Solventless Technology for Silicone PSAs

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About Dow

Dow is a material science leader committed to delivering innovative and sustainable solutions for customers in packaging, infrastructure, and consumer care.

Dow Consumer Solutions for the Pressure Sensitive Industry

Dow Consumer Solutions offer a comprehensive line of silicone-based adhesives and release coatings for pressure sensitive applications. Products are available worldwide.

Silicone pressure sensitive adhesives (PSAs) are used in a diverse range of large and fast-growing applications. This includes tape products where excellent performance at high temperature and resistance to chemicals, moisture, weathering, and UV are required. Silicone tapes excel in applications such as plasma spray, flame spray, and electronic circuit board masking where conventional, organic-based PSAs are unable to perform satisfactorily under the elevated temperatures required in use. Additionally, the ability to adhere to low-energy surfaces make silicone PSAs suitable for use as splicing tapes for silicone-coated release liners (Table 1).

Table 1. General PSA performance comparison of silicone and organic PSAs.

	Silicone PSA		Organic PSA	
Type (Material / Cure)	**Addition / Pt**	**Peroxide / BPO**	**Acrylic**	**Rubber**
System	Solvent Solventless	Solvent	Solvent Emulsion Hot Melt	Solvent Emulsion Hot Melt
Heat Resistance	260°C	288°C	150°C	100°C
Low Temperature Resistance	-50°C	-50°C	0°C	0°C
Chemical Resistance	Good	Good	Good to poor	Good to poor
Weather Resistance	Excellent	Excellent	Good	Poor
Adhesion to PTFE	High	High	Poor	Poor
Adhesion to Si Rubber	Medium to High	High	Poor	Poor

The Composition of Silicone PSAs

The composition of silicone PSAs parallels that of many common organic-based PSAs. The two main components that determine the final performance profile of the silicone PSA are a medium to high molecular weight, linear siloxane polymer ("gum") and a highly condensed, silicate tackifier ("MQ") resin. Silicone PSAs are produced using siloxane polymers with either silanol (SiOH) or vinyl (Vi) functionality at the polymer chain ends (Figure 1).

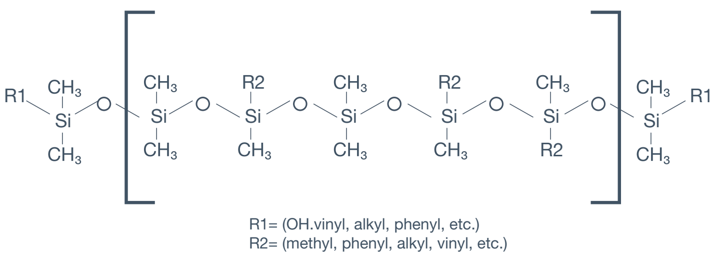

Figure 1. Structure of a generic siloxane polymer used in silicone PSAs.

The MQ resin contains a level of silanol functionality on the surface. The MQ name derives from its structure which consists of a core of three-dimensional Q units ($SiO_{4/2}$) surrounded by a shell of M units ($R_3SiO_{1/2}$) (Figure 2). The MQ resin is generally supplied as a dispersion in a hydrocarbon solvent.

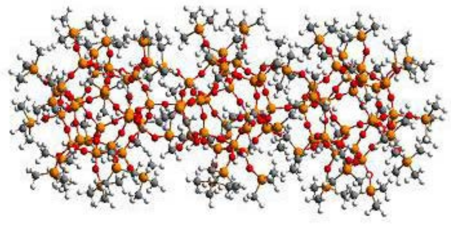

Figure 2. Model structure of a MQ Silicate Tackifier Resin used in silicone PSAs.

Silicone PSAs are produced by blending together a specified ratio of the MQ resin and siloxane polymer. The Resin-to-Polymer ratio (R/P) is one of the most important factors when optimizing the balance of performance properties of a given adhesive. Figure 3 shows the relationship between the R/P ratio and resulting performance properties of adhesion, tack, and shear.

