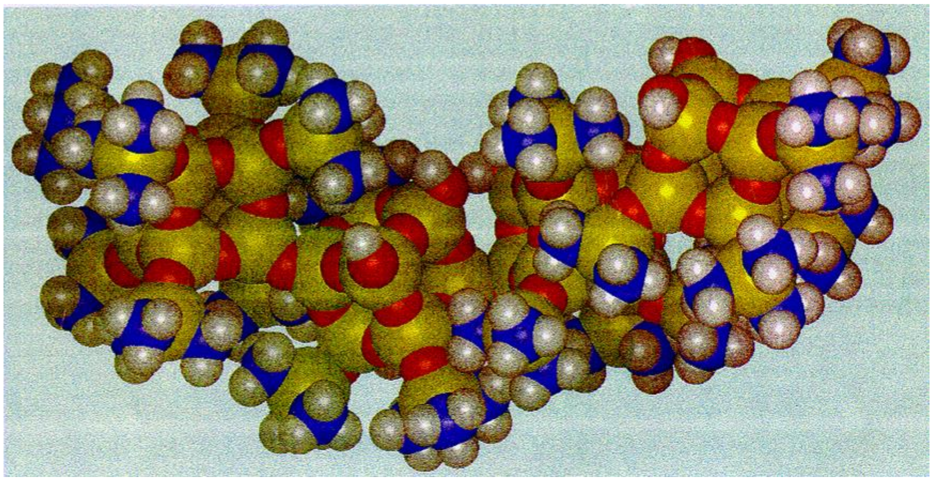


Figure 3. Typical Structure of MQ resin

Silicone Gum and MQ resin are the main components of Silicone PSAs. An important step of the PSA production process is the condensation enabled by silanol functionality, normally catalyzed by a base or an acid. The condensation proceeds rapidly at the solvent reflux temperature, while the H_2O by-product is separated by azeotrope distillation. As the condensation proceeds, the reaction mixture becomes clear. Figure 4 depicts the chemistry of the condensation process. Several factors influence the condensation process and the product obtained: 1) catalyst level. 2) Silanol content, differentiated as active silanol % and inactive silanol %. 3) R/G ratio (the ratio of MQ resin to silicone gum). 4) reflux temperature, which is also the condensation reaction temperature. 5) reaction time.

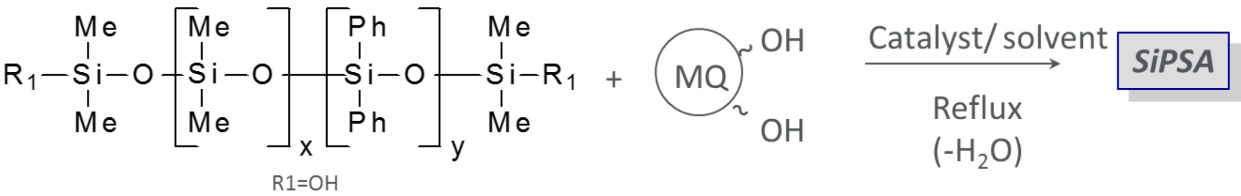


Figure 4. Chemistry of the PSA condensation process

Selecting suitable silicone gums and MQ resins is an important step in the development of a PSA tailored to particular applications. Ideally one seeks to obtain a suitable balance among several PSA performance factors, such as peel strength, tack, cohesion strength, lap shear, thermal residue. The development process often follows custom or proprietary methodology. One of the critical factors affecting performance is the R/G ratio. Figure 5 shows the relationship between R/G ratio and the silicone PSA performance.

