

COMPARISON OF QUANTITATIVE HIGH TEMPERATURE TESTING METHODS FOR SILICONE PRESSURE SENSITIVE ADHESIVES

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1.0 Abstract

Silicone Pressure Sensitive Adhesives provide high temperature resistance. A comparison will be provided of unique high temperature testing methods, including high temperature peel and thermal gradient hot plate. Silicone PSAs were evaluated using an Instron equipped with environmental chamber to test in situ high temperature peel. The thermal gradient hot plate provides a linear temperature profile, which allows for a wide range of temperatures to be studied with one sample and one test. Silicone PSAs were evaluated over the selected temperature gradient to compare their performance.

2.0 Introduction

The composition of a silicone pressure sensitive adhesive (PSA) is based on a polymer filled system. The two main components that dictate the performance of the silicone PSA are a high molecular weight, linear siloxane polymer and a highly condensed, silicate tackifying resin (MQ resin). Figure 1 shows the structure of a typical silicone polymer. Commercially available silicone PSAs utilize either a polydimethylsiloxane polymer or polydimethyldiphenylsiloxane co-polymer that may contain silanol or vinyl functionality at the polymer chain ends.

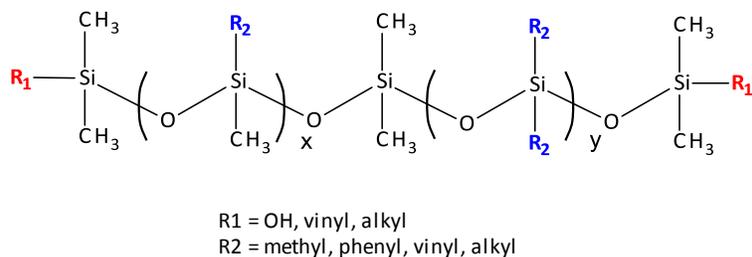


Figure 1. General chemical structure of a silicone polymer.

The silicate resin, often referred to as a MQ resin, is a solid particle supplied in a hydrocarbon solvent. The MQ name derives from the fact that its structure consists of a core of three-dimensional Q-units ($\text{SiO}_{4/2}$) surrounded by a shell of M-units ($\text{Me}_3\text{SiO}_{1/2}$). The resin also contains a low level of silanol functionality on the surface. The ratio of M:Q is typically in the range of 0.6-1.2:1. Figure 2 shows a computer generated molecular model of a silicate resin.

Silicone PSAs are produced by blending a specified ratio of MQ resin and siloxane polymer together in a hydrocarbon solvent. Heating the mixture to promote a condensation reaction between the available silanol functionality on the resin and polymer can further enhance the initial cohesive strength of the adhesive. The ratio of resin to polymer is the most important formulation detail when trying to optimize the balance of performance properties for a given adhesive. Figure 3 shows an example of how the balance of resin and polymer can affect the tack, peel adhesion, and shear performance for a silicone

PSA. The exact positioning of these curves with respect to the x and y axes and each other is determined primarily by the resin composition.

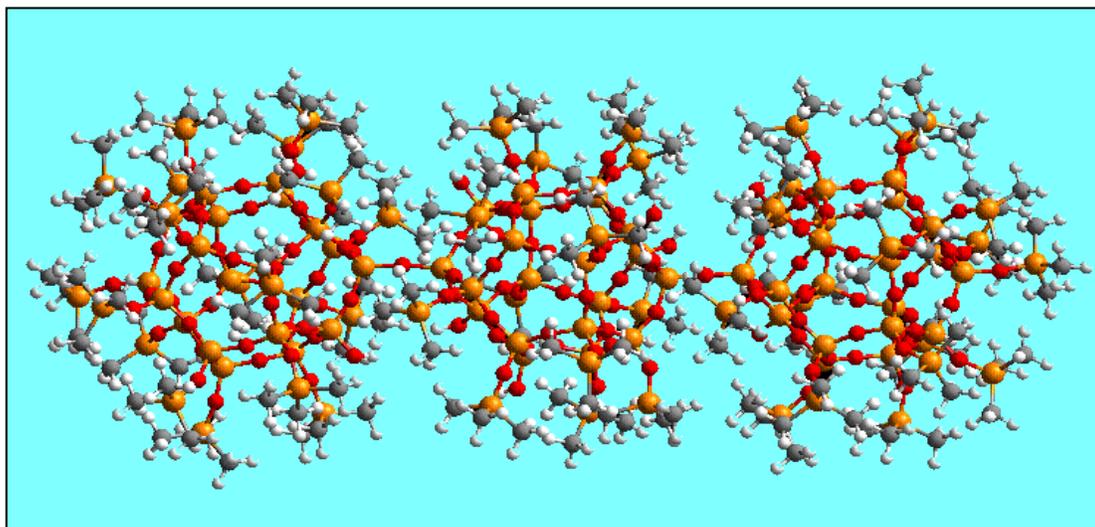


Figure 2. Molecular model of a MQ resin.

