ENVIRONMENTALLY FRIENDLY SILICONE PRESSURE SENSITIVE ADHESIVES

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1. Abstract

As the world faces the challenges of climate change, sustainability in the chemical industry grows more and more important each day. Silicone pressure sensitive adhesives (PSAs) are used to manufacture pressure sensitive tapes which features good chemical resistance, high temperature hold and good low temperature performance and adhesion to low surface energy substrates. Currently, silicone PSAs are mainly supplied in aromatic solvents. To meet the global trend on sustainability, the tapes market is asking for solvent-free PSAs and/ or environmentally friendly solvent PSAs. Furthermore, there are also demands for new applications in automotive, aeronautics and electronics markets for silicone PSA tapes with low volatile organic compounds (VOCs). The challenge here is to develop new environmentally friendly PSAs without affecting performances usually obtained when using solvent-based PSAs, such as adhesion, tack, and temperature-hold. Novel developments in this area will be presented.

2. Introduction

2.1 Why use Silicone Pressure Sensitive Adhesive (PSA)?

Silicone pressure sensitive adhesives (PSAs) offer unique properties that cannot be matched by organic adhesives such as acrylic, natural rubber, and other competing materials. Silicone PSA can be sticked to low energy surfaces, is repositionable, gas permeable and can be used in a wide range of temperatures, while keeping its properties. It is also quite resistant to weather conditions.

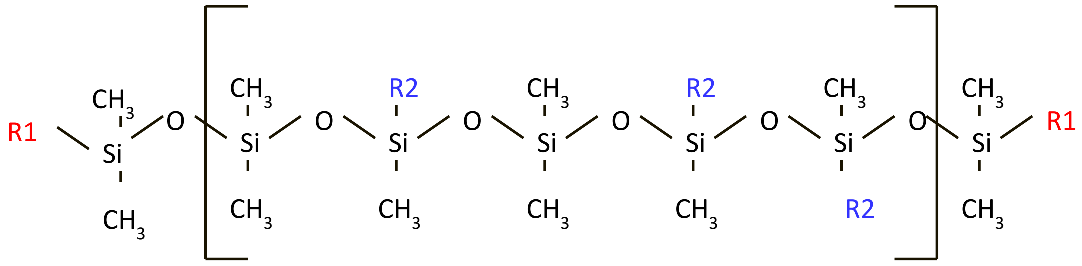
2.2 Application

Silicone PSAs are high performance adhesives used to manufacture pressure sensitive tapes which feature good chemical resistance, high temperature hold, and good low temperature performance and adhesion to low surface energy substrates. There is a wide range of application, and some of them are listed hereunder.

- Masking tapes, mica tapes or specialty tapes for cable insulation.
- Assembly tapes or specialty marking labels for Automotive.
- Protective films and tapes to temporarily decorate automotive glass or building windows and to protect electronic or industrial components.

2.3 Composition of Silicone PSA

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 use either a polydimethylsiloxane polymer or polydimethyldiphenylsiloxane co-polymer that may contain silanol or vinyl functionality at the polymer chain ends.



R1= (OH, vinyl, alkyl, phenyl, etc.)

R2= (methyl, phenyl, alkyl, vinyl, etc.)

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 ($SiO_{4/2}$) surrounded by a shell of M-units ($Me_3SiO_{1/2}$). 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 resin.

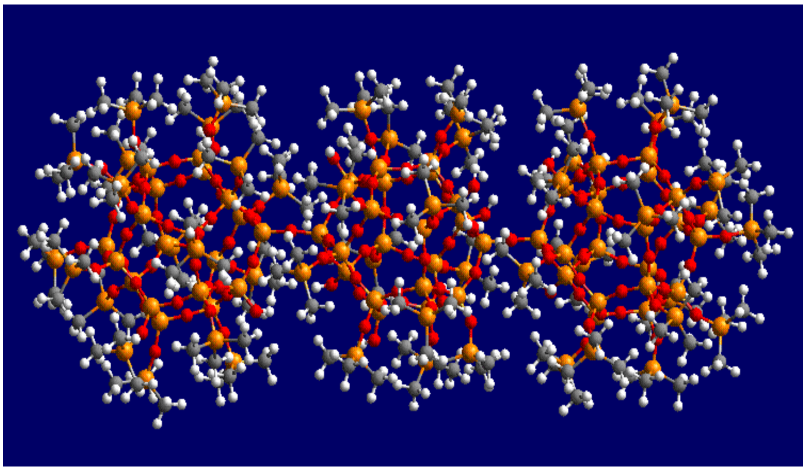


Figure 2: Molecular model of MQ resin

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.