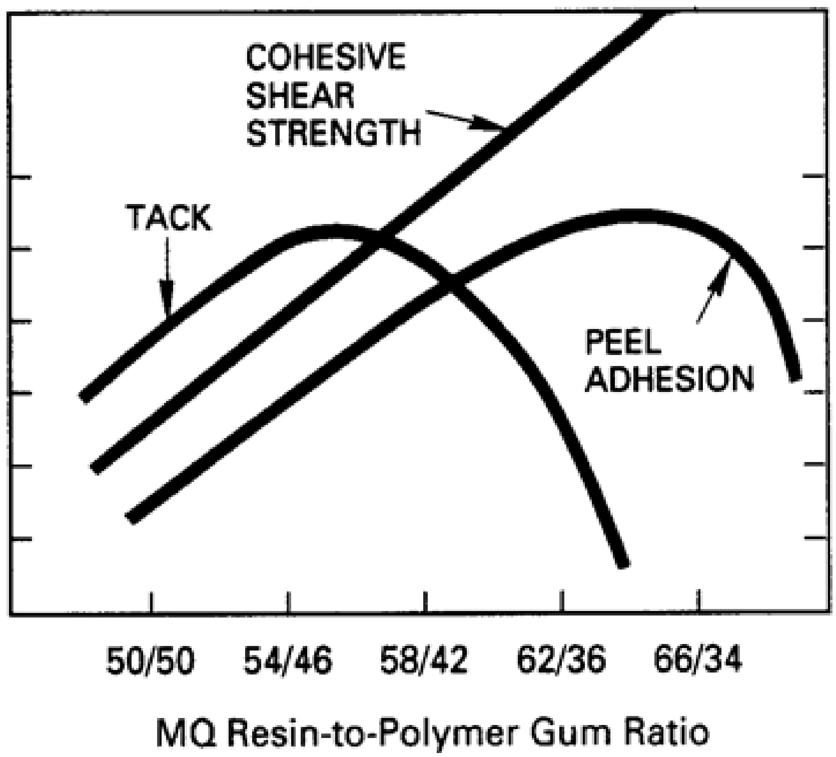


Figure 5. The relationship between R/G ratio and silicone PSA performance

At the end of the condensation reaction the PSA usually has good cohesion strength. The tape manufacturer coats the PSA on the desired substrate for a high temperature Si-Tape, requiring premium high temperature resistance and clean removability. In a subsequent curing process the customer blends a peroxide, such as BPO (Benzoyl peroxide) into the PSA in order to increase the cohesion, anchorage, and heat resistance further. The peroxide initiates the crosslinking reaction connecting different polymer chains into a network. The higher the peroxide amount, the higher the crosslinking density of the resulting PSA. In general applications, 1.0~3.0% solid/solid (BPO/PSA) satisfies final tape application requirements. In applications requiring low temperature cure, 2,4 –dichlorobenzoyl peroxide activated at 132℃ (270°F) may be used. However, 2,4-dichlorobenzoyl peroxide may generate polychlorinated biphenyls during the curing process, prohibited by certain industry regulations. In order to achieve optimum adhesive properties, it is essential to optimize the drying step of the process so as to ensure solvent removal from the adhesive film before initiating cure. Figure 6 shows the Chemistry of peroxide-initiated PSA cure.