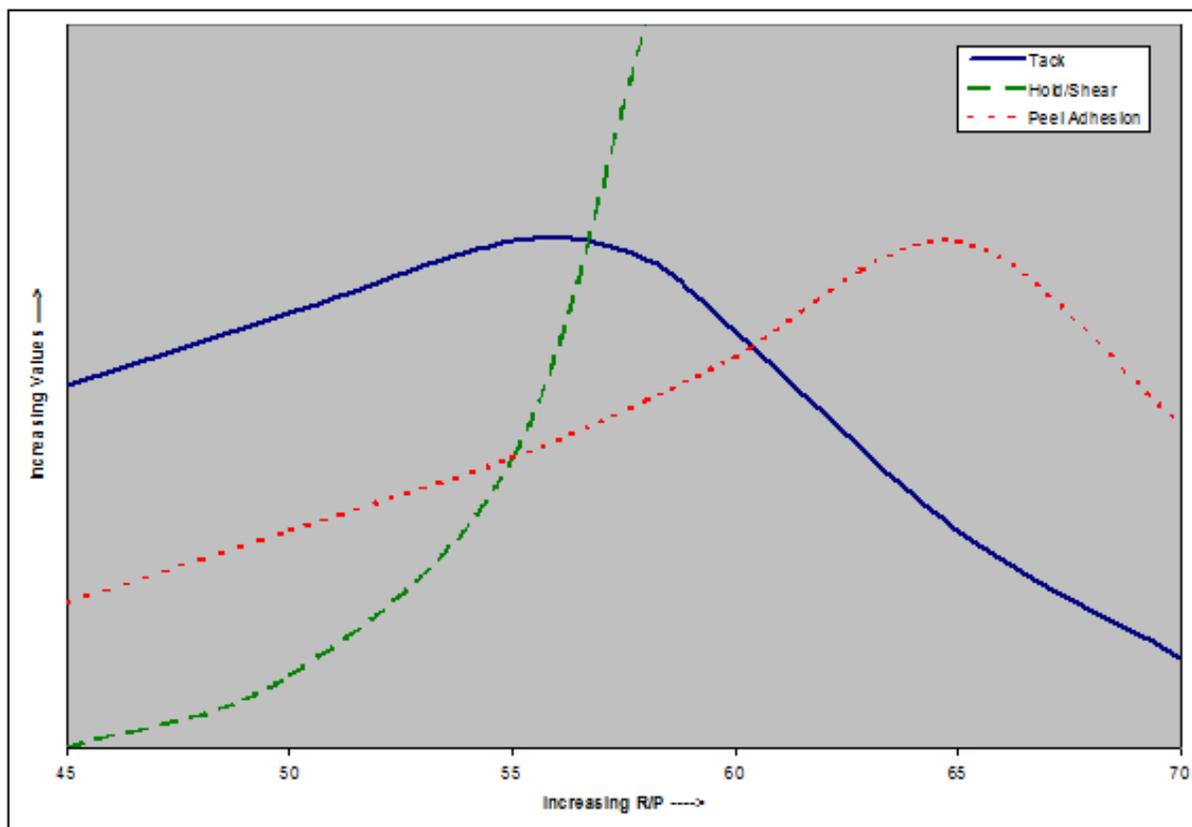


Figure 3. The effect of composition on silicone PSA properties.

2.1 Adhesive Cure Chemistry

Although most silicone PSAs will exhibit pressure sensitive behavior immediately after solvent removal, further crosslinking is done to reinforce the adhesive network. The level of additional crosslinking will depend on the intended application needs of the PSA construction. There are two basic cure systems available for silicone PSAs: peroxide catalyzed free-radical cure and platinum catalyzed silicon hydride to vinyl addition cure. The majority of commercial silicone PSAs employ the use of a peroxide catalyzed free-radical reaction to achieve additional crosslink density. Curing of these types of adhesives is done in multi-zoned ovens due to the use of non-specific peroxides. Solvent removal is first required at lower temperatures (60 to 90°C) to ensure the peroxide does not inadvertently cure solvent in the PSA matrix which would result in reduced performance and poor temperature stability. At elevated temperatures (130 to 200°C), the catalyst decomposes to form free radicals which primarily attack the organic substituents along the polymer chains to extract protons and generate free radicals¹. The free radicals then combine to form crosslinks as shown by the general reaction mechanism in Figure 4.

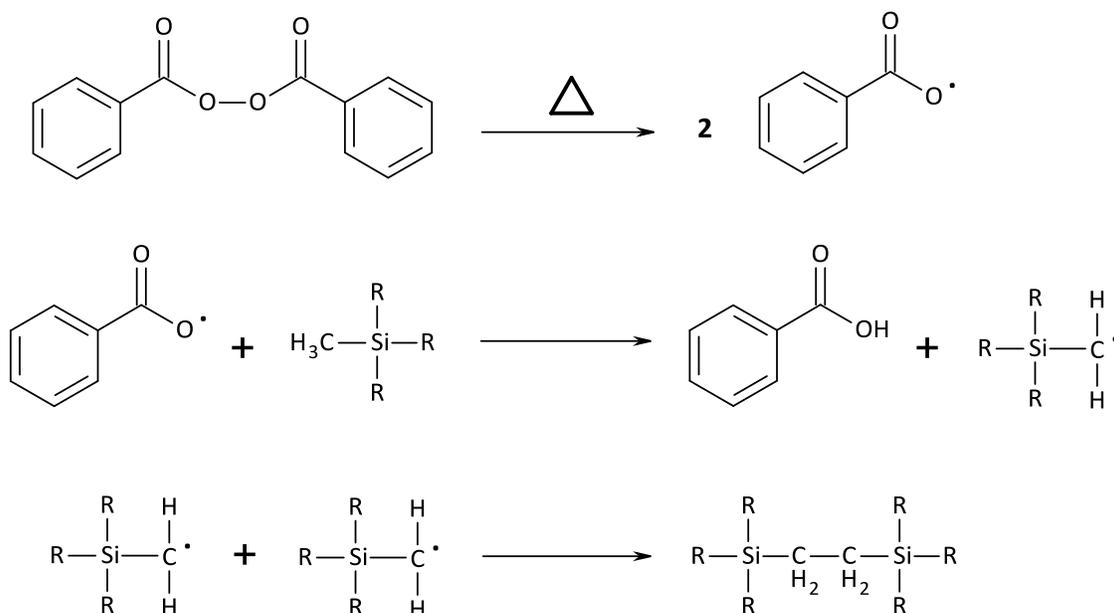


Figure 4. General steps in the peroxide catalyzed crosslinking of silicone PSAs.