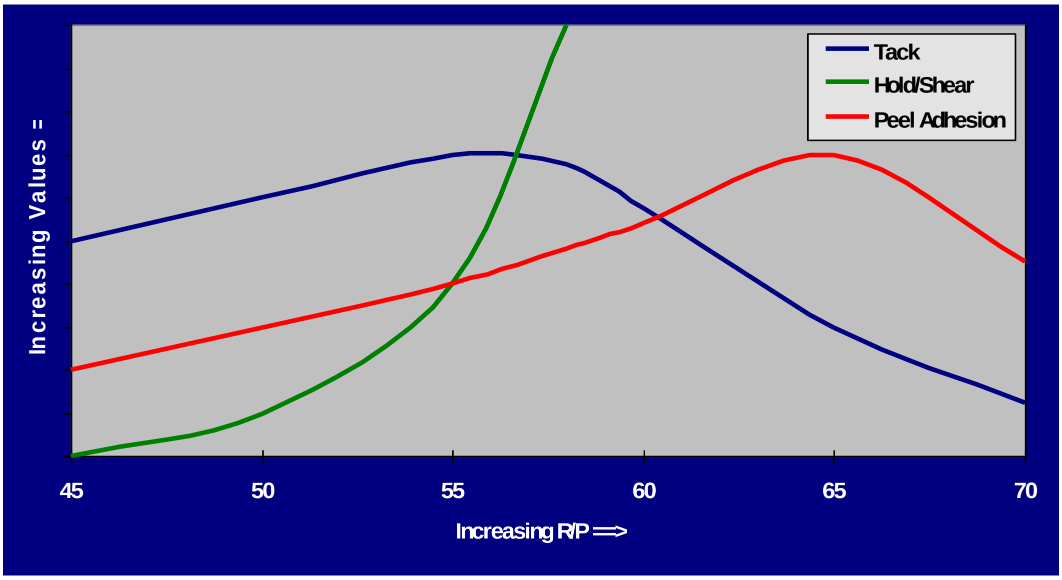


Figure 3: The effect of composition on Silicone PSA properties

2.4 Adhesive cure chemistry

Although most silicone PSAs will exhibit pressure sensitive behaviour 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 catalysed free-radical cure and platinum catalysed silicon hydride to vinyl addition cure. Most commercial silicone PSAs use a peroxide catalysed 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 (180 to 204°C), the catalyst decomposes to form free radicals which primarily attack the organic substituents along the polymer chains to extract protons and generate free radicals[1]. The free radicals then combine to form crosslinks as shown by the general reaction mechanism in Figure 4.