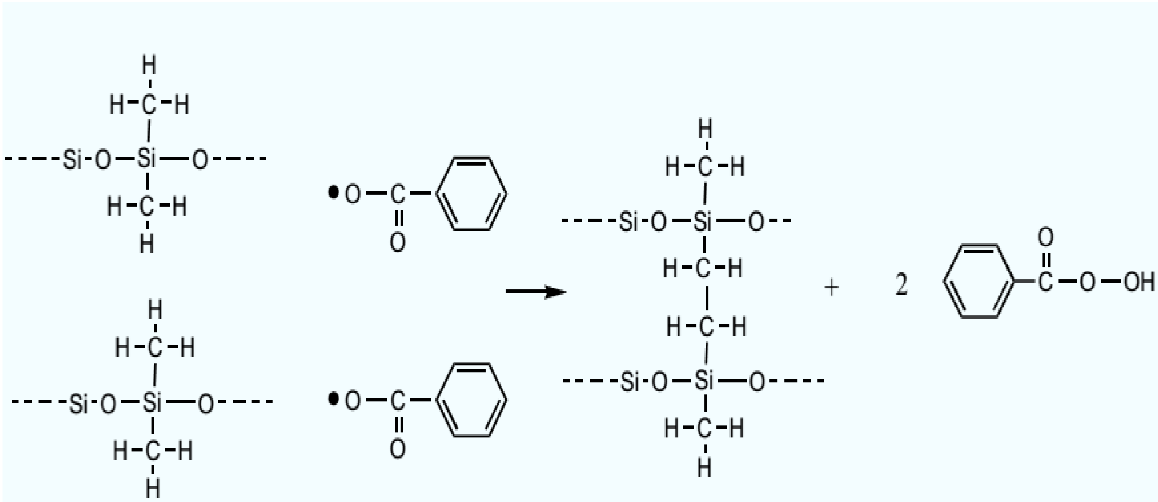


Figure 6. The chemistry of PSA curing via peroxide process

3.0 Thermally Resistance Evaluation Methods for Silicone PSA

Commercially available silicone PSA can be divided into two types based on the different silicone gums used: methyl silicone PSA and phenyl silicone PSA. Methyl silicone PSA utilizes polydimethylsiloxane polymer; phenyl silicone PSA employs polydimethyldiphenylsiloxane co-polymer as the gum, both of them contain silanol at the polymer chain ends. Both gums have silanol-terminated polymer chains. Phenyl silicone PSA have better high temperature resistance performance than methyl silicone PSA due to the silanol in methyl silicone PSA promoting a cyclization reaction under high temperature, which causes polymer degradation thus reducing the high temperature performance. By comparison, when phenyl functional groups are introduced into the silicone PSA system, silanol end functionality may cleave the Si-Ph bond, yielding benzene and a branching point. This in turn may restrain the cyclization reaction, finally controlling the polymer degradation and imparting better high temperature performance. While phenyl silicone PSA have better high temperature resistance than methyl silicone PSA, the high cost of polydimethyldiphenylsiloxane co-polymer cascades into a higher price for the final Ph-PSA. The development of a methyl-based PSA of similar performance offers the customer an application-competitive product at a better price.

High temperature lap shear and thermal residual performance ranked highest in importance among the factors evaluated in a customer survey. The customers also desired normal peel strength and tack values typical of traditional methyl-PSAs. Addressing these requirements, we developed a new thermally resistant methyl-PSA by selecting and developing new silicone gums and MQ resin materials as well as optimizing the catalyst and process conditions. The new methyl PSA uses toluene as the preferred solvent. The next section provides details regarding the test methods and actual performance.

3.1 High Temperature Lap Shear Test

Sample preparation: Arrange the needed amount of 2” x 2” Stainless Steel Panels. Cut a three (3) inch X one (1) inch tape from a sheet previously coated with pressure sensitive adhesive (PSA). Apply the cut tape for a 1” x 1” overlap onto the Stainless Steel Panel. Using a 4.5 pounds roller, roll over the tape area over and back one time. Wait 20 minutes after applying the tape to the steel panel. This is referred to as Dwell Time.

Testing Procedure: Set the oven temperature to a high temperature, such as 300 ˚C prior to sample preparation. After the temperature reaches 300C, attach the bottom 1” x 1” of the tape to the desired weight (1000 grams). Hang each sample in the oven (ensure protective wear is used for safety due to the high temperature). Record the time required for weight to drop.

3.2 SAFT (Shear Adhesion Failure Temperature) Test

Sample preparation: Arrange the needed amount of 2” x 2” Stainless Steel Panels. Cut a three (3) inch x one (1) inch tape from a sheet previously coated with pressure sensitive adhesive (PSA). Apply the cut tape for a 1” x 1” overlap onto the Stainless Steel Panel. Using a 4.5pounds roller, roll over the tape area over and back one time. Wait 20 minutes after applying the tape to the steel panel. This is referred to as Dwell Time.

Testing Procedure: Set the maximum temperature to 400 ˚C and program for increasing temperature at 2.2 ˚C per minute after a 1minute initial room temperature delay. Attach the bottom 1” x 1” of the tape to the desired weight (1000 grams). Hang duplicate samples for each tape in the oven at room temperature then start test Program. Record the temperature when the weight drops.

3.3 Thermal Residual Test

Sample preparation: Arrange the needed amount of 2” x 6” Stainless Steel Panels. Cut a three (3) inch x one (1) inch tape from a sheet previously coated with pressure sensitive adhesive (PSA). Apply the tape to the 1” x 6” Stainless Steel Panel. Using a 4.5pounds roller, roll over the tape area applied to the stainless steel panel, over and back one time. Wait 20 minutes after applying the tape to the steel panel. This is referred to as Dwell Time.

Testing Procedure: Set the oven target temperature (such as 260 ˚C). Place the panels with tape into the oven for 30mins. Remove panels and peel a portion of the tape immediately while at high temperature for hot peel. Check for adhesive residual on the panel surface. Allow these samples to cool to room temperature, then peel for a cool peel result. Also check for adhesive residual on the cool peel portion of the panel surface

4.0 Thermal Resistance of the New Methyl-PSA

Solvent-based silicone pressure sensitive adhesive covers a significant market volume in applications related to masking and insulation in the electronics, electric and automotive industry. Most of the applications need a good thermal residual and high temperature lap shear performance. Three silicone PSAs were evaluated in this study. All of them are dimethyl silicone

PSAs and peroxide cured. One is the new thermally resistant methyl silicone PSA we developed, the other two are traditional methyl silicone PSA which are popular in the industry.

For comparable testing all three methyl silicone PSAs used the same BPO ratio based on solids. The samples were formulated by adding a toluene solution of BPO in an amount to yield 2 wt% per silicone solids. All of the formulations were diluted with toluene to 40% as the final solids.