The main benefit of the peroxide catalyzed system is the ability to control properties by addition level of peroxide used. The tape producer has the flexibility to use a range from 0 to 4 wt.% peroxide. The additional curing with the peroxide results in a more tightly crosslinked PSA. An increase in cohesive strength, as evidenced by performance in shear tests, is generally observed. The increase in cohesive strength is accompanied by a slight decrease in adhesion and tack. Some of the disadvantages of this type of silicone PSA system include the handling of volatile solvents, generation of peroxide by-products, more sophisticated curing ovens, and the need for priming of certain substrates to improve adhesive anchorage in the construction of self-wound tapes.

As an alternative to the peroxide catalyzed system, silicone PSAs can utilize a platinum catalyzed addition cure in which a silicon hydride reacts with a silicon vinyl to form a crosslink site. This chemistry is analogous to the typical solvent-based and solventless platinum catalyzed silicone release coating systems used for release liners of organic PSAs. The curing of this type of silicone PSA can be accomplished in a single-zone oven at lower overall temperatures (100 to 150°C) even though these

3.2 Proposed

Proposed high temperature testing methods include thermal gradient hot plate and high temperature peel adhesion. A thermal gradient hot plate was used to expose a sample to a thermal gradient at steady state for thirty minutes. The set points of the thermal gradient were set to 40°C and 315°C, resulting in a temperature range of ~195°C to ~302°C over the length of each sample. Embedded thermocouples allow for verification of the gradient's linearity. After thirty minutes of exposure to the gradient, the sample was removed from the hot plate and allowed to cool to room temperature. The sample was then characterized by 180° peel adhesion per PSTC-101. At the low temperature end of the sample, the mode of failure was adhesive. The temperature at which the failure mode changed to 100% cohesive failure will be termed T_{cf} . The position where the failure mode changes is measured, then converted to T_{cf} using the linear regression fit of the gradient².

High temperature peel was achieved using an Instron equipped with environmental chamber³. The environmental chamber was set to 300°C. A sample was placed in the grips, environmental chamber door closed, and environmental chamber allowed to again reach 300°C. The average time required to reach temperature was 7:44 minutes. This allowed the sample to equilibrate as well. Once 300°C was reached, the sample was characterized by 180° peel adhesion at a rate of 12 inches/minute. Room temperature data was also collected. Each condition was tested in triplicate.

4.0 Cured Adhesive Characterization

4.1 Formulating, Laminate Preparation, and PSA Testing Procedures

Three different types of silicone PSAs were evaluated in this study. A polydimethylsiloxane peroxide cure PSA (Dimethyl Peroxide), two polydimethyldiphenylsiloxane peroxide cure PSAs (Diphenyl Peroxide), and a polydimethylsiloxane platinum cure PSA (Dimethyl Platinum). The Dimethyl Peroxide PSA would be considered a general purpose adhesive with excellent high temperature properties for electrical tapes and other very high temperature tapes. The Diphenyl Peroxide PSA would be considered for applications that require performance in extremely high temperature applications, such as plasma spray masking tapes. The Dimethyl Platinum PSA is designed to have adhesion and clean removability properties for applications such as electronic masking and assembly.

The peroxide catalyzed materials were formulated by adding a solvent solution of benzoyl peroxide (BPO) in an amount to yield 1, 2, or 3 wt.% BPO per silicone solids. Each formulation was subsequently diluted with additional solvent to reach a final solids content of 50 wt.%. The platinum catalyzed materials were formulated by adding a platinum catalyst in an amount to yield 0.1, 0.3, or 0.4 wt.%. Each formulation was subsequently diluted with additional solvent to reach a final solids content of 50 wt.%.

PSA laminates were prepared by coating the formulated adhesives onto 2-mil fluorosilicone treated PET and 1-mil untreated polyimide (PI) films using a vacuum coating table with an appropriate application bar to target a 1.5-mil dry adhesive thickness. The PET films coated with the peroxide catalyzed formulations were placed in an air-circulating oven at 80°C for two minutes to remove the solvent followed by 180°C for 2 minutes to cure. The second cure zone was increased to 204°C when PI films were coated. The platinum catalyzed formulations were cured at 150°C for 3 minutes on all film types. Each prepared laminate was cut into test strips using a 1" specimen tape cutter.

The 2-mil fluorosilicone treated PET laminates were used to prepare rheology samples by stacking several of the transfer adhesives together until a target thickness of 1.5 mm was reached. The fluorosilicone liner remained on both sides of the rheology sample until testing. The 1-mil untreated PI laminates were characterized by 180° peel adhesion per PSTC-101, probe tack per ASTM D-2979, high temperature static shear, thermal gradient hot plate and high temperature peel.

4.2 Dimethyl Peroxide PSA

Samples of a Dimethyl Peroxide PSA were prepared at levels of BPO catalyst varying from 1 to 3 wt.%. The laminate thickness, peel adhesion, and tack results on 1-mil Kapton® are shown in Table 1.

Table 1. Laminate thickness, peel adhesion, and tack results for the Dimethyl Peroxide PSA.

BPO (%)	Avg Thickness (mil)	Adhesion (g/in)	Tack (g)
1	1.50	785	557
2	1.47	655	430
3	1.49	590	423

As the level of catalyst was increased for the Dimethyl Peroxide PSA, it was found that there was a decreasing trend in both the adhesion and tack performance. This indicates that increasing the crosslink density of the Dimethyl Peroxide PSA has a direct, inverse relationship to these performance properties.

The high temperature static shear performance was tested at 300°C using a 1 kilogram weight. The laminates were tested until 5 days high temperature was reached. The results are shown in Table 2.

