Silicone sealants and adhesives as used in the construction industry were introduced approximately forty years ago, and many of the silicones applied in the early days are still performing today. Products are available in a variety of forms, from paste-like materials to flowable adhesives. Both single- and multi-component versions are available, each with several different cure chemistries.

The commercial importance of silicone sealants and adhesives is based on their unique combination of properties that permit them to satisfy important needs in a broad variety of markets. These properties include excellent weather and thermal stability, ozone and oxidation resistance, extreme low temperature flexibility, high gas permeability, good electrical properties, physiological inertness and curability by a variety of methods at both elevated and ambient temperatures. Because of their low surface energy, they wet most substrates, even under difficult conditions, and when formulated with suitable adhesion promoters, they exhibit very good adhesion. These unique characteristics are the result of a scientific endeavour to combine some of the most stable chemical and physical attributes of the inorganic world with the highly utilizable aspects of organic materials.

A qualitative list of the features of siloxane polymers that contribute to the unique combination of properties of silicone sealants and adhesives relevant in construction applications is given in Table 1. Almost all these inherent attributes are a consequence of four fundamental aspects: the low intermolecular forces between dialkylsiloxane molecules, the dipolar nature and the strength of the siloxane bond and the flexibility of the siloxane backbone.

Probably the most important properties of silicone sealants for construction are durability and adhesion.

Table 1. Silicone Attributes Contributing to Durability

<table>
<thead>
<tr>
<th>Sealant Property</th>
<th>Silicone Attribute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent substrate wetting (adhesion)</td>
<td>Low surface tension</td>
</tr>
<tr>
<td>High water repellence</td>
<td>Low surface tension</td>
</tr>
<tr>
<td>Excellent flexibility</td>
<td>Low glass transition temperature</td>
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<tr>
<td></td>
<td>Large free volume</td>
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<tr>
<td></td>
<td>Low apparent energy of activation for viscous flow</td>
</tr>
<tr>
<td></td>
<td>Low activation energy of Si-O-Si bond rotation</td>
</tr>
<tr>
<td>Small temperature variation of physical</td>
<td>Configuration of siloxane polymer chain and small interaction between methyl groups</td>
</tr>
<tr>
<td></td>
<td>Low activation energy of Si-O-Si bond rotation</td>
</tr>
<tr>
<td>Low reactivity</td>
<td>Configuration of siloxane polymer chain and small interaction between methyl groups</td>
</tr>
<tr>
<td>High gas permeability</td>
<td>Large free volume</td>
</tr>
<tr>
<td></td>
<td>Low activation energy of Si-O-Si bond rotation</td>
</tr>
<tr>
<td>High thermal and oxidative stability</td>
<td>High Si-methyl bond energy</td>
</tr>
<tr>
<td>Ultraviolet light resistance</td>
<td>High Si-O bond energy</td>
</tr>
</tbody>
</table>
Adhesion

Although the primary function of sealants is to seal, in most applications they cannot provide this function without proper and durable adhesion to the substrate(s). Furthermore, in many applications, it is difficult to distinguish between an adhesive and a sealant. For example, structural silicone adhesives are used in the building construction industry owing to their sealing, adhesive and elastomeric properties, as well as their resistance to harsh environmental conditions.

The type of application dictates the adhesion requirements. For instance, sealants and adhesives for general use are expected to achieve primerless adhesion to a broad variety of substrates.

Siloxane polymers spread easily on most surfaces as their surface tensions are less than the critical surface tensions of most substrates. This thermodynamically driven property ensures that surface irregularities and pores are filled with sealant or adhesive, giving an interfacial phase that is continuous and without voids. Thus, maximum van der Waals and London dispersion intermolecular interactions are obtained at the silicone-substrate interface. However, these initial interactions are purely physical in nature. Theoretically, these physical intermolecular interactions would provide adhesion energy on the order of several mJ/m². This would be sufficient to provide some basic adhesion between the adhesive and the substrate. However, the energy of adhesion required in many applications is on the order of kJ/m². Therefore, physical intermolecular forces across the interphase are not sufficient to sustain a high stress under severe environmental conditions. However, chemisorption also plays an important role in the adhesion of reactive silicone sealants and adhesives; thus, physisorption and chemisorption both account for bond strength [1].

Obviously, the ideal silicone adhesive or sealant is one that is self-priming; that is, the adhesion promoter is included in the formulation and is generally part of the curing reaction system. This is the most common type of commercial silicone sealant or adhesive, as it often provides adhesion without the need of a complicated pretreatment procedure such as priming, corona- or plasma-treatment. However, even with self-priming systems, proper cleaning of the substrate prior to application is required to eliminate weak boundary layers and to achieve strong and durable adhesion.

Durability

Properly formulated silicone sealants and adhesives exhibit outstanding durability in a variety of environments. They are known for their high movement capability; their excellent resistance to ultraviolet light, high temperature and ozone; their low water absorption and low temperature flexibility, as well as their ability to form strong chemical bonds to the surface of typical construction and industrial substrates [2]. The outstanding UV stability of silicones is derived from the bond strength of the silicon-oxygen linkages in the polymer chain, as well as the absence of any double-bond or other ultraviolet (UV) light-absorbing groups.