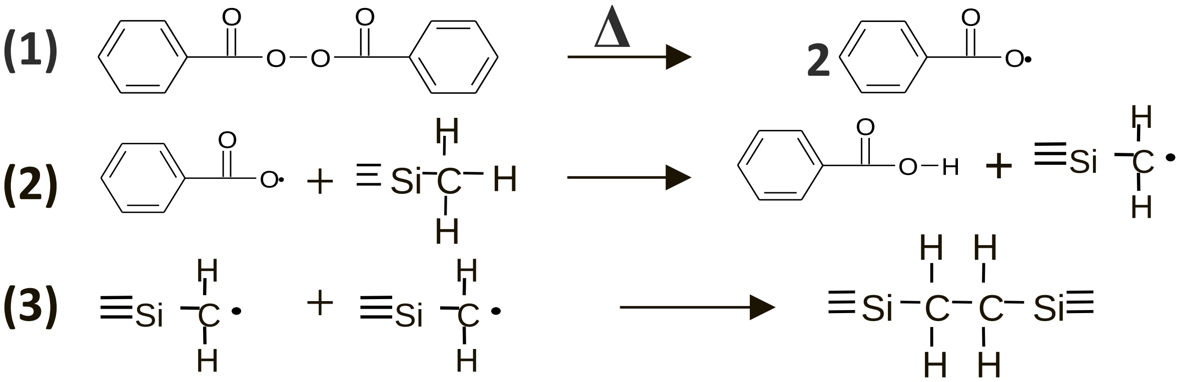


Figure 4: General steps in the peroxide catalysed crosslinking of silicone PSAs

The main benefit of the peroxide catalysed 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 catalysed system, silicone PSAs can utilize a platinum catalysed 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 catalysed silicone release coating systems used as release liners for organic PSAs. 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 systems are supplied in hydrocarbon solvents. As the solvent evaporates, the platinum catalysed reaction occurs without any generation of by-products as shown in Figure 5.

The ability of the system to be cured at a single, lower temperature offers benefits that are not seen with a peroxide catalysed system. These benefits include faster line speeds (or cure time), lower sensitivity to temperature variation, ability to use substrates with lower thermal stability (polyethylene, polypropylene, etc.) and no generation of volatile by-products. Another benefit of the platinum catalysed silicone system is the fact that it does not inherently need the hydrocarbon solvent for anything other than viscosity control. The peroxide catalysed system not only needs the solvent for viscosity control, but the solvent also keeps the peroxide dissolved within the adhesive bath prior to coating on the web. This advantage of the platinum catalysed system allows for the ability to manufacture solventless platinum catalysed silicone PSAs.

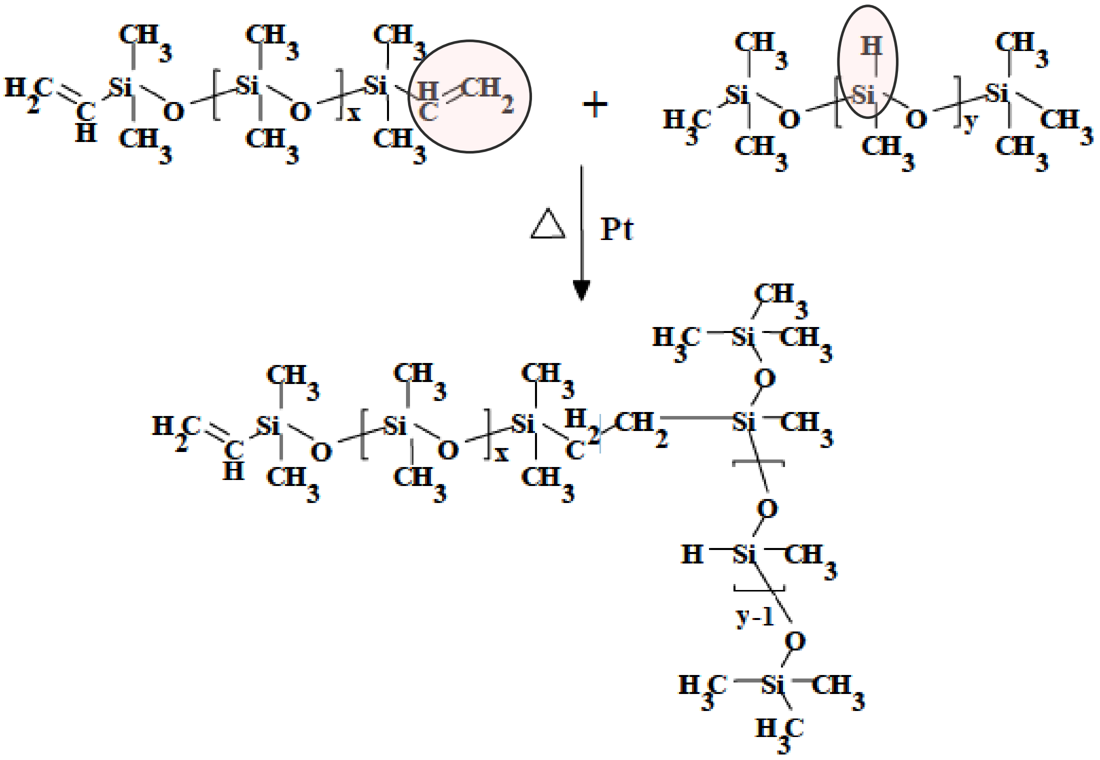


Figure 5: General reaction mechanism in the Platinum catalysed crosslinking of silicone PSAs