Table 2. High temperature static shear results for the Dimethyl Peroxide PSA.

BPO (%)	Fail Time	Failure Mode
1	1 hour	Cohesive
2	5 day pass	NA
3	5 day pass	NA

As the level of catalyst was increased from 1 to 2 wt.% for the Dimethyl Peroxide PSA, the static shear performance exhibited an increasing trend while there was little improvement increasing the concentration to 3 wt.%. This indicates that increasing the crosslink density of the Dimethyl Peroxide PSA has a direct relationship to increasing static shear performance.

Understanding the viscoelastic nature of silicone PSAs can help guide the proper selection of PSA type (dimethyl, diphenyl, etc.), crosslink density, and additives for a particular application. In addition, the rheological profile of a system can be used as a troubleshooting tool for determining sources of performance failures, as well as correlating against other performance tests. The rheology of each formulation was conducted using a dynamic temperature ramp at a rate of 2°C per minute. Each sample was tested using 8 mm stainless steel parallel plates at a frequency of 10 radians per second and a constant strain of 0.1%. The results are shown in Figure 6 and Table 3.

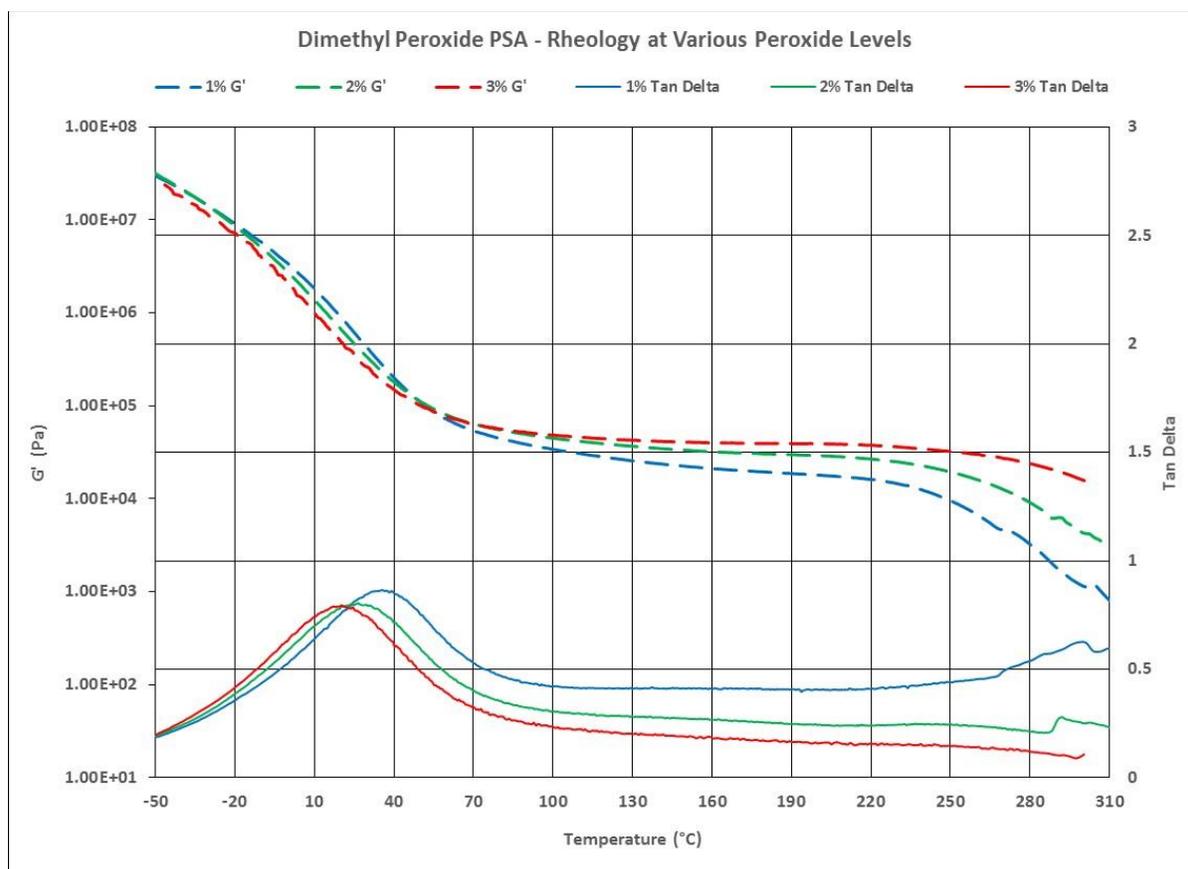


Figure 6. G' and tan delta curves for the temperature ramp testing of the Dimethyl Peroxide PSA.

Table 3. Selected rheology values for the Dimethyl Peroxide PSA.

BPO (%)	Tg (°C)	Tan Delta at Tg
1	35.5	0.87
2	26.4	0.80
3	20.1	0.79

The impact of crosslink density through catalyst addition for the Dimethyl Peroxide PSA becomes evident by the rheology analysis. As the catalyst concentration increases, the position of the Tg decreases to a lower temperature and the overall magnitude of the tan delta peak decreases. The largest effect of the increased crosslinked density is exhibited in the rubbery plateau regions where the storage modulus increases with increasing catalyst concentrations. This reduces the ability of the PSA to dissipate energy and results in lower peel adhesion and tack. The tan delta profile at temperatures greater than 220°C demonstrate how lowering the crosslink density can increase the flow behavior at elevated temperatures.

The thermal gradient settings on the gradient hot plate were set to 40°C and 315°C. Each sample was exposed to the thermal gradient for thirty minutes. The T_{cf} values are shown in Table 4.

Table 4. T_{cf} values for the Dimethyl Peroxide PSA.