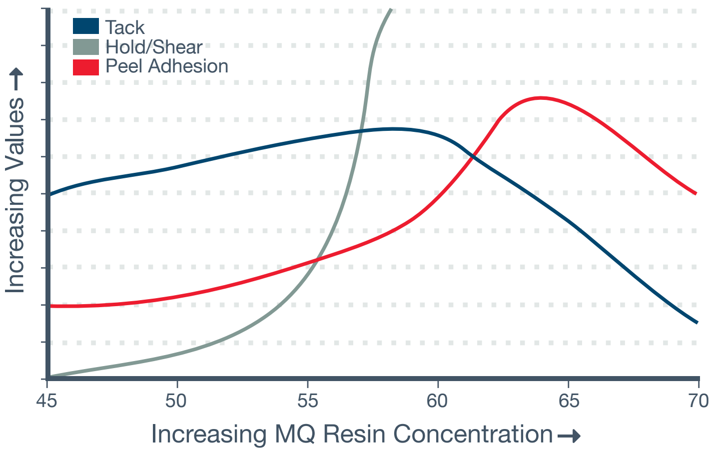

Figure 3. Relationship between the R/P ratio and performance properties of silicone PSAs.

The resin, by its three-dimensional nature, can act as a cross-linker between polymer chains. As additional resin is added to a composition, a more tightly crosslinked network is achieved. A point is reached where sufficient crosslink density provides the cohesive strength required to give substantial resistance to shear under a load. In addition, higher resin levels produce a PSA with increasing peel adhesion strength. The increase in peel adhesion and internal cohesive strength are accompanied by lower tack of the cured adhesive.

The highly viscous to solid-like state of the MQ resin and siloxane polymer often requires that silicone PSAs are produced by blending in a hydrocarbon solvent carrier. The solvent helps to lower the formulation viscosity for ease in the initial manufacturing and subsequently downstream in coating processes. Currently, most commercial silicone PSAs are supplied in aromatic solvents such as toluene and xylene.

Adhesive Cure Chemistry

Although most silicone PSAs will exhibit pressure sensitive behavior immediately after solvent removal, additional crosslinking is done to reinforce the adhesive network. There are two basic cure systems commercially available for silicone PSAs: peroxide-catalyzed free-radical cure and platinum-catalyzed silicon hydride to vinyl addition cure. Many silicone PSAs employ the use of a peroxide-catalyzed (dibenzoyl peroxide) free-radical reaction to achieve the additional crosslink density. Curing of these types of adhesives is completed 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. These radicals primarily attack the organic substituents along the polymer chains to extract protons and generate additional free radicals. The free radicals then combine to form crosslinks as shown below:

1) $C_6H_5C(=O)OO(O=)CC_6H_5 \xrightarrow{\Delta} 2\ C_6H_5C(=O)O\bullet$

2) $C_6H_5C(=O)O\bullet + \equiv SiCH_3 \longrightarrow C_6H_5C(=O)OH + \equiv SiCH_2\bullet$

3) $\equiv SiCH_2\bullet + \equiv SiCH_2\bullet \longrightarrow \equiv SiCH_2CH_2Si\equiv$

The main benefit of the peroxide-catalyzed system is the ability to control properties by addition level of peroxide. The tape producer has the flexibility to use a range from 0 to 4 weight% peroxide. The additional curing with the peroxide results in a more tightly cured PSA. An increase in cohesive strength, as evidenced by performance in shear tests, is observed. The increase in cohesive strength is accompanied by a slight decrease in adhesion and tack. 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 have been introduced which utilize a different type of curing mechanism. These adhesives are cured by a platinum-catalyzed reaction of silicon hydride to vinyl. 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 systems are supplied in hydrocarbon solvents. As the solvent evaporates, the platinum-catalyzed reaction occurs without any generation of catalytic by-products as shown in Figure 4.