3. Formulating & PSA testing procedures

In this study, we are going to look at both peroxide and addition cure PSAs. Environmentally friendly PSA cured with peroxide will first be evaluated. Currently, silicone PSAs are mainly supplied in aromatic solvents such as benzene, toluene, or xylene. Owing to strict environmental requirements to limit BTX solvent emission as well as improved EHS measures in production environments with regards to solvents exposure, a silicone PSA with an alternative solvent, heptane, was developed. To follow sustainability trend, it is to be noted that heptane is produced through distillation of crude oil at low temperature as compared to catalytic reforming of crude oil with very high temperatures for aromatic solvents. For this study it was important to keep performances, high adhesion, or high temperature resistance, obtained with a conventional peroxide cure PSA.

Secondly, we will focus on solvent-free PSA cured with platinum. Addition-cure silicone PSA products are also supplied in aromatic solvents. The continued restrictions involved in the use and handling of solvents and the trend for sustainability make it appropriate to offer an alternative delivery system such as solvent-free PSA[2].

3.1 Formulating

Samples of BTX and Heptane PSAs were prepared using 2 wt% BPO catalyst. Backings were 25µm PET and PI (polyimide) films. Cure conditions were the following: 2 minutes at 80°C followed by 2 minutes at 180°C.
Samples of solvent-based and solvent free PSAs were prepared using 0.4 wt% of Platinum catalyst. Backing was 50 µm PET film. Cure condition was 3 minutes at 150°C.

3.2 PSA testing procedures

Adhesion and tack are collected with 40 µm tapes.

- Adhesion: 180° peel using Chem Instruments AR-1500.
- Probe tack using ChemInstruments PT-1000. Test method applied: CTM0091
- Heat-resistance on BTX/ heptane PSAs was done in following conditions: 40µm PSA on 25µm PI (polyimide) backing. Put PSA tapes on SUS plate, leave at room temperature for 30 minutes before putting plate in oven at 260°C/ 30 min. Remove plate from oven and immediately peel off tape (hot peel). When plate reaches room temperature, peel off tape (cold peel).
  Same testing protocol was used on Solvent-based/solvent-free PSAs. However, tapes were made with 40µm adhesive on 50µm PET and temperature resistance was evaluated at 200°C.
  - Rheology using TA instruments DHR-2 Rheometer. Use 2 wt% BPO catalyst and cure conditions at 80°C/ 2 min followed by 180°C/ 4 min. For second study, 0.4 wt% Pt catalyst was used and cure was 150°C during 3 min. Data was collected 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%.