BPO (%)	T _{cf} (°C)
1	256
2	292
3	293

The observed cohesive failure followed an expected trend with lower peroxide levels (lower crosslink density) exhibiting failure at lower temperatures. The T_{cf} for 2% and 3% peroxide loading did not show an appreciable difference indicating that 2% BPO is sufficient for applications where the gradient hot plate testing is applicable.

An Instron equipped with environmental chamber was used to test peel adhesion in situ at elevated temperature. Peel adhesion values at room temperature and 300°C are shown in Table 5.

Table 5. Instron peel adhesion at Room Temp and 300°C for the Dimethyl Peroxide PSA.

BPO (%)	Room Temp	300°C
	Adhesion (g/in)	Adhesion (g/in)
1	900	52
2	691	61
3	632	62

The failure mode for room temperature samples was adhesive. As with the peel adhesion tested in the conventional manner, values for room temperature adhesion decreased with increasing BPO. The failure mode for 300°C samples was cohesive for 1% BPO samples and adhesive for 2 and 3% BPO samples. As the adhesive moved from 1% to 2% BPO, it built enough cohesive strength to remain intact and peel adhesively.

4.3 Diphenyl Peroxide PSAs

Samples of two Diphenyl Peroxide PSAs were prepared at levels of BPO catalyst varying from 1 to 3 wt.%. The laminate thickness, peel adhesion, and tack results on 1-mil Kapton® are shown in Tables 6 and 7.

Table 6. Laminate thickness, peel adhesion, and tack results for Diphenyl Peroxide PSA 1.

BPO (%)	Avg Thickness (mil)	Adhesion (g/in)	Tack (g)
1	1.49	1076	760
2	1.48	966	578
3	1.48	922	572

Table 7. Laminate thickness, peel adhesion, and tack results for Diphenyl Peroxide PSA 2.

BPO (%)	Avg Thickness (mil)	Adhesion (g/in)	Tack (g)
1	1.58	959	957
2	1.58	889	864
3	1.48	731	716

As the level of catalyst was increased for the Diphenyl Peroxide PSAs, it was found that there was a decreasing trend in both the adhesion and tack performance. Diphenyl Peroxide PSA 1 had higher levels of adhesion and lower levels of tack compared to Diphenyl Peroxide PSA 2.

The high temperature static shear performance for the Diphenyl Peroxide PSAs are shown in Tables 8 and 9.

Table 8. High temperature static shear results for Diphenyl Peroxide PSA 1.

BPO (%)	Fail Time	Failure Mode
1	1 hour	Cohesive
2	1 hour	Cohesive
3	5 day pass	NA

Table 9. High temperature static shear results for Diphenyl Peroxide PSA 2.

BPO (%)	Fail Time	Failure Mode
1	1 hour	Cohesive
2	1 hour	Cohesive
3	5 day pass	NA

As the level of catalyst was increased from 2 to 3 wt.% for the Diphenyl Peroxide PSAs, the static shear performance exhibited an increasing trend. This indicates that increasing the crosslink density of the Diphenyl Peroxide PSA has a direct relationship to the increase in static shear performance. Diphenyl Peroxide PSA 1 and Diphenyl Peroxide PSA 2 performed similarly in this test.

The rheology of each Diphenyl Peroxide PSA formulation was conducted using a dynamic temperature ramp at a rate of 2°C per minute. Each sample was tested using 8 mm stainless steel parallel plates at a frequency of 10 radians per second and a constant strain of 0.1%. The results are shown in Figures 7 and 8 and Tables 10 and 11.