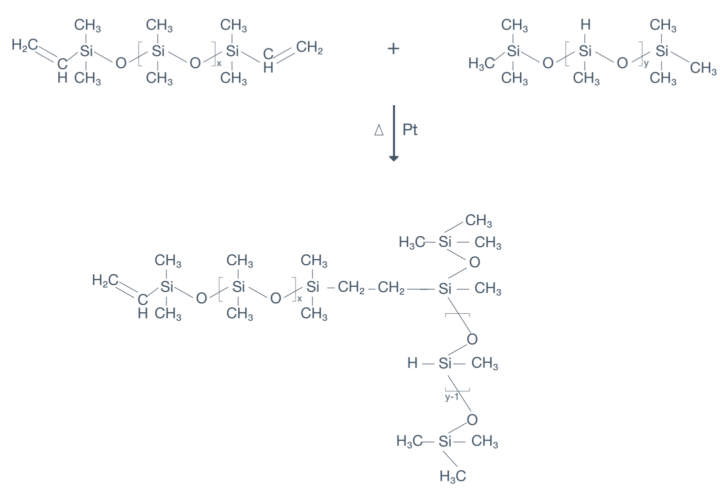

Figure 4. Scheme for the platinum-catalyzed addition cure reaction of silicone PSAs.

The ability of this type of system to be cured at a single, lower temperature offers benefits that are not seen with a peroxide-catalyzed system. These benefits include faster line speeds (or cure time), lower sensitivity to temperature variation, the ability to use substrates with lower thermal stability (PE, PP, etc.), and no generation of volatile by-products.

Another benefit of the platinum-catalyzed silicone system is the fact that it does not inherently need the hydrocarbon solvent for any purpose other than viscosity control. The peroxide-catalyzed system not only needs the solvent for viscosity control, but it is also required to ensure the peroxide remains dissolved within the adhesive bath prior to coating on the web. This advantage for the platinum-catalyzed chemistry has led to the successful commercialization of many solventless silicone systems including silicone release coatings.

Unfortunately, limited success has been made in producing an industrial solventless silicone PSA for tape applications. In the early 1990's, Dow commercialized a VOC compliant silicone PSA that was meant to address the market need for the reduction of solvents. This product was based on the platinum-catalyzed chemistry and showed significant performance advantages such as high peel adhesion, high tack, primer-less adhesion to multiple substrates, and a lower volatile siloxane content. The one disadvantage that it had in comparison to traditional silicone PSAs was its inferior high temperature shear performance. To be commercially viable, a silicone PSA ultimately needs to be able to perform in temperature extremes where an organic PSA fails. This product was eventually removed from the commercial market. As time has moved forward, silicone raw materials have continued to evolve much like any other chemistry. This evolution with time has ultimately expanded the toolbox for the development chemist. Extensive work has led to the development of solventless silicone PSAs that have the tack, adhesion, and high temperature shear performance of common solvent-based silicone PSAs.

Comparative Performance of Solventless PSA Product Family

In recent years, the family of solventless silicone PSAs has expanded into a series of products with broad performance attributes. Figure 5 shows the full range of solventless silicone PSAs offered by Dow today.

The product line covers a span of low to high adhesion/tack performance to address the application needs of protective films, specialty tapes, and electronic assembly. The product offerings can be separated into two categories: 1) High adhesion solventless silicone PSAs (DOWSIL™ 2013, 2014, and 2015 Adhesives) and 2) Low adhesion solventless silicone PSAs (DOWSIL™ 2102 and 2110 Adhesives).

High Adhesion Solventless Silicone PSAs

The basic physical properties of the high adhesion solventless PSAs are summarized in Table 2.

Table 2. Physical properties of high adhesion solventless silicone PSAs.

Property	Unit	DOWSIL™ 2013 Adhesive	DOWSIL™ 2014 Adhesive	DOWSIL™ 2015 Adhesive
Appearance		Clear	Clear	Clear
Physical form		Liquid	Liquid	Liquid
Active content	%	>97	>97	>97
Viscosity at 25°C	mPa.s	8,000-15,000	8,000-15,000	8,000-15,000
Cure system		Platinum	Platinum	Platinum

In some applications, a lower viscosity may be required by customers to produce thin films when using these solventless PSAs. Figure 6 provides a general guidance for the viscosity of DOWSIL™ 2014 and 2015 Adhesives when low levels of heptane are used to dilute the catalyzed adhesive bath prior to coating.

