Waterborne Silicone PSA Emulsions

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About Dow

Dow is a materials 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

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. A general property comparison of silicone and organic PSAs is shown in 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 a silicone PSA is based on a polymer filled system. The two main components that determine the final performance profile of the silicone PSA are: 1) a medium to high molecular weight, linear siloxane polymer ("gum") and 2) a highly condensed, silicate tackifier ("MQ") resin[1]. The highly viscous to solid-like state of these components often requires that silicone PSAs are produced by blending in a hydrocarbon solvent carier. The solvent lowers the formulation viscosity for ease in the initial manufacturing and, subsequently, downstream in coating processes. Most commercial silicone PSAs are currently supplied in aromatic solvents such as toluene and xylene.

Waterborne Silicone PSA Emulsions

To meet the global trend on sustainability, the tape market is asking for solvent-free silicone PSAs and/or environmentally friendly solvent silicone PSAs. An emulsion silicone PSA would be favored as the alternative solution versus any given solvent-based system.

Due to the highly viscous and solid-like states of the gum polymer and MQ resin, it has been extremely difficult to emulsify these compositions without some type of processing aide. Past attempts at producing an emulsion silicone PSA often left residual aromatic solvent in the final product or replaced the solvent with a volatile siloxane[2]. These attempts fell short of making a truly solvent-free system and, in the case of the volatile siloxane approach, created secondary issues such as emulsion instability and potential for oven dusting.

Rather than using processing aides to make the emulsification more manageable, process research has shifted focus to studies on the manufacturing of these high viscosity materials through mechanical emulsion processes. Silicone emulsions can be produced with numerous shear devices. The choice of process equipment is dependent on the formulation viscosity of the starting silicone. The common types of mechanical dispersion equipment are listed in Table 2.

Table 2. Commonly used mechanical dispersion technologies for silicone emulsions.

Shear Devices	High Pressure Sonolator	Homogenizer	Rotor / Stator	Change Can
Formulation Viscosity	< 5,000 cP	< 1,000 cP	5,000 cP to Gum	5,000 cP to Gum

The extremely high viscosity of the silicone polymer and MQ resin blend limits the choice of equipment to those that can handle these high viscosity regimes. Intensive process studies at Dow has led to the ability to consistently manufacture a solvent-free, emulsion silicone PSA with a unimodal particle size distribution of Dv(50) around 350 nm and Dv(90) around 700 nm (Figure 1).

Figure 1. Scheme of a typical waterborne silicone PSA emulsion.

Some basic emulsion silicone PSA properties are summarized in Table 3.

Table 3. Typical emulsion silicone PSA physical properties.

Property	Specification
Non-Volatile Content[(1)]	55 - 60%
pH, 25°C	7 - 9
Appearance	White liquid
Viscosity[(2)]	1000 - 5000 cP
Shelf life[(3)]	360 days

[(1)]Non-Volatile content was measured at 105°C for 1 hour.
[(2)]Viscosity was measured at 6 rpm with #62 plate at 25°C.
[(3)]Stored below 40°C/104°F and avoided freezing.

It must be noted that the emulsion silicone PSA properties are tunable based on the initial composition of the silicone phase. Table 3 is only listing the preliminary data for a few specific emulsion silicone PSAs currently produced by Dow.

Laminate Preparation of Emulsion Silicone PSAs

The emulsion silicone PSAs are cured by the addition of a novel dibenzoyl peroxide (BPO) suspension developed by Dow. The PSAs can be formulated by adding the peroxide suspension in an amount of 2 to 4 weight% peroxide compound per silicone solids. The formulated emulsions can be further diluted to 45 weight% solids content to control final PSA coat weights. It has been found that if the solids content is lower than 45 weight%, the wet film may exhibit shrinkage during the drying and curing steps which could result in a poor tape surface.

All the prepared PSA laminates for this paper were based on the addition of 3 weight% peroxide per silicone solids. PSA laminates were prepared by coating the formulated adhesives onto 50 µm primer treated (Table 4) polyester (PET) film using a vacuum coating table with an appropriate application bar to target a 35 to 40 µm dry adhesive thickness. The coated films were placed in an air-circulating oven at 90°C for one minute to remove water followed by 170°C for 3 minutes to cure.

Table 4. Silicone primer formulation used for polyester (PET) film treatment.