4. PSA performances

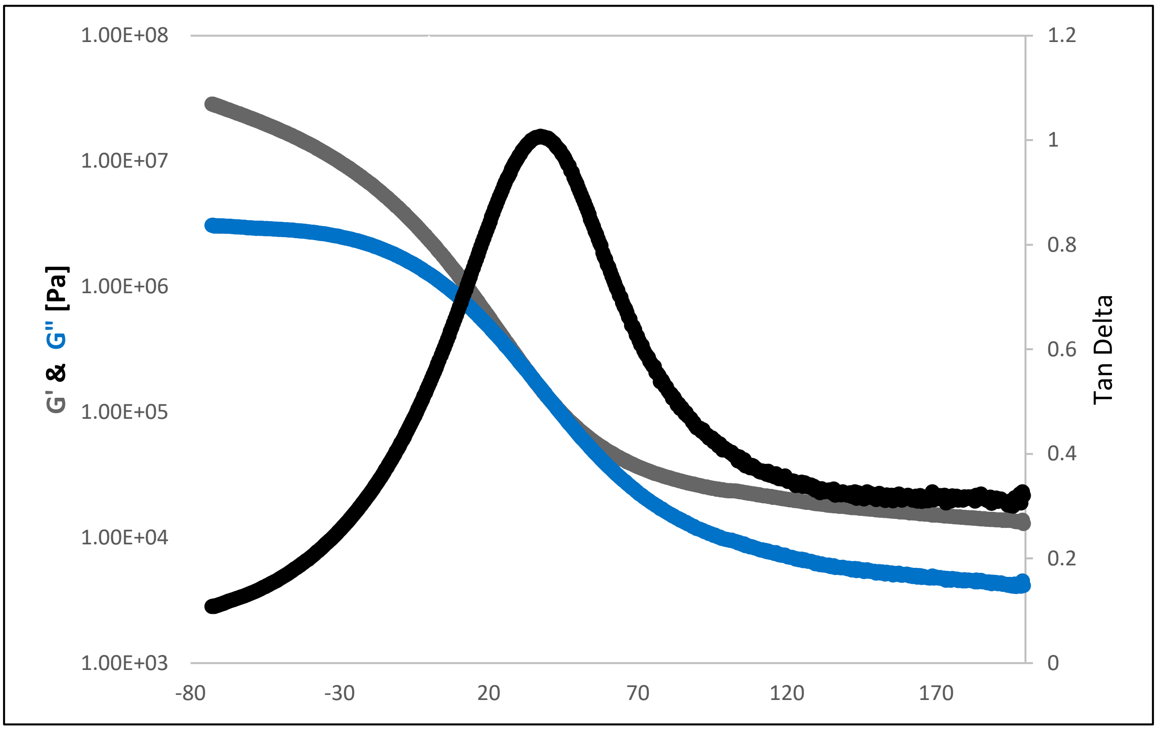
4.1 Environmentally friendly PSAs

Adhesion and tack data can be seen in Table1 hereunder. Heptane-PSA shows high tack performance and reasonable adhesion as compared to BTX-PSA. Crosslinking density can be adjusted to increase adhesion if needed.

Table 1: Adhesion and tack

PSA	Adhesion (gf/ Inch)	Tack (g)
BTX	1200	202
Heptane	1050	292

Rheology curves can be seen in Figure 6 and data in Table2. Lower Tg as well as G’ at 25°C are to be seen for heptane PSA. These values confirm high tack and lower adhesion as opposed to BTX PSA. High temperature resistance also seem similar as observed on plateau of G’ and tan delta. It would also be interesting to see how these two PSAs behave at much higher temperatures.