The PSA samples were coated on 25um polyimide (PI) film, the PI film was treated by methyl based silicone primer before adhesive coating. The target dry adhesive thickness is 40um, after drying and curing, the adhesive surface was covered with 50um fluorine polyethylene terephthalate (PET) liner as the final tape product.

4.1 High Temperature Lap Shear Test

Figure 1 shows the high temperature lap shear results for the three different methyl-PSAs at a fixed temperature of 300℃ prior to samples being placed in oven. The results show the new methyl PSA has much better high temperature lap shear performance than other two traditional methyl PSAs, the new methyl PSA can hold more than 6 hours without slipping while traditional methyl PSA 1 dropped at 18 minutes and methyl PSA 2 dropped at 30 minutes. Both of their failure mode were cohesion failure. Figure 7 shows the difference.

300°C Lap Shear Test	Traditional Methyl-PSA 1	Traditional Methyl-PSA 2	New Methyl-PSA
Time (hrs)	0.3	0.5	6

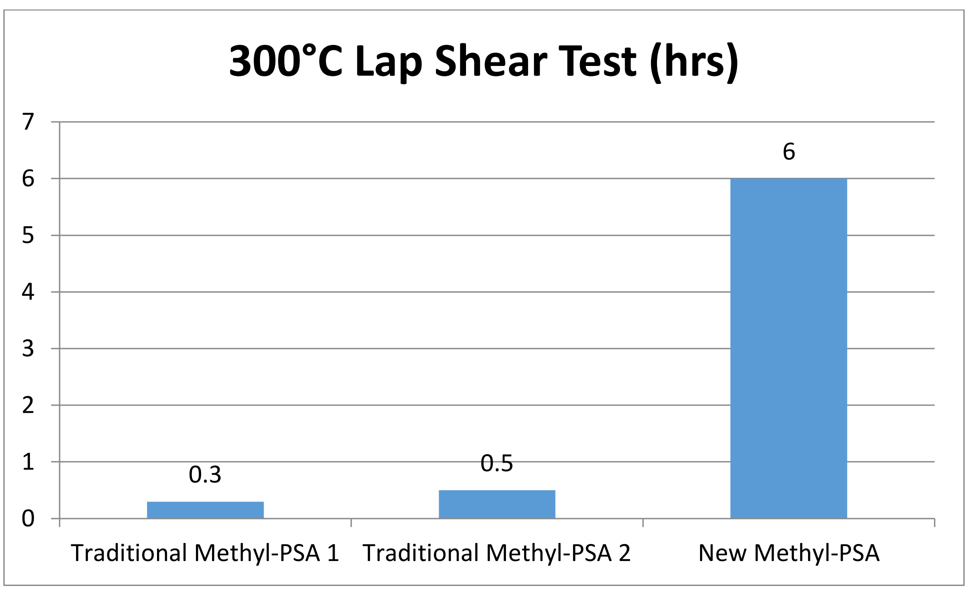


Figure 7. 300°C Lap shear test result

4.2 SAFT (Shear Adhesion Failure Temperature) Test

Compared with High temperature lap shear test, SAFT test shows the three different methyl-PSAs shear and cohesion performance under different temperatures based on a given temperature ramp rate of 2.2 ˚C per minute, so the test results are the final temperature when the test tapes dropped from the SS panels. The SAFT test result also shows the new methyl PSA has much better high temperature resistance performance than other two traditional methyl PSAs. Figure 8 shows the detail test result.

SAFT Test	Traditional Methyl-PSA 1	Traditional Methyl-PSA 2	New Methyl-PSA
Temperature (°C)	299	314	365