Material	Amount / Parts
DOWSIL™ 7499 PSA Primer	100
SYL-OFF™ 7215 PSA Crosslinker	1.5
SYL-OFF™ 297 Anchorage Additive	0.5
SYL-OFF™ 4000 Catalyst	0.5
Toluene	500

Curing condition (On 50 µm PET): 150°C for 45 seconds.
Dry primer thickness: 2-5 µm.

Adhesion and Probe Tack of Emulsion Silicone PSAs

The influence of compositional changes on final tape performance properties was evaluated by modification of the MQ resin. Figure 2 shows the MQ resin type and Resin-to-Polymer ratio (R/P) impact on peel adhesion and probe tack of the emulsion silicone PSA.

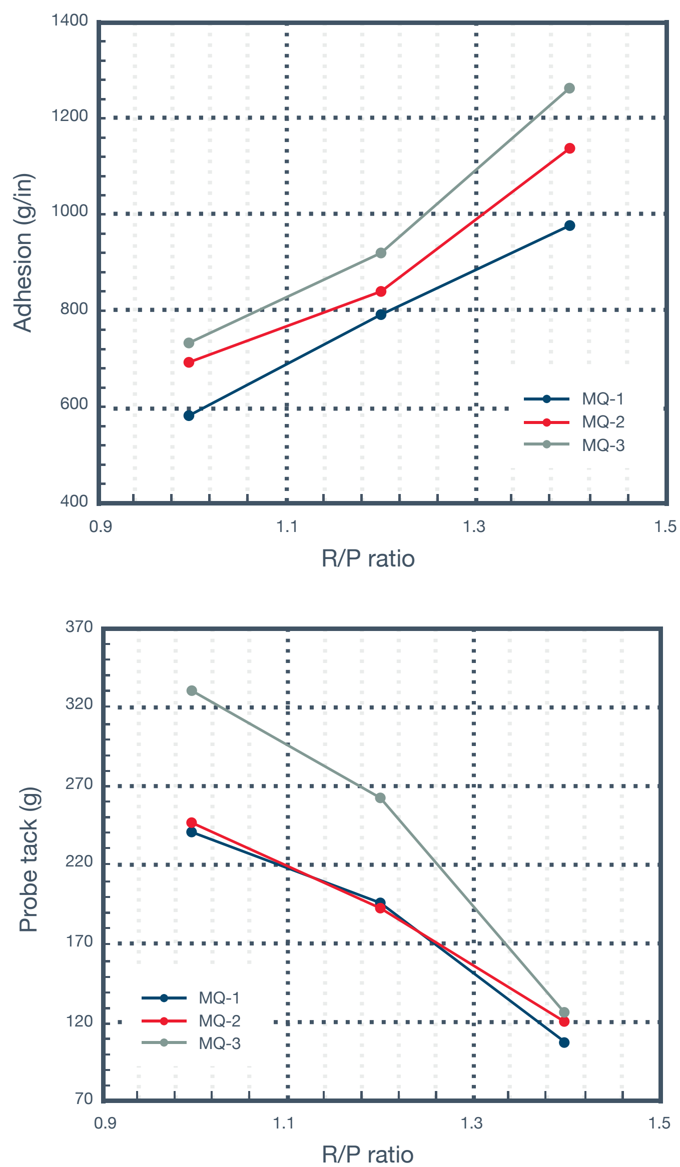

Figure 2. MQ resin type and R/P ratio impact on adhesion and tack performance.

As the R/P ratio was increased for a given MQ resin type, the resulting adhesion increased, and probe tack decreased. This behavior follows trends seen when formulating traditional solvent-based silicone PSAs. Changing the type of MQ resin (MQ-1 → MQ-3) allowed the effective performance level of adhesion and probe tack to be increased at a given R/P ratio. The achievable level of adhesion ranged between 550 – 1300 g/inch and the probe tack reached levels up to 330 grams based on the silicone PSA composition.

Rheological Behavior of Emulsion Silicone PSAs

The rheological impact of changing the R/P ratio for the emulsion silicone PSAs was evaluated by running a dynamic temperature sweep. Figure 3 shows three emulsion silicone PSAs based on R/P ratios of 1.0, 1.2, and 1.4.