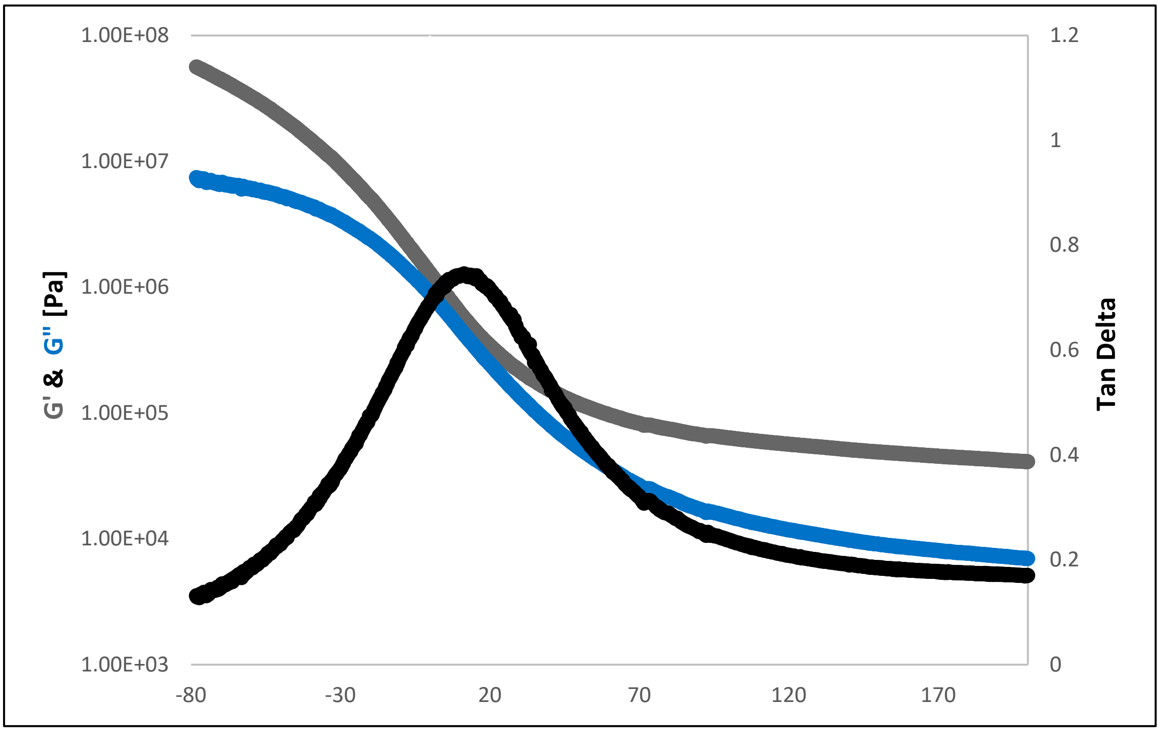


Figure 6: G’, G” & tan Δ curves for BTX (top) and heptane PSA (bottom)

Table 2: Selected rheology values

PSA	Tg (°C)	G’ at 25°C (MPa)
BTX	39	5.7
Heptane	11.3	2.7

Heat resistance was evaluated at 260°C and the test performance can be seen in Figure 7. BTX PSAs (on the left) clearly show cohesive failure at high temperature as compared to heptane-PSA. On the other hand, both families of PSA show good performances when at room temperature.

Hot peel

Cold peel

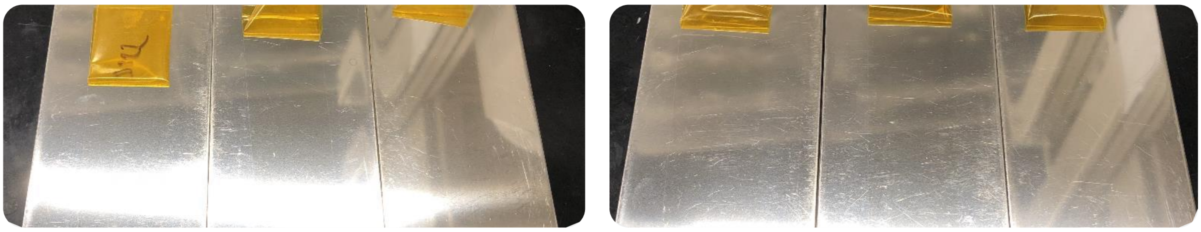


Figure 7: Heat resistance at 260°C BTX PSA (left) & heptane PSA (right)

4.2 Solvent-free PSA

Adhesion and tack data can be found in Table 3. Both solvent-based and solvent-free PSAs show high adhesion, higher than 1000 gf/ Inch. On the other hand, solvent-free PSA seems to be a low tack adhesive.