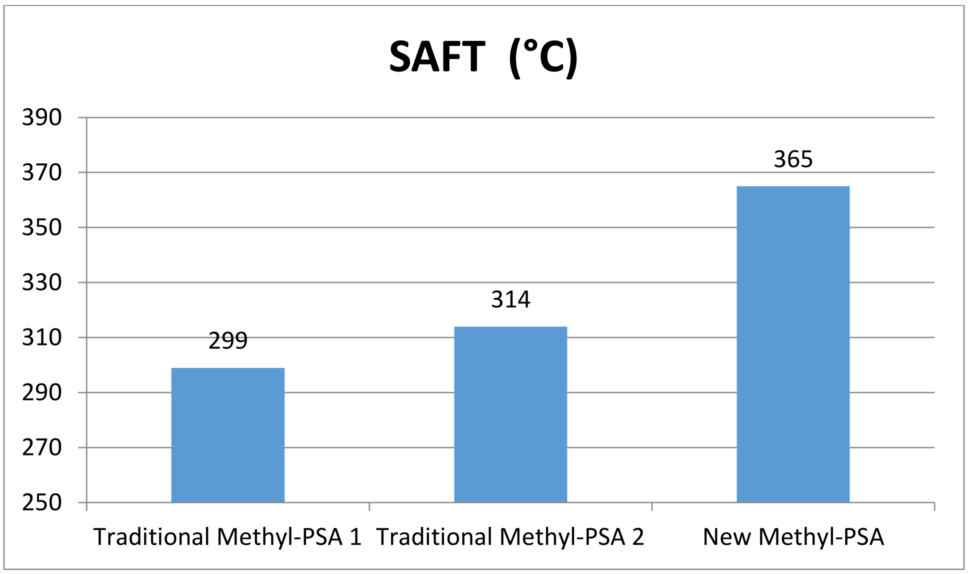


Figure 8. SAFT test result

4.3 Thermal residual performance

The thermal residual test conditions were 240 ˚C/30mins, 250 ˚C/30mins, 260 ˚C/30mins, 270 ˚C/30mins and 280 ˚C/30mins. This test protocol determines adhesive residual on the SS panel after high temperature aging and is based on customers' actual application. The test can be divided into two parts: hot peel and cool peel. Normally hot peel is much stricter than cool peel regardless of aging temperature. From the test result it can be seen that the new methyl PSA's thermal residual performance is very stable, only showing a slight adhesive residual only at 280 ˚C by hot peel. Traditional methyl PSA 1 shows adhesive residual at 240 ˚C by hot peel and 250 ˚C by cool peel. Traditional methyl PSA 2 shows adhesive residual at 270 ˚C by both hot peel and cool peel. Figure 9 shows the detailed results and appearance.

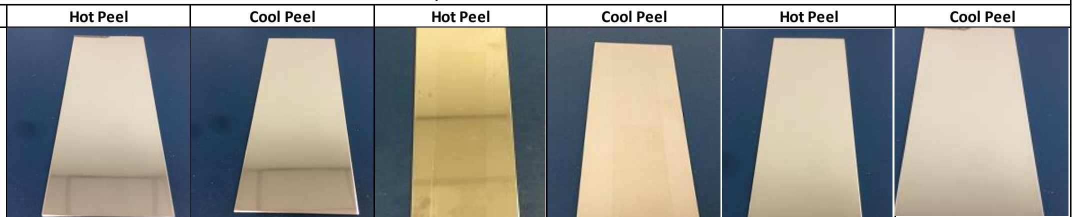
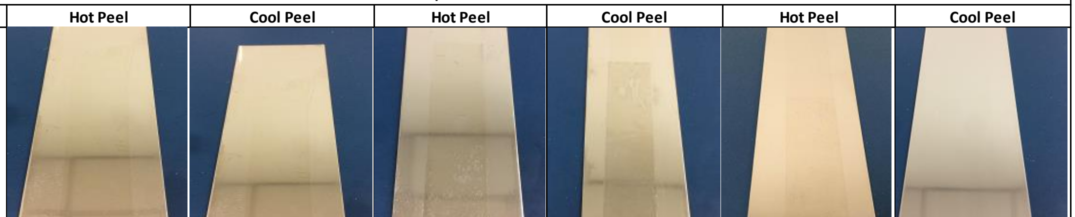
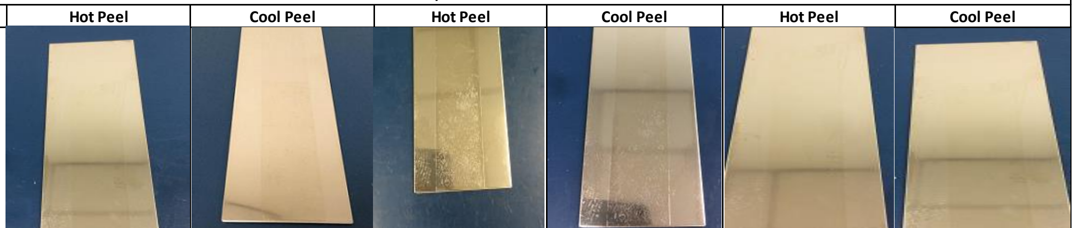
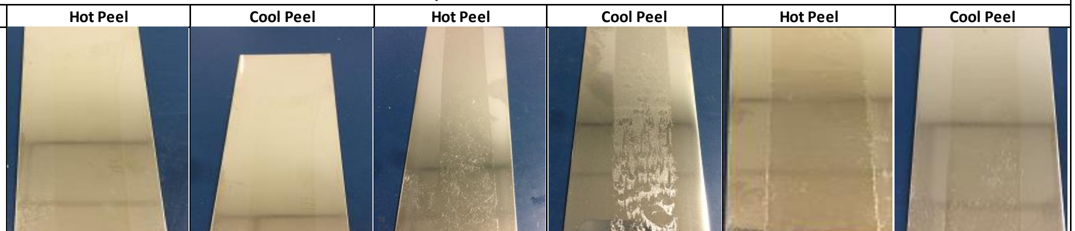
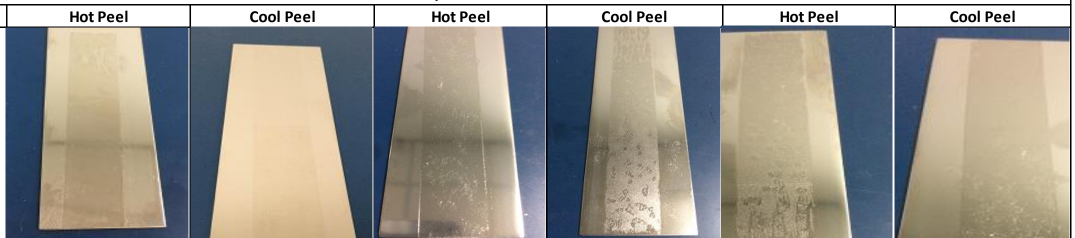
Thermal Residual Test						