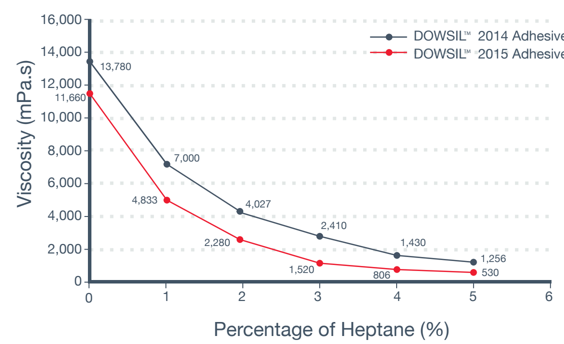

Figure 6. Impact of heptane addition on the viscosity of DOWSIL™ 2014 and 2015 Adhesives.

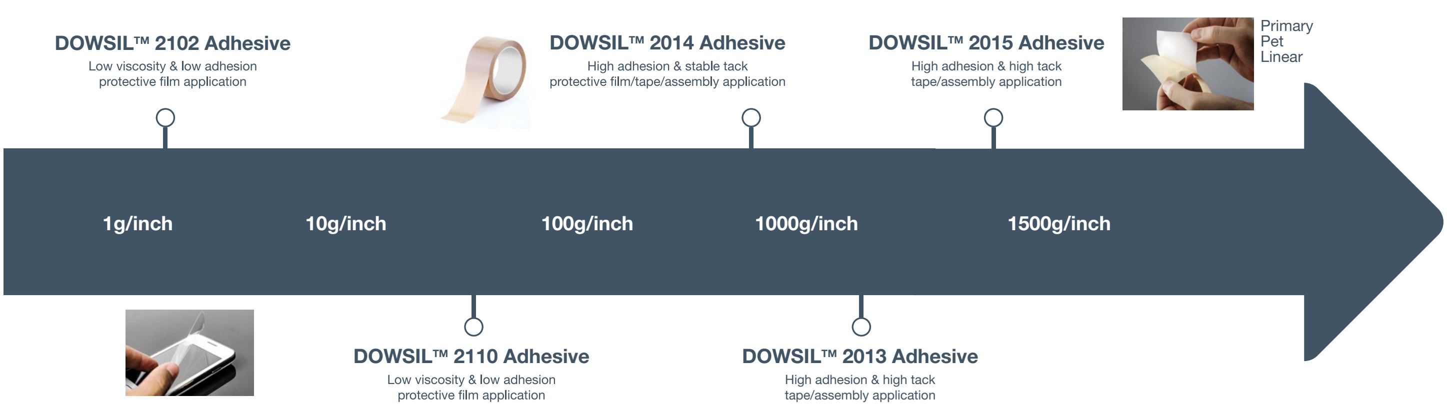

Figure 5. Performance spectrum of Dow's solventless silicone PSA product family.

It should be noted that the solventless silicone PSAs can meet general coaters' requirements for a solvent-free PSA solution. Figure 6 only provides a guidance when special cases require the need for low viscosity processing. The results demonstrate that low levels of heptane can remarkably decrease the formulation viscosity of DOWSIL™ 2014 and 2015 Adhesives.

A performance comparison of the three high adhesion solventless silicone PSAs was conducted against DOWSIL™ 7657 Adhesive. This adhesive is a commercial solvent-based, platinum catalyzed silicone PSA. The 180° peel adhesion performance for the three solventless silicone and single solvent-based adhesives is shown in Figure 7.

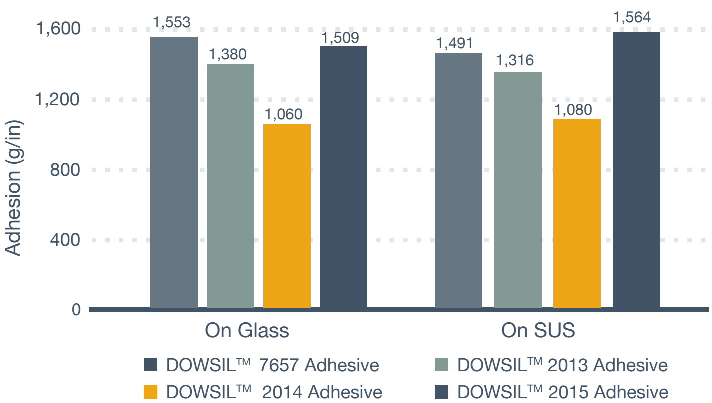

Figure 7. 180° peel adhesion results on glass and stainless-steel (SUS) substrates (40µm thick adhesive on a 50µm polyester backing substrate).