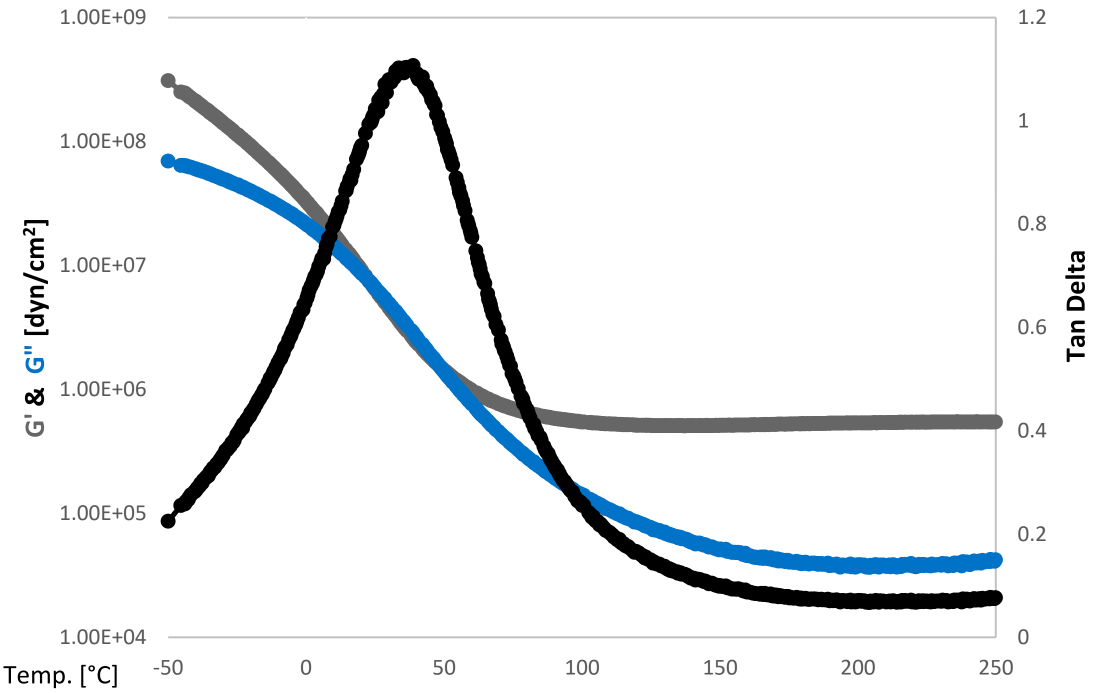
Table 3: Adhesion and tack

PSA	Adhesion (gf/ Inch)	Tack (g)
Solvent-based	1500	1160
Solvent-free	1100	223

Rheology curves can be seen in Figure 8 and selected data in Table4. Both PSAs have similar profiles. However, glass transition and G’ at 25°C are much higher for solvent-free adhesive. Furthermore, solvent-free does not seem to have the rubbery plateau observed on solvent-based PSA. Adhesion and tack performances collected are clearly confirmed with rheology. Both PSAs appear to show good high temperature performances which is crucial for silicone PSAs.