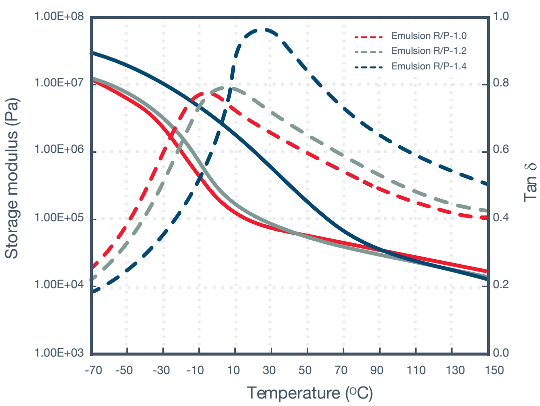

Figure 3. Rheology profiles of emulsion silicone PSAs with R/P ratios of 1.0, 1.2, and 1.4.

All three rheology profiles exhibit a typical silicone PSA rheology window with the plateau modulus in the range of 10^4 - 10^5 Pa. The glass transition temperature (Tg) increases from -23°C to +30°C as the R/P ratio increases from 1.0 to 1.4. The corresponding plateau modulus decreases with the higher concentration of MQ resin in the PSA matrix.

A comparison of the rheology behavior between a solvent-based and emulsion silicone PSA was carried out using the same testing conditions. The solvent-based silicone PSA was formulated with the same raw materials and composition as the emulsion silicone PSA. The results are shown in Figure 4.

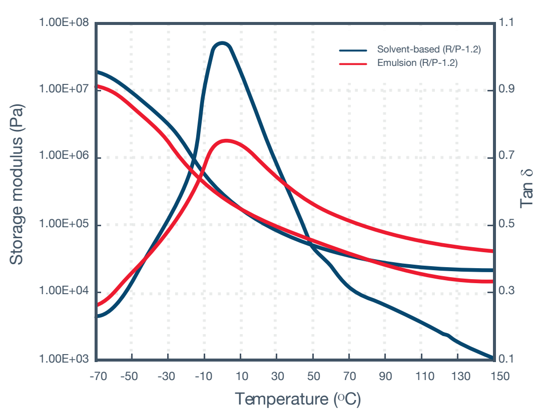

Figure 4. Rheology profile comparison of solvent-based and emulsion silicone PSAs.

The two PSAs exhibited a similar rheology profile with Tg at ~0°C. However, the tan δ value and plateau modulus were higher for the solvent-based PSA. This was an indication that the two PSAs had a difference in crosslink density, with the emulsion PSA having a relatively weaker degree of cure. The surfactant in the emulsion PSA could be an additional contributing factor in the differences seen between technology types.

Performance Comparison of Solvent-based and Emulsion Silicone PSAs

As the emulsion silicone PSA is a new product in the PSA market, the initial application would likely target masking tapes. A performance comparison of two select emulsion silicone PSAs was conducted against two common solvent-based silicone PSAs (DOWSIL™ 7366 and 7268 Adhesives) used in masking applications. The results are shown in Figure 5.

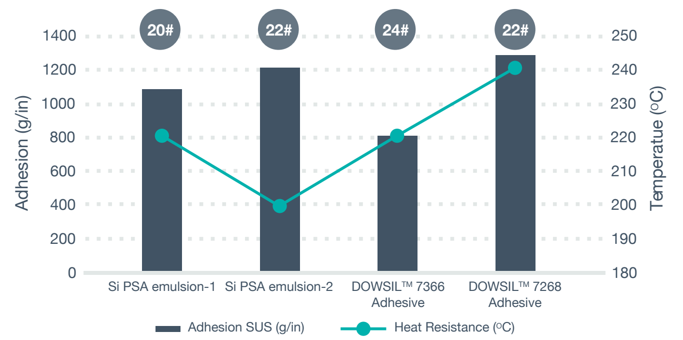

Figure 5. PSA performance comparison of solvent and emulsion silicone PSAs.

The emulsion silicone PSAs have similar adhesion and ball tack performance as the selected solvent-based silicone PSAs. The upper heat resistance for the emulsion silicone PSAs was 220°C. For the selected solvent-based silicone PSAs, DOWSIL™ 7268 Adhesive slightly outperformed the emulsion silicone PSAs. However, the overall emulsion silicone PSA performance was very close to the solvent-based silicone PSAs. The study gives promise that the emulsion silicone PSA can be applied in masking tape applications.