Adhesive	New Methyl-PSA		Traditional Methyl-PSA 1		Traditional Methyl-PSA 2	
Substrate	PI film (25um)		PI film (25um)		PI film (25um)	
Adhesive thickness (dry)	40um		40um		40um	
BPO (Dry:Dry)	2%		2%		2%	
240C/30mins						
Test Items	Hot Peel	Cool Peel	Hot Peel	Cool Peel	Hot Peel	Cool Peel
Appearance						
Performance	No Residual	No Residual	Slight Residual	No Residual	No Residual	No Residual
250C/30mins						
Test Items	Hot Peel	Cool Peel	Hot Peel	Cool Peel	Hot Peel	Cool Peel
Appearance						
Performance	No Residual	No Residual	Medium Residual	Slight Residual	No Residual	No Residual
260C/30mins						
	Hot Peel	Cool Peel	Hot Peel	Cool Peel	Hot Peel	Cool Peel
Appearance						
Performance	No Residual	No Residual	Serious Residual	Medium Residual	No Residual	No Residual
270C/30mins						
	Hot Peel	Cool Peel	Hot Peel	Cool Peel	Hot Peel	Cool Peel
Appearance						
Performance	No Residual	No Residual	Serious Residual	Serious Residual	Medium Residual	Slight Residual
280C/30mins						
	Hot Peel	Cool Peel	Hot Peel	Cool Peel	Hot Peel	Cool Peel
Appearance						
Performance	Slight Residual	No Residual	Serious Residual	Serious Residual	Serious Residual	Medium Residual