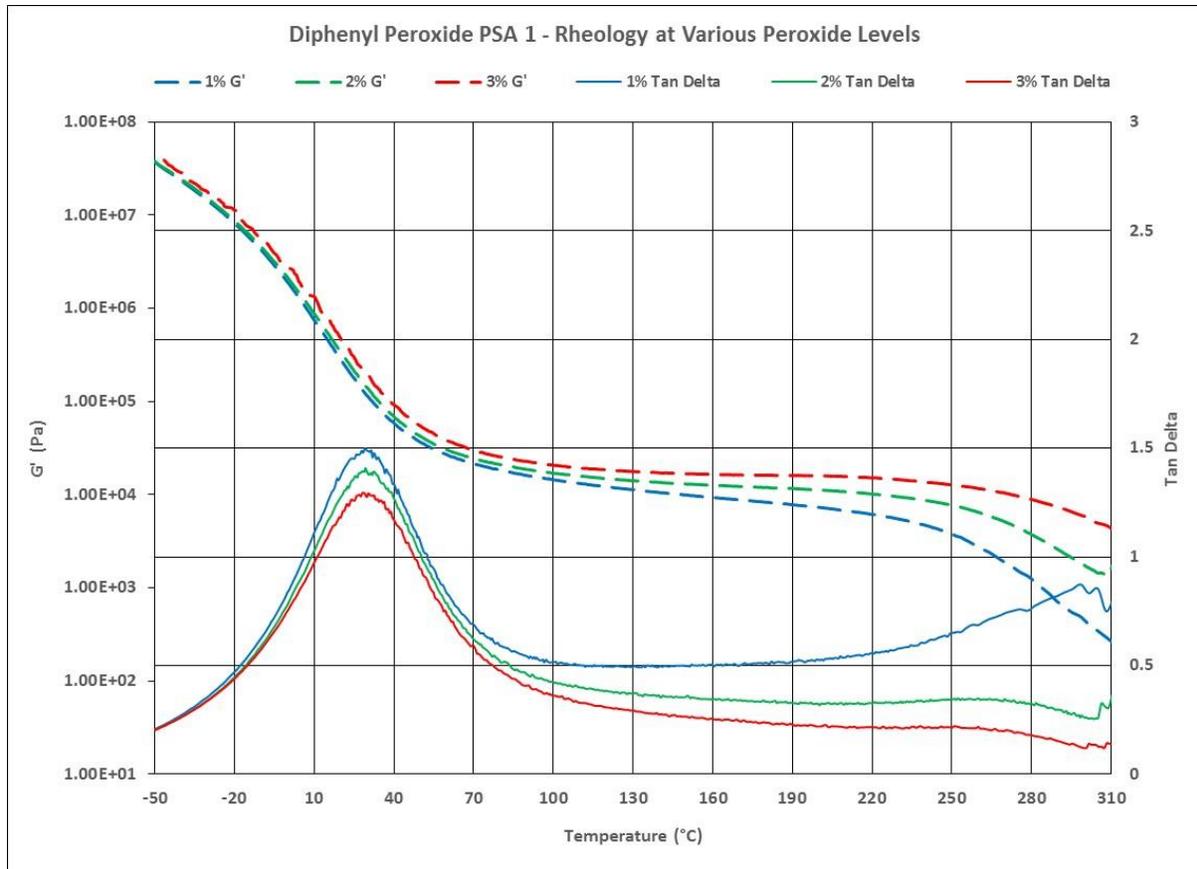


Figure 7. G' and tan delta curves for the temperature ramp testing of Diphenyl Peroxide PSA 1.

Table 10. Selected rheology values for Diphenyl Peroxide PSA 1.

BPO (%)	Tg (°C)	Tan Delta at Tg
1	29.2	1.50
2	29.3	1.41
3	28.1	1.29

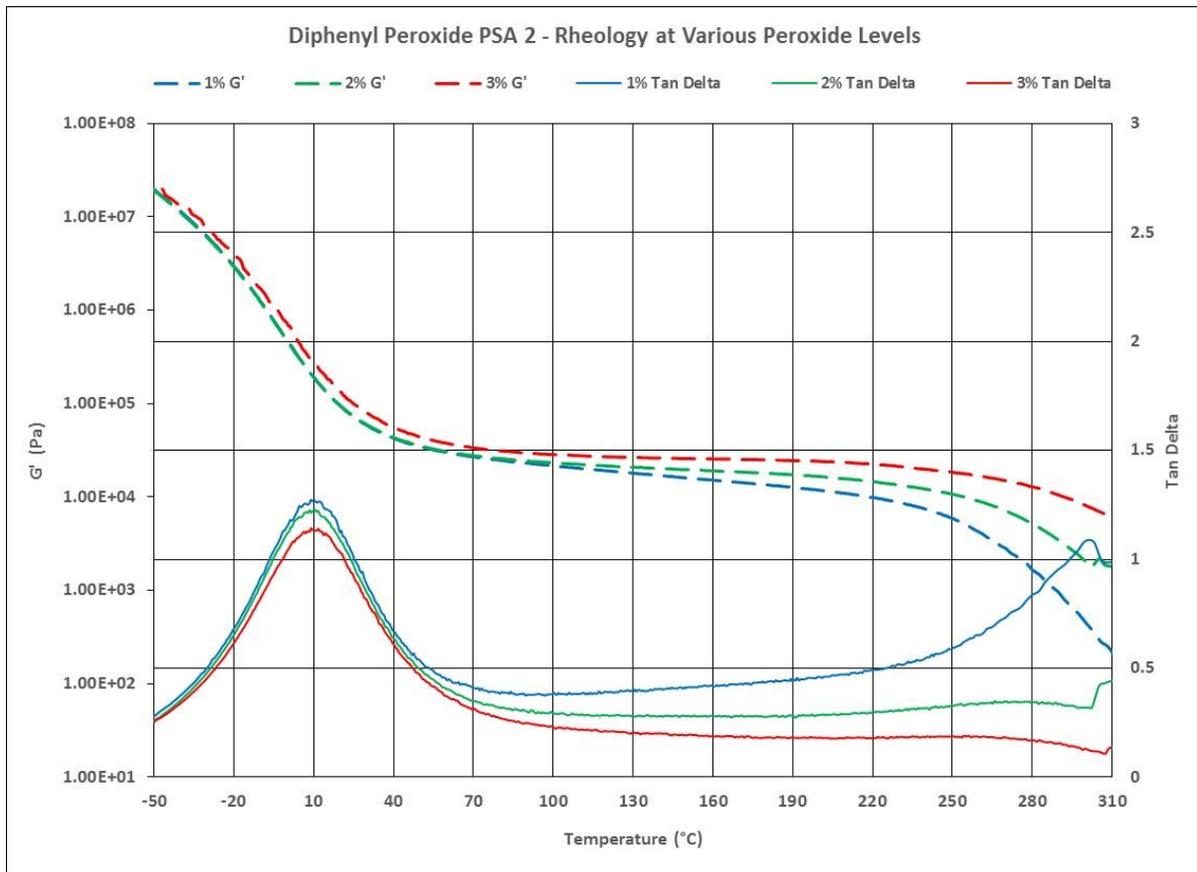


Figure 8. G' and tan delta curves for the temperature ramp testing of Diphenyl Peroxide PSA 2.

Table 11. Selected rheology values for Diphenyl Peroxide PSA 2.

BPO (%)	Tg (°C)	Tan Delta at Tg
1	8.8	1.27
2	10.4	1.23
3	9.0	1.14

The rheology profiles of the Diphenyl Peroxide PSAs are similar to each other. The Tg temperature for Diphenyl Peroxide PSA 2 is lower and mainly due to compositional differences in the starting raw materials. The impact of crosslink density for the Diphenyl Peroxide PSAs follows the trend seen with the Dimethyl Peroxide PSA. As the catalyst concentration increases, the magnitude of the tan delta peak decreases. The magnitude of tan delta is greater for the Diphenyl Peroxide PSAs at similar levels of peroxide concentration when compared to the Dimethyl Peroxide PSA. The largest effect is found in the rubbery plateau regions where the higher crosslink density increases the storage modulus. The tan delta profile at temperatures greater than 190°C demonstrate how lowering the crosslink density can increase the flow behavior at elevated temperatures.