An overall emulsion silicone PSA (hollow dots) performance map is shown in Figure 6. Two solvent-based peroxide-cure (DOWSIL™ 7388 and 7268 Adhesives) and one solvent-based platinum-cure (DOWSIL™ 7657 Adhesive) silicone PSAs are shown for reference.

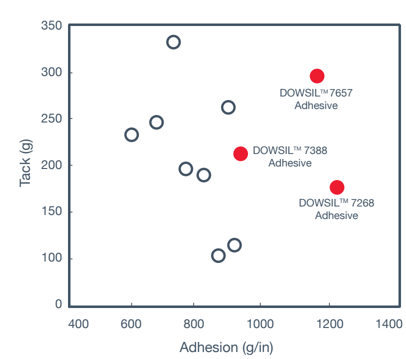

Figure 6. Emulsion silicone PSA performance map.

A broad range of adhesion and tack performance can be achieved by the emulsion silicone PSAs by effective control of the base silicone composition. This allows the technology to target the varied performance requirements desired in many masking applications.

Blending with Emulsion Acrylic PSAs

The delivery form of the emulsion silicone PSA allows for the possibility of new downstream applications where the PSA can be blended with other organic PSA emulsions. It is well known that silicone materials by nature are generally incompatible with most organic PSAs. Simple blending of the non-aqueous systems will commonly result in visual phase separation of the bulk sample. On the contrary, the emulsion form of the silicone PSA can allow for the formation of a compatible system. The combination of suitable drying and curing processes can result in a continuous hybrid PSA film in the nano-to-micro size scale.

Emulsion acrylic PSAs can achieve high adhesion but often exhibit unstable adhesion force as the sample ages. Figure 7 shows the rate of change in adhesion force of an emulsion acrylic PSA by blending with different levels of emulsion silicone PSA.

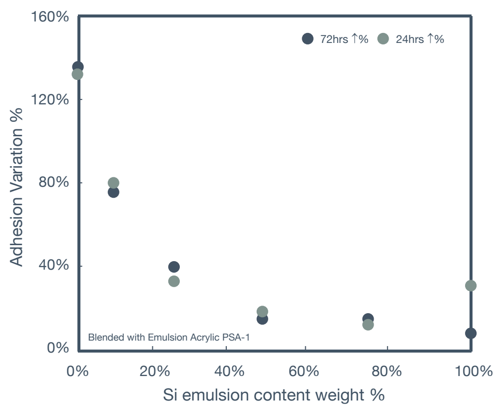

Figure 7. Adhesion stability of emulsion acrylic/silicone PSA blends.

The pure acrylic PSA adhesion increased by more than double after aging on a stainless-steel panel for 24 hours. However, the adhesion force becomes more stable by blending with an emulsion silicone PSA. While the absolute adhesion level of the acrylic PSA may decrease with increasing levels of silicone PSA, these types of blends may address applications that require stable adhesion with some sacrifice of starting adhesion force.

Depending on the acrylic PSA composition, blending with an emulsion silicone PSA can boost the adhesion, enhance the aging stability, and improve the thermal resistance.

Table 5. Thermal resistance performance of emulsion acrylic/silicone PSA blends.

	Emulsion acrylic/silicone PSA ratio			
Blended with Emulsion Acrylic PSA-2	100/0	50/50	30/70	0/100
Heat Resistance 30 minutes @ 180°C	Adhesive residual	Light ghosting	Pass	Pass

In Table 5, it demonstrates that the thermal stability of a second emulsion acrylic PSA was improved with the stepwise addition of emulsion silicone PSA when evaluated by hot/cold peel adhesion testing. The adhesion force and aging stability of the emulsion acrylic PSA was also improved as shown in Figure 8.

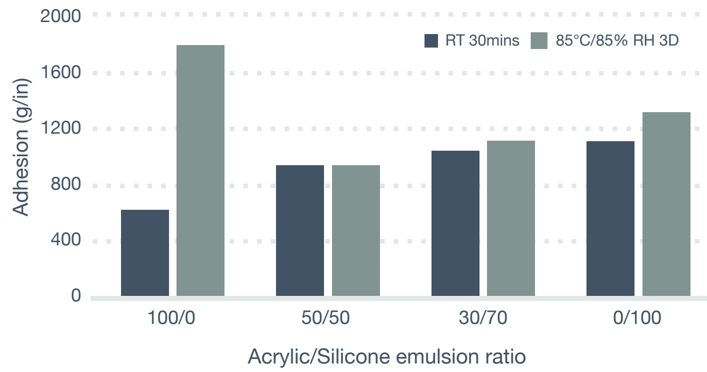

Figure 8. Aged adhesion stability of emulsion acrylic/silicone PSA blends.