Figure 9. Thermal residual test result

4.4 Peel strength on SS panel

Based on High Temperature Lap Shear, SAFT and Thermal residual tests, the new thermally resistant methyl-PSA shows significantly improved high temperature performance compared to two traditional methyl-PSAs. Additional important factors for a silicone PSA are peel strength and tack on final product performance at the customer.

For comparable testing, all of the three methyl silicone PSAs used the same BPO ratio 2wt% based on solids diluted with toluene to 40% as the final solids. The PSA samples were coated on 50um Polyethylene terephthalate (PET) film without surface treatment. The target dry adhesive thickness is 40um after drying and curing were laminated with 50um fluorine PET liner as the final tape product. Tapes are cut and removed from the liner then applied onto standard Stainless Steel (SS) panel. After a 20 minutes dwell time the 180˚ peel strength at a peel speed of 12inch/minute was determined.

The results confirmed the new thermally resistant methyl silicone PSA has similar peel strength performance as the two traditional methyl PSAs as shown in Figure 10.

Product Name	**Traditional Methyl-PSA 1**	**Traditional Methyl-PSA 2**	**New Methyl-PSA**
Peel from SS Panel(g/inch)	1140	1075	1125

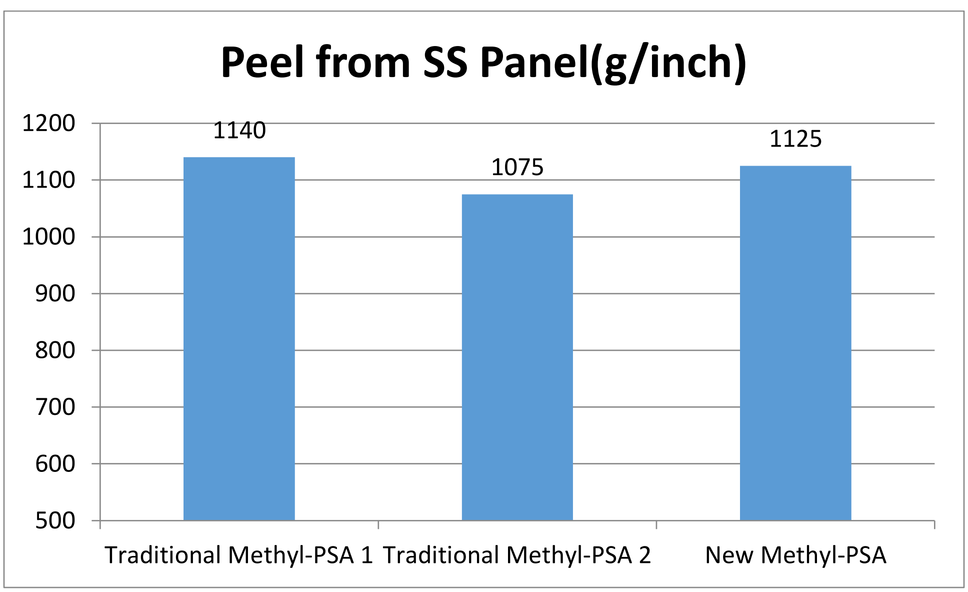


Figure 10. Peel strength test result

4.5 Probe tack test

Prepared PET tape samples used for peel strength were tested for probe tack by a Lab Master Probe Tack Tester. The tester brings together the rough tip of the probe (0.5 cm diameter) and the adhesive layer of the tape for 0.5 seconds. It then pulls them apart at the rate of 0.5 cm/second and measures the force required for separation. The weight atop of a test specimen corresponded to 1000 gram per cm^2 contact force.

From the test results we also confirm that the new thermally resistant methyl PSA has similar probe tack values as the two traditional methyl PSAs. This confirmed that the final composition determined for increased high temperature performance did not impact the new thermally resistant methyl silicone PSA's tack performance as shown in Figure 11.

Product Name	**Traditional Methyl-PSA 1**	**Traditional Methyl-PSA 2**	**New Methyl-PSA**
Probe Tack(g/cm^2)	515	520	510

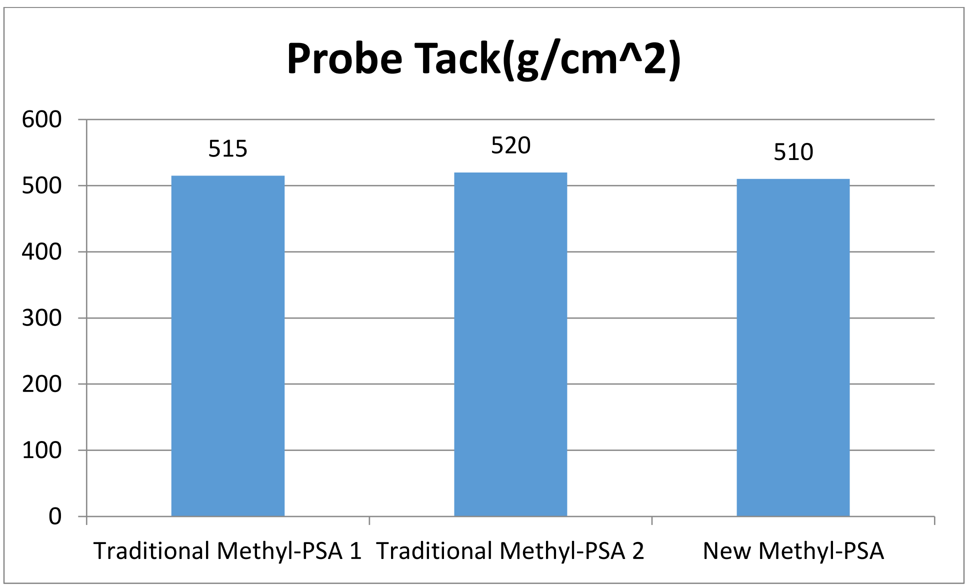


Figure 11. Probe tack test result

4.6 Thermal Gravimetric Analysis (TGA) test

For new thermally resistant methyl silicone PSAs, thermal gravimetric analysis may show polymer stability from room temperature to high temperature. The new thermally resistant methyl silicone PSA was characterized by Thermal Gravimetric Analysis (TGA) under a high purity air environment. A Q5000 TGA from TA Instruments Inc. was used. The gas purge rate was set at 10 ml/min and the sample purge rate at 25 ml/min. A ramp rate of 20 ˚C /min to 800 ˚C was used. The table below gives the weight retention at three temperature points, showing a remaining weight at 800 ˚C of 59.91%. Figure 12 shows the detailed TGA curve and test result.