Table 4: Selected rheology values

PSA	Tg (°C)	G’ at 25°C (MPa)
Solvent-based	38.8	0.6
Solvent-free	69.1	2.8



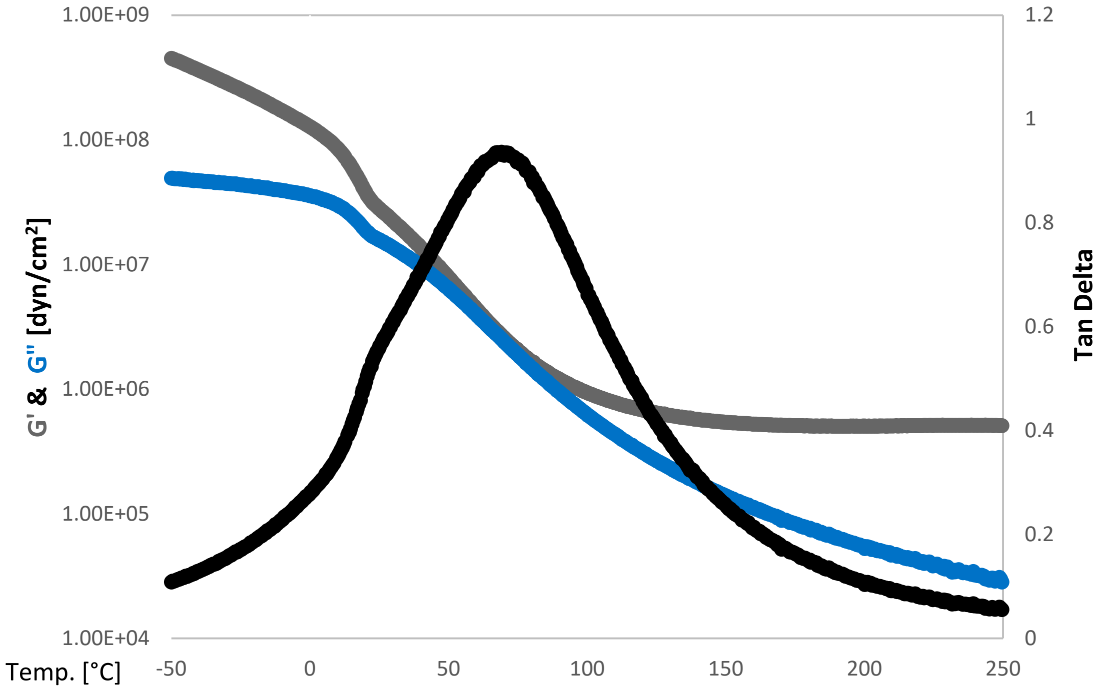


Figure 8: G’, G” & tan Δ curves for Solvent-based (top) and solvent-free PSA (bottom)

High temperature resistance was evaluated at 200°C. The pictures taken of SUS plates after hot and cold peel are to be seen in Figure 9. Both technologies pass the evaluation, no residues are seen on SUS plates after hot and cold peels. Solvent-free PSA can hence be used in applications where high temperature resistance is required.

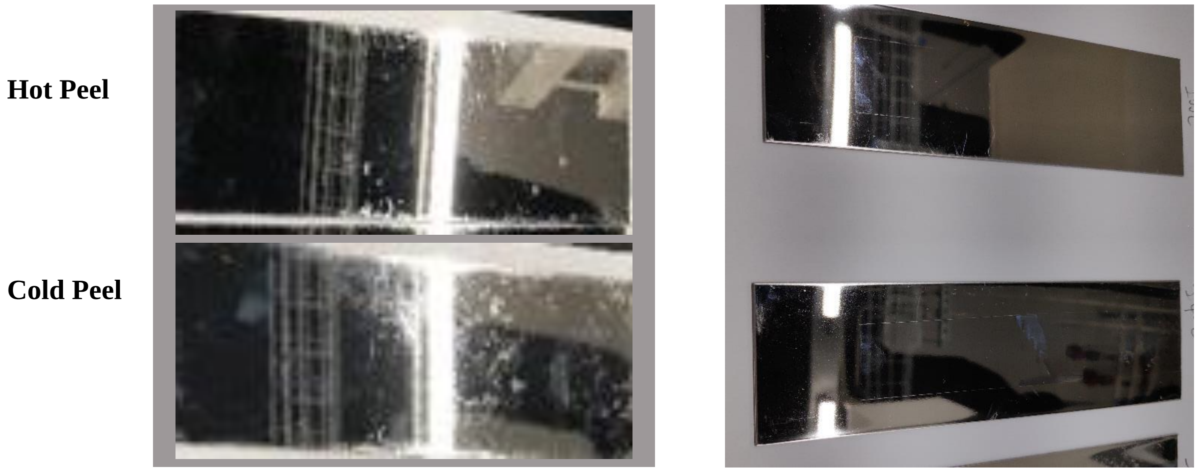


Figure 9: Heat resistance at 200°C solvent-based PSA (left) & solvent-free PSA (right)

5. Summary

This paper shows sustainable PSA solutions to meet a wide range of application needs. Peroxide cure PSA, with heptane, showed comparable and good performances to BTX conventional PSAs, while decreasing environmental impact from carrier solvent. Addition cure PSA showed that traditional PSAs have high adhesion and tack. However, solvent-free PSAs can also achieve high adhesion and good high temperature resistance. It could also be a perfect fit for applications with low volatile organic components (VOCs) requirements and for energy efficient processes. Moreover, major improvements in EHS could be achieved in production facilities using non-BTX solvent and solvent-free PSAs.

6. Literature citations

1. Sobieski, L. A. and Tangney, T. J. Silicone Pressure Sensitive Adhesives. Handbook of Pressure Sensitive Adhesive Technology, (D. Satas, ed.). 2nd Edition, Van Nostrand Reinhold, New York, 1989, 508-517.
2. Lin S.B., Durfee L.D., Ekeland R.A., McVie J., Schalau II G.K. (2007), “Recent advances in silicone pressure sensitive adhesives”, J.Adhesion Sci. Technol., Vol.21, N°7, 605-623.

7. Acknowledgements

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