The thermal gradient settings on the gradient hot plate were set to 40°C and 315°C. Each sample was exposed to the thermal gradient for thirty minutes. The T_{cf} values are shown in Tables 12 and 13.

Table 12. T_{cf} values for Diphenyl Peroxide PSA 1.

BPO (%)	T_{cf} (°C)
1	264
2	281
3	274

Table 13. T_{cf} values for Diphenyl Peroxide PSA 2.

BPO (%)	T_{cf} (°C)
1	257
2	275
3	287

The observed cohesive failure followed an expected trend with lower peroxide levels (lower crosslink density) exhibiting failure at lower temperatures in the majority of data points.

An Instron equipped with environmental chamber was used to test peel adhesion in situ at elevated temperature. Peel adhesion values at room temperature and 300°C are shown in Tables 14 and 15.

Table 14. Instron peel adhesion at Room Temp and 300°C for Diphenyl Peroxide PSA 1.

BPO (%)	Room Temp Adhesion (g/in)	300°C Adhesion (g/in)
1	1080	22
2	945	80
3	874	41

Table 15. Instron peel adhesion at Room Temp and 300°C for Diphenyl Peroxide PSA 2.

BPO (%)	Room Temp Adhesion (g/in)	300°C Adhesion (g/in)
1	977	17
2	849	81
3	728	55

The failure mode for room temperature samples was adhesive. As with peel adhesion tested in the conventional manner, values for room temperature adhesion decreased with increasing BPO. The failure mode for 300°C PSA 1 and 2 samples was cohesive for 1 and 2 wt.% BPO samples and adhesive for 3 wt.% BPO samples. The move from 2 to 3 wt.% BPO was required to build enough cohesive strength to remain intact and peel adhesively. Both Diphenyl Peroxide PSAs showed higher adhesion at room temperature compared to Dimethyl Peroxide PSA. Compared to each other, Diphenyl Peroxide PSA 1 exhibited higher adhesion at room temperature. The diphenyl PSAs were comparable at 300°C.

4.4 Dimethyl Platinum PSA

Samples of a Dimethyl Platinum PSA were prepared at levels of platinum catalyst in an amount to yield 0.1, 0.3, and 0.4 wt.%. The laminate thickness, peel adhesion, and tack results on 1-mil Kapton® are shown in Table 16.

Table 16. Laminate thickness, peel adhesion, and tack results for the Dimethyl Platinum PSA.

Pt (%)	Avg Thickness (mil)	Adhesion (g/in)	Tack (g)
0.1	1.59	916	581
0.3	1.57	949	559
0.4	1.58	945	555

As the level of platinum was increased from 0.1 to 0.3 wt.%, an increase in adhesion and a decrease in tack was observed. Increasing the platinum from 0.3 to 0.4 wt.% had minimal effect on adhesion and tack.

The high temperature static shear performance for the Dimethyl Platinum PSA is shown in Table 17.

Table 17. High temperature static shear results for the Dimethyl Platinum PSA.

Pt (%)	Fail Time	Failure Mode
0.1	16 hours	Cohesive
0.3	16 hours	Cohesive
0.4	16 hours	Cohesive

The change in platinum concentration did not affect high temperature static shear performance, which was lower overall than the peroxide cured systems.

The rheology of each Dimethyl Platinum PSA formulation was conducted using a dynamic temperature ramp at a rate of 2°C per minute. Each sample was tested using 8 mm stainless steel parallel plates at a frequency of 10 radians per second and a constant strain of 0.1%. The results are shown in Figures 9 and Table 18.

