Silicone Release Coatings for the Pressure Sensitive Industry – Overview and Trends

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Part 1 – An Introduction to Silicone

The Versatile Nature of Silicone

Silicone applications are diverse and essential to many industries. The inorganic nature of silicone comes from a semi-organic form of silicon known as silicone or organosiloxane polymer. The initial synthesis and use of silicones as oils and resins began in the 1940s. For 60 years, Dow Corning has dedicated itself to silicone industry development, and silicone applications have now expanded into almost every market.

Various applications involving synthetic materials have utilized silicone technology. This has been possible because of the versatile nature of silicones, which are available as low-molecular-weight volatile liquids as well as high-molecular-weight fluid-like gums, solid resins and cured elastomers. The organosiloxane polymer, more commonly known as polydimethlysiloxane (PDMS), is shown below. Figure 1 is a molecular simulation of the PDMS polymer, while Figure 2 is dimethyl silicone resin.

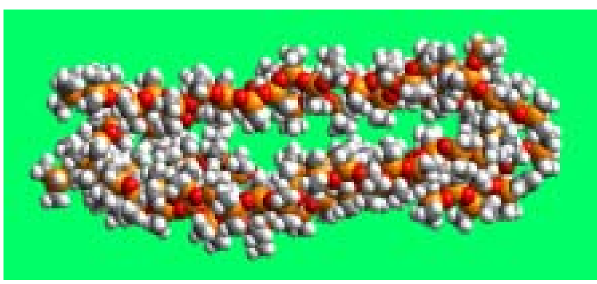


Figure 1 – PDMS Polymer.

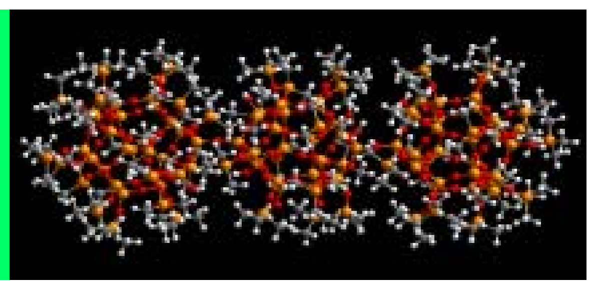


Figure 2 – Dimethyl Silicone Resin.

Silicones can perform as sealants, lubricants, surfactants, rubbers, coatings and adhesives. In addition, silicones have become essential, and even irreplaceable, ingredients in many applications. This is because silicone has unique physico-chemical properties compared to other materials. (See Table 1.)

Table 1 – Silicone Forms and Properties.

Fluids	Elastomers	Resins
Properties		
Heat stable	Elastic/stretchable	Hard/tough/solid
Low vapor pressure	Bounce	Oxidatively stable
High flash point	Retraction	Rigid
Flexible and flowable		
Applications		
Surfactant	Sealants	Coatings
Damping fluids	Rubber molded parts	Paints
Lubricants/release agents	Release coatings	Polishes
Water repellent additives	Gaskets	Laminates/finishes
Cosmetic additives	Adhesives/PSAs	Adhesives/PSAs

Structure and Characteristics

Silicone has been recognized as one of the pressure sensitive industry's key materials for the design of release coatings and pressure sensitive adhesives. The reasons range from the material's distinctive basic siloxane molecular structure and bond strength to its intrinsic surface properties and viscoelastic characteristics. Table 2 shows that the semi-organic molecular siloxane bond provides a highly flexible backbone with large bond angles, long bond lengths and extreme freedom of rotation. The energy required for bond rotation is near zero. Its notable viscoelastic characteristics were often used as a standard material for rheology testing. The freedom of rotation allows for the siloxane polymer orientation, a helix polymeric structure consisting of an inorganic Si-O-Si backbone (high surface energy) with a pendant methyl group (low surface energy) shown in Figures 1 and 2. The pendent methyl groups form a regular, apolar, hydrophobic arrangement of low intermolecular interaction and unique surface properties.

Table 2 – Molecular Characteristics of Polydimethylsiloxanes.

Energy of Rotation About Bonds		
Silicone-to-oxygen	Polydimethylsiloxane	→ 0 kJ/mol
Carbon-to-carbon	Polystyrene	13.8 kJ/mol
	Polytetrafluoroethylene	19.7 kJ/mol
Bond Angles		
Si-O-Si	$[(CH_3)_2SiO]_4$ at -50°C	145º
	Hexamethyldisiloxane	145-150º
O-Si-O	$[(CH_3)_2SiO]_4$ at -50°C	109º
C-O-C	Dimethyl ether	111º
C-C-C	Propane	112º
Bond Lengths		
Si-O	Hxamethyldilsioxane	0.163 nm
Si-C	$[(CH_3)_2SiO]_4$ at -50°C	0.192 nm
C-O	Dimethyl ether	0.142 nm
C-C	Propane	0.154 nm
Bond Energies		
Silicon-to-oxygen		443 kJ/mol
Silicone-to-carbon		326 kJ/mol
Carbon-to-carbon		356 kJ/mol

In addition, the methyl groups of PDMS are spread out at the interface, yielding a typically low surface energy (20 to 23 dyne/cm for a cured PDMS film) and inert properties. The low solubility parameter of PDMS shows immiscibility to most organic polymers and organic-substituted methlysiloxanes. However, the substitution of methyl with other organic groups provides modified reactivity, adhesion, surface energy, thermostability, hydrophilicity, etc. Some organo-functional groups, such as silanol, Si-H and Si-vinyl, provide robust reactions for silicone networking under controlled temperature with a catalyst.