DOWSIL™ 2013 and 2014 Adhesives are lower in peel adhesion than DOWSIL™ 7657 Adhesive, while DOWSIL™ 2015 Adhesive has equivalent adhesion performance to the solvent-based product. Both the solvent-based and solventless PSAs exhibit a similar adhesion performance when laminated on either a glass or stainless-steel substrate.

After the initial measurements, the peel adhesion stability of the tape with room temperature aging was monitored for 2 months to evaluate the long-term performance of the adhesives (Figure 8).

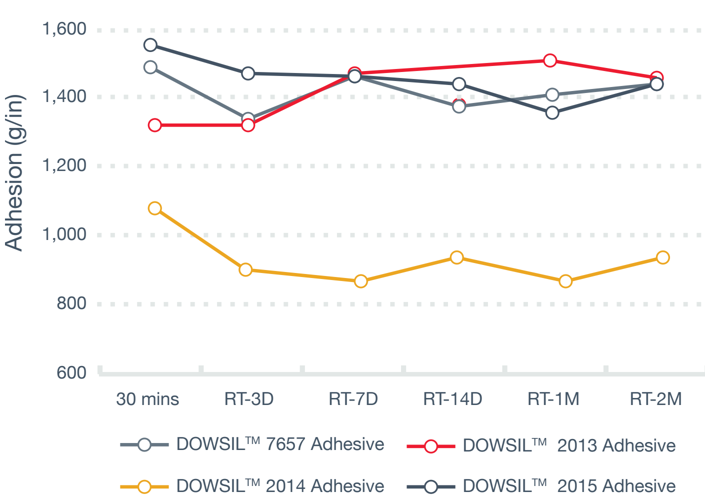

Figure 8. Peel adhesion stability on stainless-steel (SUS) with room temperature aging.

All the solventless adhesives demonstrate an equivalent adhesion stability to that of the solvent-based silicone PSA. DOWSIL™ 2014 Adhesive showed a slight drop of the adhesion within the two-month tracking period while DOWSIL™ 2013 Adhesive showed a slight increase.

Ball tack measurements of the four silicone PSAs show that the solvent-based PSA exhibits a greater ball tack than the three solventless adhesives. In terms of the tack stability, three of the four silicone PSAs show fairly stable ball tack performance after 3 days aging with DOWSIL™ 2015 Adhesive demonstrating a decrease (Figure 9).

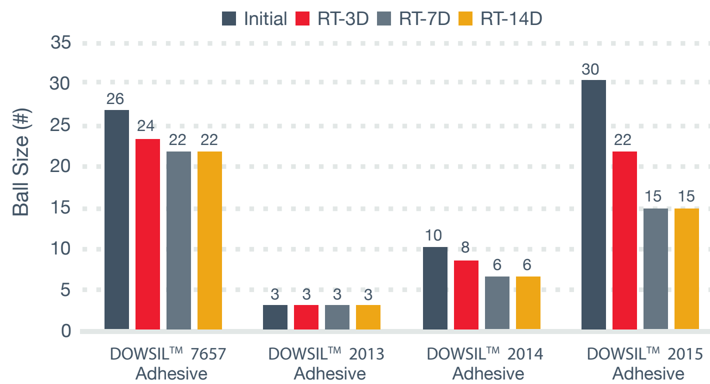

Figure 9. Ball tack and tack stability of the tapes with room temperature aging.

The thermal resistance of the four silicone PSAs was measured through hot and cold peel testing on stainless-steel plates under two thermal aging conditions. The results are shown in Table 3.

Table 3. Heat resistance performance of four silicone PSAs.

Product	Heat Resistance (Hot/Cold Peel) (Ranking 0-5:5 is the best, 0 is the worst)			
	Hot Peel 180°C / 30 min	**Cold Peel** 180°C / 30 min	**Hot Peel** 260°C / 30 min	**Cold Peel** 260°C / 30 min
DOWSIL™ 7657 Adhesive	5	5	5	5
DOWSIL™ 2013 Adhesive	5	5	4	4
DOWSIL™ 2014 Adhesive	5	5	4	4
DOWSIL™ 2015 Adhesive	5	5	3	3

DOWSIL™ 2013 and 2014 Adhesives exhibit the same thermal resistance as DOWSIL™ 7657 Adhesive. DOWSIL™ 2015 Adhesive exhibits much lower thermal resistance than the other three silicone PSAs.