Temp	Weight
T 400˚C	92.637%
T 450˚C	85.085%
T 800˚C	59.910%

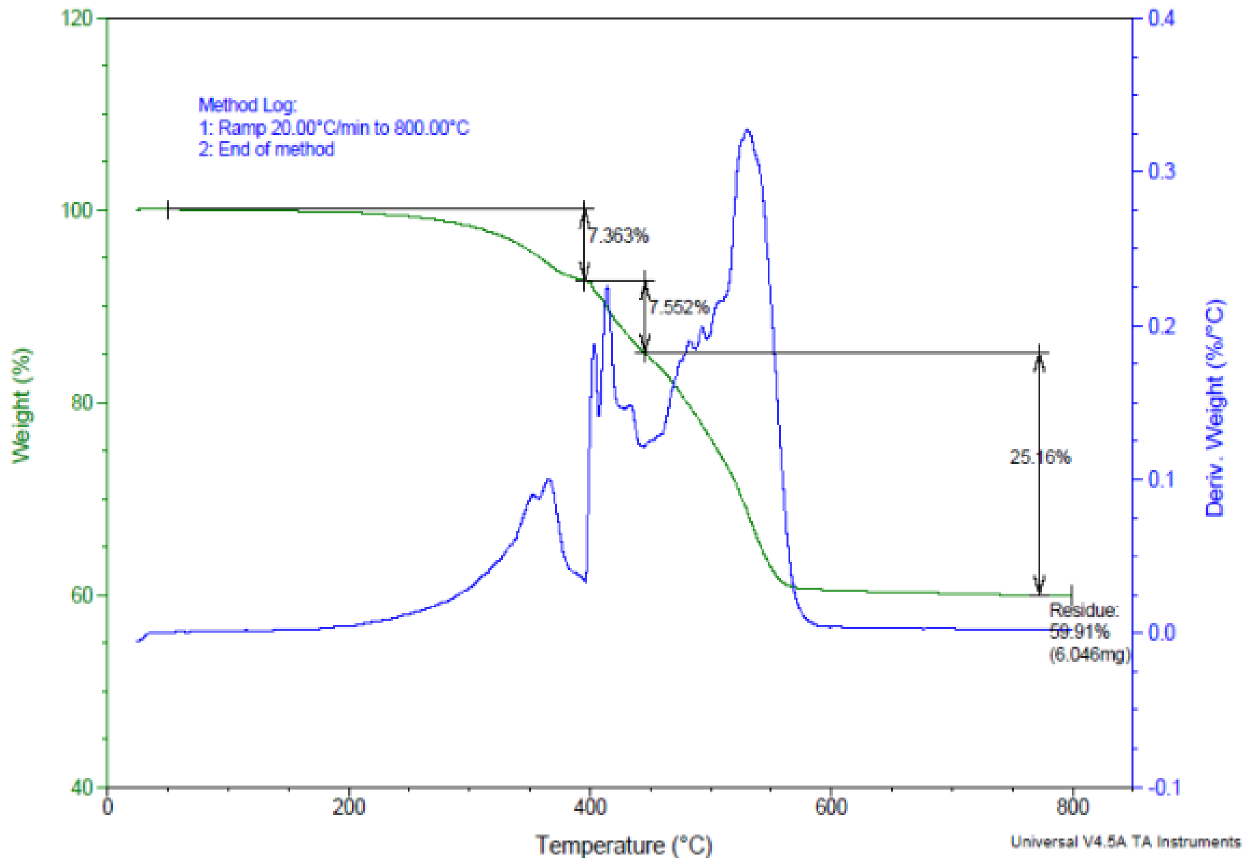


Figure 12. TGA curve of new methyl-PSA

5.0 Conclusion

We have developed a new solvent based thermally resistant methyl silicone PSA by synthesizing new raw materials and optimizing the formulation and process. Compared with traditional methyl PSAs, the new PSA has better high temperature performance such as high temperature lap shear, SAFT and thermal residual results while retaining peel strength and tack values similar to those of traditional silicone PSAs. This new thermally resistant methyl silicone PSA offers customers new options in actual applications related to masking and insulation in the electronics, electric and automotive industry.

6.0 Acknowledgments

The author would like to acknowledge Tiberiu Siclovan, Jos Delis, Roy Griswold and Mark Fraser for their help and suggestion.