The selected emulsion acrylic PSA exhibited ~600 g/in of adhesion which increased to 1800 g/in after aging at 85°C/85% RH conditions for 3 days. By blending in 50 parts of the emulsion silicone PSA, the initial adhesion increased to ~900 g/in with improved stability after aging.

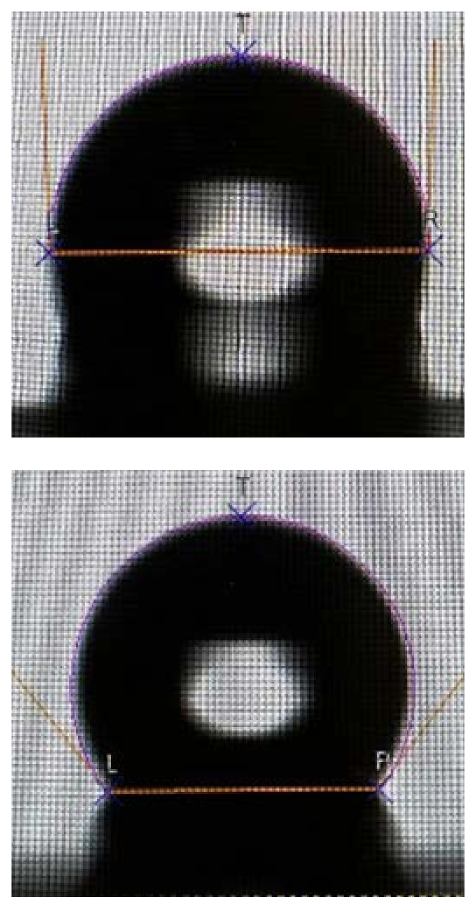

Figure 9. Water contact angle (WCA) on films of emulsion acrylic/silicone PSA blends – Pure acrylic (top); 50/50 (bottom).

As shown in Figure 9, the water contact angle (WCA) on the emulsion acrylic/silicone PSA film increased over that of the pure acrylic PSA film. In some cost sensitive applications, a tape may need to bond to a low-energy surface. A pure acrylic PSA masking tape may not bond to the surface while a pure silicone PSA may not be affordable. The emulsion acrylic/silicone PSA blends could offer a price competitive solution to address these applications.

Summary

A series of waterborne silicone pressure sensitive adhesive emulsions were prepared via a mechanical dispersion process in Dow. The PSA composition and processing conditions were studied systematically to yield an emulsion silicone PSA which performed comparably to traditional commercial solvent-based silicone PSAs. The new environmentally sound silicone PSAs reduce the need for undesirable solvents used in the incumbent solution-based silicone PSAs while still maintaining the inherent benefit of a silicone PSA.

Depending on the starting silicone composition, the emulsion silicone PSAs can achieve up to 1200 g/in of adhesion and 300 grams of tack. The PSA films can also hold up to 220°C of thermal resistance. The adhesion and tack performance trends follow the same formulating rules observed with solvent-based silicone PSAs. A higher R/P ratio leads to higher adhesion and lower tack. However, changing the MQ resin type was found to result in an overall improvement in both adhesion and tack performance.

Additionally, hybrid formulations with organic emulsion PSAs can be prepared more practically via simple blending with the emulsion silicone PSA. Emulsion acrylic PSAs can gain improved adhesion stability, thermal resistance, and low energy surface bonding by blending with an emulsion silicone PSA. These blends offer a competitive window between acrylic and silicone PSAs based on performance and cost.

The development work and resulting emulsion silicone PSAs provide the tape and film market with much safer materials by eliminating solvent usage with a more sustainable solution.

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).

The 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 emulsions.
- Development of organic/silicone PSA hybrids to combine the technical advantages of both types of adhesives into a single solution.

Literature Citation

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. Kosal, Jeffery Alan. Silicone Pressure Sensitive Adhesive Compositions. US 6,545,086 B1. April 8th, 2003.

Acknowledgements

The authors would like to thank Qiangqiang Yan and Zheng Zhang for their help in the mechanical dispersion process and gathering of data for this paper.

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