The rheology of the adhesives was evaluated by running dynamic temperature sweeps with 8mm stainless-steel parallel plates. The rheology profiles are shown in Figure 10.

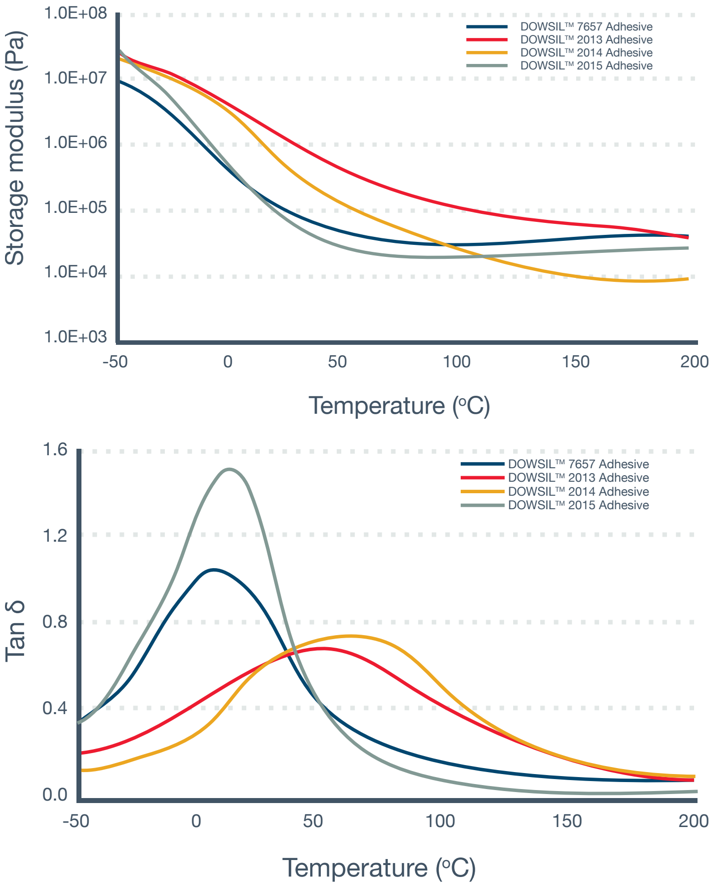

Figure 10. Storage modulus and tan δ comparison of four silicone PSAs.

DOWSIL™ 2015 Adhesive exhibits a similar modulus and tan δ profile to that of DOWSIL™ 7657 Adhesive. DOWSIL™ 2013 and 2014 Adhesives exhibit a higher glass transition temperature (Tg) and lower tan δ maximum than DOWSIL™ 2015 and 7657 Adhesives. DOWSIL™ 2014 Adhesive also has the lowest plateau modulus.

Low Adhesion Solventless Silicone PSAs

Low adhesion solventless silicone PSAs are designed to perform in protective film applications for screen and displays. The basic physical properties of the low adhesion solventless PSAs are summarized in Table 4.

Table 4. Physical properties of low adhesion solventless silicone PSAs.

Product	Unit	DOWSIL™ 2102 Adhesive	DOWSIL™ 2110 Adhesive
Appearance		Clear to slight hazy	Clear to slight hazy
Physical form		Liquid	Liquid
Active content	%	>97	>91
Vicosity at 25°C	mPa.s	1,500 - 2,500	2,500 - 3,500
Cure system		Platinum	Platinum

Additionally, a recommended formulation to target the proper adhesion for protective film applications in given in Table 5.

Table 5. Recommended low adhesion solventless PSA formulations.

Material	Amount / Parts	
DOWSIL™ 2102 Adhesive	100	---
DOWSIL™ 2110 Adhesive	---	100
SYL-OFF™ SL 7028 CROSSLINKER	2.0 - 2.2	1.0 - 1.2
SYL-OFF™ 297 Anchorage Additive	1.5	1.5
SYL-OFF™ 4000 Catalyst	1.8	1.5

Cure conditions (on 50μm PET): 140°C for 2 minutes
Dry film thickness: 10 - 15 μm

Using the recommended formulations in Table 5, the peel adhesion performance of the low adhesion silicone PSAs was conducted on a glass substrate at room temperature and with aging at 70°C / 80% relative humidity (Figure 11).