The principal environmental factors acting on a sealant or adhesive in outdoor exposures are:
- Temperature extremes (high and low)
- Water
- Solar radiation (UV and IR)
- Oxygen/ozone
- Corrosive gases (sulphur dioxide, nitrogen oxides)
- Mechanical stress

For radiation energy to initiate chemical changes, the molecules of the material in question must absorb it. Silicones absorb very little ultraviolet radiation in the 300-400 nm region, which is the wavelength range that causes problems with most other polymers at, or near, ground level. When irradiated under conditions of natural photo-aging, silicones are slowly oxidised. The oxidation of the hydrocarbon side-groups results in the formation of carbonyl groups [3-4-5-6]. Since carbonyl groups do not interact strongly, the oxidation has little effect on the mechanical properties of the sealant or adhesive. This is consistent with the fact that, even after 20 years of outdoor weathering in sunny climates, silicone elastomers show comparatively little change in physical properties [7-8].

Under natural weathering conditions, the effects of oxygen and ozone are inextricably connected to those of elevated temperatures and sunlight. At room temperature, oxidation by oxygen is not noticeable. The excellent oxidation resistance of silicones is a consequence of the dipolar character of the siloxane backbone. The positively polarised silicon atom acts as an electron drain for the methyl group, rendering it less susceptible to oxidation [9]. Oxidation in air generally becomes noticeable above 200ºC, resulting in cleavage of the Si-C bond. However, one can raise the upper service temperature by using suitable oxidation inhibitors.

Changes in the physical properties of silicones under artificial or natural weathering conditions, involving alternating periods of wet and dry conditions, are mainly due to the physical effects of water [10]. Since the hydrolysis reaction is reversible, some of the siloxane bonds that were ruptured by hydrolysis are formed again by the condensation of silanol groups upon drying [11]. Thus, during alternating periods of wet and dry conditions, a relatively small number of siloxane bonds in the bulk of the sealant or adhesive are constantly broken and reformed.

Silicone sealants and adhesives show excellent resistance to the combined effect of the key weathering factors: water, heat and ultraviolet light [12-13]. Compared to organic sealants and adhesives, silicones are more thermally stable, perform over a wider range of temperatures, have a higher movement capability and are less susceptible to fatigue resulting from cyclic mechanical strain. They are also more resistant to UV light as well as oxygen and ozone attack. They are also known for their low water absorption and the ability to form strong chemical bonds to typical construction substrates.

A weaker aspect of the environmental stability of silicones is their susceptibility to hydrolysis reactions, particularly at the extremes of acidity or alkalinity and at elevated temperatures. Exposure to strong acids and bases as well as to super-heated steam are detrimental to the stability of silicone sealants. Under natural weathering conditions (involving small amounts of water incorporated in the bulk of the sealant or adhesive), mass action effects keep the hydrolysis reaction within limits, a condition much aided by the low water wettability of the siloxane polymer.

**Applications**
The construction industry represents the largest market segment for silicones. Silicone
Sealants, primarily as one-part room temperature vulcanisable (RTV) products, are widely used by the construction industry for applications such as sealing building and highway expansion joints, general weatherproofing of joints in porous and nonporous substrates, sanitary joints around bathroom and kitchen fixtures, as well as fire-rated joints around pipes, electrical conduits, ducts, and electrical wiring within building walls and ceilings. In a variety of applications, silicone sealants also perform the functions of an adhesive (i.e., they act as structural sealants). For example, silicones are used in structural glazing, where the cured sealant becomes part of the overall load-bearing design, or in insulating glass secondary seals, which structurally bond two panes of glass together. Structural glazing is the application that most importantly is enabled by the outstanding durability of silicone sealants.

Structural silicone glazing (SSG) is the method of bonding glass, ceramic, metal, stone or composite panels to the frame of a building by using the bond strength, movement capability and durability of a silicone structural sealant. Figure 1 shows the Burj-Al-Arab hotel in Dubai as one example of the many exceptionally well-designed buildings sporting silicone structural glazing façades.

![Burj-Al-Arab Hotel](image)

**Figure 1. Burj-Al-Arab Hotel, Dubai; a tribute to the use of structural glazing silicone adhesive in a high-rise façade.**

Because of the elastomeric character and the chemical adhesion of silicone structural bonding seals, SSG design concepts offer a number of performance benefits [14]:

- Effective air- and weather-sealing of the facade
- Improved thermal and sound insulation
- Protection of the supporting structure from the elements by a durable glass skin
- Increased rigidity and stability of the facade, resulting in the ability to withstand higher wind-loads
- Ability to absorb differential movements between glass and building frame, resulting
in superior performance of SSG facades during seismic events

For the facade designer, SSG provides the possibility to construct facades with free-flowing, uninterrupted bands of glass or smooth, uninterrupted total glass surfaces.

The SSG technique uses both the adhesive and sealing properties of structural silicone sealants. Medium modulus, good elastomeric properties, and excellent, highly durable adhesion are important to support the weight of glazed panels and to resist wind load, while simultaneously being able to absorb differential movements between dissimilar materials induced by thermal fluctuations, seismic loading or other forces. It is essential for the success of SSG design to use a structural sealant and not a rigid adhesive because the structural seal needs to resist both loads and movements without creating unduly high stresses at the glass interface or failing cohesively [15]. Since the interface between structural seal and glass is directly exposed to sunlight, the sealant must develop extremely UV-stable bonds to the glass substrate to achieve an expected service life of 30 to 50 years. Because of this requirement, only silicone sealants are allowed for structural glazing applications.
References


This article has been published in the chapter “Silicones in Industrial Applications” in Inorganic Polymers, an advanced research book by Nova Science Publishers (www.novapublishers.com); edited by Roger De Jaeger (Lab. de Spechtochemistry Infrarouge et Raman, Univ. des Sciences and Tecn. de Lille, France) and Mario Gleria (Inst. di Scienze e Tecn. Molecolari, Univ. di Padoa, Italy). Reproduced here with the permission of the publisher.