The resulting properties of this unique molecular structure are summarized in Table 3. When we apply silicone in the pressure sensitive industry, formulated silicone compounds can act both as release agents for most organic adhesives and as pressure sensitive adhesives. Three major requirements for these functions are: 1) the ability of the silicone polymer to wet nearly any substrate surface, 2) crosslinkable siloxane polymer to make available a non-flowable cured film for various process needs and 3) appropriate viscoelastic behavior when modifying the structure of the siloxane network or incorporating silicone resin to adjust peeling release force, tack, adhesion and cohesive strength of the adhesive.

Commercial silicone release products include a PDMS base and a fluoro-alkyl substituted polysiloxane release coating. The latter is used as a release liner for silicone-based PSAs. Dow Corning offers industrial-grade and medical-grade PSAs for various applications.

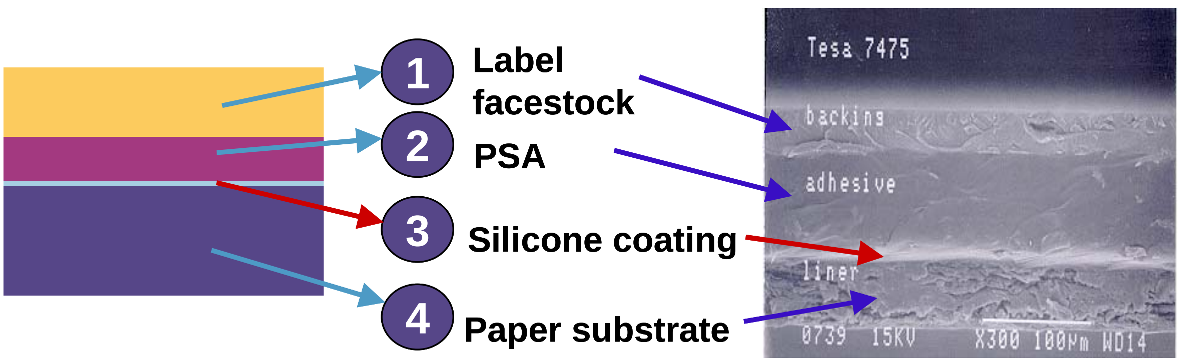
Table 3 – Physical-Chemical Properties of Polydimethlysiloxane Fluid

Properties	**Value**
Low surface characteristics (PDMS)	
• Surface tension at 20ºC	20.4
• Critical surface tension of wetting	24 mN/m
Low glass transition temperature, Tg	
• PDMS	-123ºC
High gas permeability	
• Highest permeability coefficient for N2 and O2	
Flowability to form a film and excellent low-temperature resistance	
• Crystallized polymer	Tc = - 90ºC
• Low pour point	Tm = - 50ºC
Excellent viscoelasticity behavior	
• Unique phase transition for polymer and resin	
• Poisson's ratio of cure network near 0.5	
• Crosslinkable siloxane network at RT or controlled temperature cure	
Lubricating, antifoaming, water repelling and release	
• Lowest surface share viscosity	
Constant physical properties within a wide temperature range in air	
• Very good thermal stability from strength of Si-O-Si linkage	
• Excellent stable dielectric properties	
Good UV and oxidative stability	
• Low UV absorption from methyl groups	
Chemical inertness to many substrate	
• Low solubility parameter	15 $(MPa)^{1/2}$
Transparency of polymer and rubber	
Biocompability	

Release Coating Uses and Functions

Release coating is an enabling technology that allows you to deliver a product identification label or an adhesive to bond two materials together. Other uses are to facilitate handling of materials, including industrial materials and food goods. Silicone release coating was developed by Dow Corning in mid-1950. Silicones remain the most commonly used release agent for pressure sensitive adhesive applications. A release liner with a thin-layer coating of a cured siloxane polymer is an essential feature of a typical self-adhesive label construction. The ultra-thin and uniform silicone coat (approximately 0.4 to 1 µm) is essential to the quality of the release behavior.

The release liner function is to ensure the specific adhesion between the silicone surface and the adhesive so the laminate is held together and can be peeled apart by hand or a specified automatic-equipment force. The release layer also maintains a stable bond with the substrate under any storage and application condition. Figure 2 shows the construction of *Tesa*® 7454, a commercial tape composed of a glassine paper, silicone layer, acrylic adhesive and plastic tape backing.



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