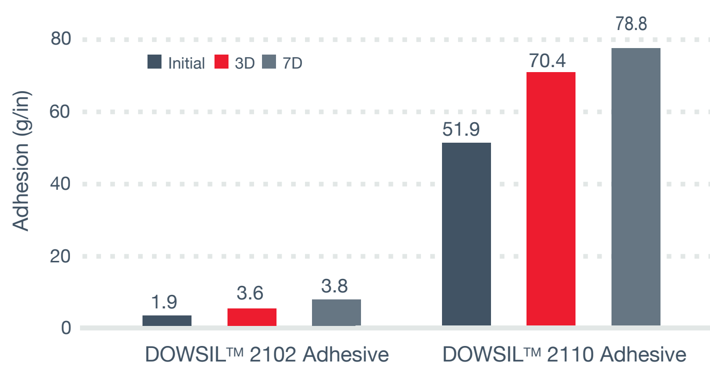

Figure 11. Low adhesion solventless PSA adhesion and 70°C/80% RH aging stability.

The peel adhesion of the recommended formulations was in the range of 1-4 g/in and 50-80 g/in for DOWSIL™ 2102 and 2110 Adhesives, respectively. The peel adhesion for DOWSIL™ 2102 Adhesive remained stable for 7 days while DOWSIL™ 2110 Adhesive showed a slight increase with aging.

In many protective film applications, a combination of low adhesion and high adhesion adhesive blends are commonly used to target tunable adhesion to meet varying performance requirements. Figure 12 provides several examples as a guide for blending adhesives DOWSIL™ 7687 and 2014 Adhesives are representative DOWSIL™ brand adhesives and the ratio is given by weight.

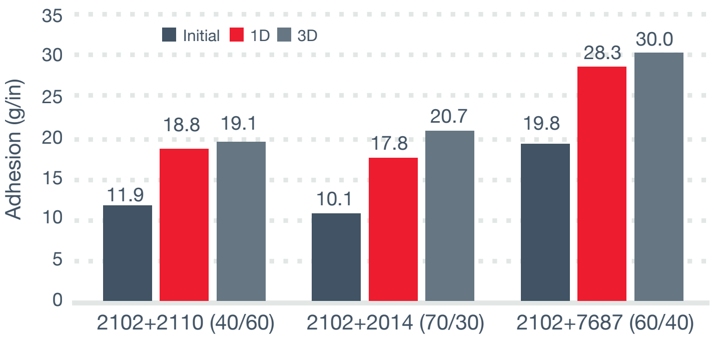

Figure 12. Adhesion and 70°C/80% RH aged stability of low/high adhesion PSA blends.

Blends of the two solventless low adhesion PSA can achieve similar peel adhesion performance when compared to blending with both solventless and solvent-based high adhesion silicone PSAs. All three adhesive blends exhibit an adhesion increase after 1 day of aging then remain relatively stable up to 3 days.

Changing Trends, Future Developments

A number of changing trends in the use of tapes are likely to impact silicone PSA applications. These include the continuing trend away from aromatic solvent-based PSA products, and the increasing demand for assembly tapes that permanently bond electronic parts and reduce process steps. The global plastic usage restriction also requires PSAs that can laminate on alternative substrates, such as paper, rather than a traditional plastic like polyester (PET).

These application trends impact the use of silicone PSAs. The above-mentioned changes create a greater need for adhesives with safer/sustainable materials, lower cure temperature, and superior reliability.

Several developments in silicone PSA technology at Dow are already underway to support some of these transitions and market trends. These include:

- Development of solventless silicone PSAs to provide safe and sustainable adhesives. These products can address novel electronic assembly processes such as permanent bonding and thicker films.
- Continued development of alternative delivery systems for silicone PSAs such as waterborne silicone PSA dispersions.
- Development of lower temperature-curing silicone PSAs for use on temperature-sensitive substrates, such as paper, to minimize the plastic usage in downstream applications.

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