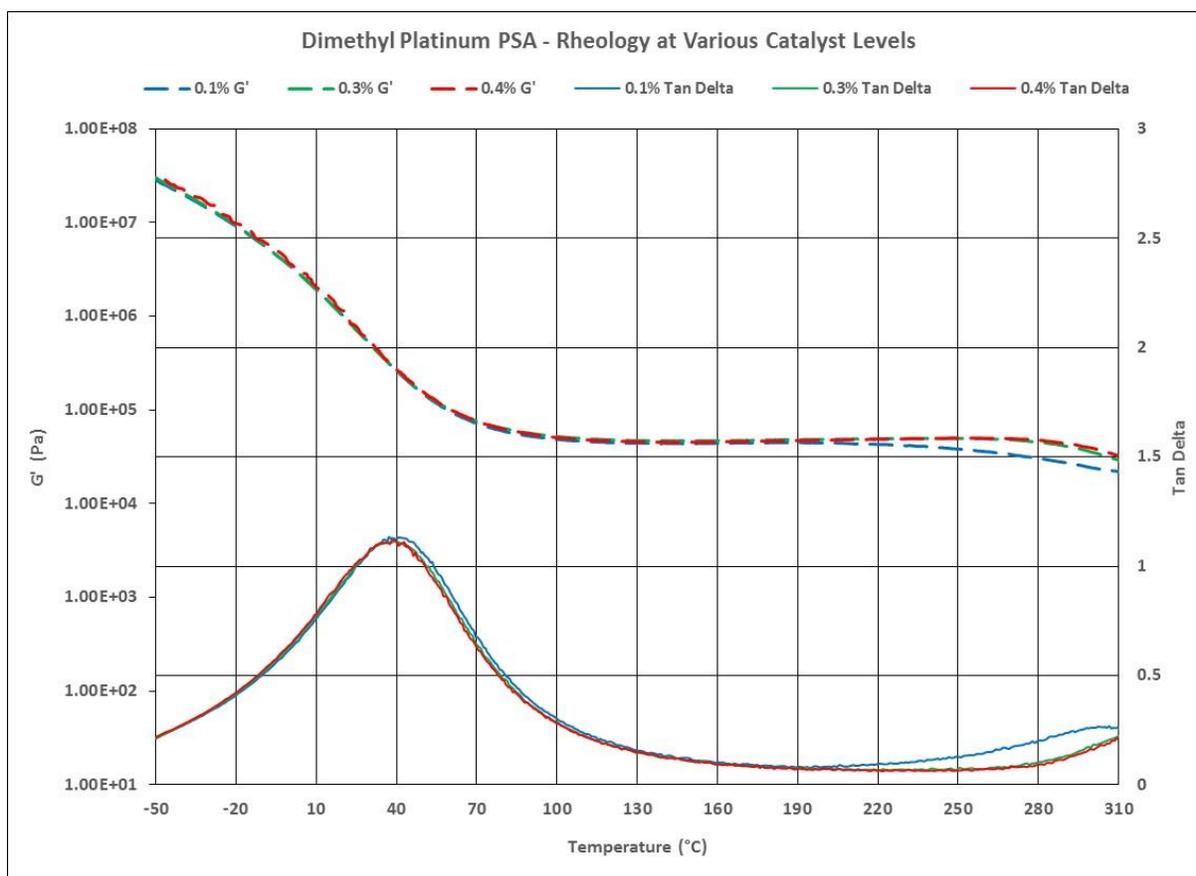


Figure 9. G' and tan delta curves for the temperature ramp testing of the Dimethyl Platinum PSA.

Table 18. Selected rheology values for the Dimethyl Platinum PSA.

Pt (%)	T _g (°C)	Tan Delta at T _g
0.1	41.2	1.13
0.3	39.3	1.12
0.4	38.8	1.12

As opposed to the peroxide cured systems, the Dimethyl Platinum PSA does not show appreciable variation when changing catalyst concentrations. The vinyl and hydride functionality available on the polymer and crosslinker portion of the PSA is finite. Therefore, adding the additional catalyst mainly impacts the cure kinetics under the conditions used to prepare the samples. There is a slight decrease in the storage modulus of the 0.1 wt.% catalyst at temperatures greater than 200°C which is likely due to incomplete cure.

The thermal gradient settings on the gradient hot plate were set to 40°C and 315°C. Each sample was exposed to the thermal gradient for thirty minutes. The T_{cf} values are shown in Table 19.

Table 19. T_{cf} values for the Dimethyl Platinum PSA.

Pt (%)	T _{cf} (°C)
0.1	277
0.3	282
0.4	283

The observed cohesive failure followed an expected trend with lower catalyst levels (lower crosslink density) exhibiting failure at lower temperatures. The T_{cf} for 0.3% and 0.4% platinum catalyst loading did not show an appreciable difference indicating that the extent of crosslinking needed to achieve high temperature cohesive performance is not influenced by the addition of catalyst beyond 0.3%.

An Instron equipped with environmental chamber was used to peel adhesion in situ at elevated temperature. Peel adhesion values at room temperature and 300°C are shown in Table 20.

Table 20. Instron peel adhesion at Room Temp and 300°C for the Dimethyl Platinum PSA.

Pt (%)	Room Temp Adhesion (g/in)	300°C Adhesion (g/in)
0.1	1025	166
0.3	987	208
0.4	981	202

The failure mode for room temperature and 300°C samples was adhesive. Room temperature adhesion decreased with increasing catalyst concentration. Adhesion at 300°C increased as catalyst concentration increased from 0.1 to 0.3 wt.% and did not change from 0.3 to 0.4 wt.%.

5.0 Summary

Quantitative high temperature testing methods were employed for three different types of silicone PSAs at increasing catalyst levels. The thermal gradient hot plate provided T_{cf} values, using the linear regression fit of the gradient. This type of data helps to provide the temperature at which a tape can survive and still deliver clean removability. High temperature peel was achieved using an Instron equipped with environmental chamber, providing peel adhesion values at elevated “in-use” temperatures.

Increasing crosslink density through peroxide addition provides a silicone PSA with higher temperature stability for applications such as heat seal and plating tapes. Applications that would require more tack and adhesion from the same PSA, such as splicing tape, may benefit from a lower peroxide loading. Decreasing the amount of peroxide also has the effect of lowering the storage modulus of the PSA allowing for more flow and subsequent wetting of the PSA on low energy substrates. High temperature static shear, thermal gradient hot plate, and high temperature peel adhesion testing for the Dimethyl Peroxide PSA did not show an appreciable difference between 2 and 3 wt.% BPO. Optimal high temperature properties for the Diphenyl Peroxide PSAs were achieved at 3 wt.% BPO. The Diphenyl Peroxide PSAs exhibited the highest room temperature adhesion and tack of the adhesives studied.

Whereas the crosslink density of the peroxide catalyzed PSAs can be modified through incremental catalyst addition, the platinum catalyzed PSAs are more limited due to the dependence on the availability of vinyl and hydride functionality on the polymers used in the formulation. It was demonstrated that the extent of crosslinking needed to achieve performance properties was not influenced by the addition of catalyst beyond 0.3 wt.%. The adhesion and clean removability performance of Dimethyl Platinum PSAs make them ideal for use in applications such as electronic masking and assembly.

Understanding high temperature performance will provide the researcher with necessary information to design a PSA for high temperature applications.

6.0 Literature Citations

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7.0 Acknowledgments

The authors would like to acknowledge Dave Dingman and Lacey Brissette for their help preparing and testing adhesives, as well as Andrew Diehl for his help with Instron equipment.