SEALANTS

1. Introduction

A sealant is a material that is installed into a gap or joint to prevent water, wind, dirt, or other contaminants from passing through the joint or gap. This joint or gap may be a fixed joint, but is often an expansion joint which may also be called a working joint. Sealants, which can also be defined by how they are tested, are rated by their ability to stretch, twist, bend, and be compressed while maintaining their bulk properties so that they do not tear apart under stress. A most important rating of a sealant in many applications is the movement ability of the sealant. The adhesion required of a sealant is simply the strength to hold the sealant in position as it is stressed and strained.

Adhesives are used to transfer loads and are typically designed with much higher tensile and shear strengths than sealants. The most important rating of an adhesive in many applications is the determination of how much load it can handle. Some sealants are used as adhesives and some adhesives as sealants and thus arises the occasional blurring of their roles. If the material's primary function is the exclusion of wind, water, dirt, etc, it is a sealant.

2. Performance Characteristics

2.1. Movement Capabilities. The movement capability of a sealant is the amount of displacement the sealant can endure in extension or compression without failing. One standard test used to rate movement capability is ASTM C719, Standard Test Method for Adhesion and Cohesion of Elastomeric Joint Sealants Under Cyclic Movement. This test subjects a sealant to cyclic movement of 3.2 mm/h under alternating conditions of high and low temperatures as well as water immersion. The movement capability is typically reported at $\pm x\%$, where the positive value refers to extension and the negative value to compression. A sealant with $+50/-25\%$ rating can be repeatedly extended by 50% or compressed to 25% of the original joint width after initial cure. In general, sealants with lower modulus of elasticity can handle higher movements.

Sealants can be broadly divided into classes according to the amount of movement they can successfully handle. High performance sealants, eg, silicones, urethanes, polysulfides, and silicone hybrids, can typically handle movements of 25% or higher. Medium performance sealants, eg, some acrylics, can handle movements of 10–25%. Low performance sealants, eg, butyls, putties, and caulks, accommodate movements $<10\%$. Movement ratings are commonly reported by sealant manufacturers, but these ratings are dependent on the substrate, cure time, rate of movement, etc. Any manufacturer's literature must be interpreted with care, some have exaggerations and some manufacturers' literature, for instance, may only test their sealant dry, at room temperature, and claim a large movement ability. If an application in question has a working joint that will be exposed to high and low temperature as well as water, the sealant to be specified should be tested to the full rigors of the ASTM C719 test. Such testing should be done by an independent laboratory validated by an independent validating organization, such as Sealants Weatherproofing and Restoration

Institute (SWRI). Outside the United States, other countries also have national validating bodies. An international norm (ISO 11600) for sealant movement capability both on glass (G) and construction materials (F) has been issued in 2002 [Reference number ISO 11600:2002 (E)]. This norm resulted from the combination of several ISO norms: the most significant ones being ISO 9047 and ISO 11431. For 25% movement capability, the sealant needs to pass several cycles of 25% compression at 70°C followed by 25% extension at −20°C (ISO 9047) and needs to withstand 100% elongation during 24 h after 500 h QUV exposure. Japan has also adopted the ISO standard but has maintain a rapid cycling test (2000 cycles at 5 cycles/min).

Movement ratings and tests, eg, ASTM C719 are useful in that they expose the sealant to conditions close to actual field conditions. However, these tests are typically carried out on freshly cured sealants, cured without any stress. In actual installations, sealants are installed in working joints and cure while joint movement occurs. More recent studies have evaluated the performance of sealants under movement during cure (1–4). Results indicate that it is possible to have a premature sealant failure on account of movement during cure. This failure may be one of several possible modes. One of the more serious modes of failure is the cracking or splitting of the sealant surface. This seems to be related to the length of time needed for a sealant surface to develop an elastic skin; sealants that develop elastic surfaces rapidly seem to resist cracking better. However, even with one-part sealants that form elastic surfaces rapidly, continuous movements of >15% during cure can cause failures. If large movements during cure are expected, two-part sealants that cure uniformly in depth may provide better resistance to failure because two-part sealants generally cure faster than corresponding one-part sealants. Another technique for reducing large joint movement on outdoor applications in hot weather is to seal during early evening hours. This allows ~12 h of cure to take place before significant joint movement occurs.

2.2. Modulus.

The measure of the stress of a sealant at a specific strain is referred to as the modulus of elasticity, sometimes called the secant modulus. This important sealant property describes the force exerted by a sealant as it is stressed. Because a primary function of a sealant is to adhere to the substrates it is in contact with, the forces generated by a joint opening or closing are transmitted by the sealant to the substrate–sealant bond line. For this reason, it is important to know the modulus of the sealant and also the strength of the substrate. The use of a high modulus sealant on a weak substrate, such as asphalt, concrete, or sandstone, can result in stresses higher than those that the substrate can tolerate, and has a higher potential for failure, often through cohesive failure of the substrate. Normally, concrete is thought of as a high strength substrate, which it is in compression. However, by comparison it is quite weak in tension. Sometimes, upon closer inspection, perceived adhesive failures are actually cohesive failure of the substrate near the substrate–sealant interface caused by such a modulus mismatch.

Although sealant manufacturer's literature commonly reports modulus values, these values must be interpreted carefully. Specimen sizes, test rate, cure conditions, and the time a sealant has been allowed to cure when tested can all have a significant effect on modulus. Therefore, for a true comparison, sealants should be evaluated by a standard test that examines all sealants by the same procedure. In general, the longer a sealant has been allowed to cure, the more realistic the modulus data.

2.3. Durability. A primary factor in sealant durability is its ability to resist decay from environmental elements. For most typical applications this includes extremes of high and low temperature, water, oxidation, and sunlight.

Temperature Stability. Sealants are used in all kinds of industries and in many of those applications temperature stability is a major concern. Some appliance applications can see 200°C (400°F) for prolonged periods of time and even mondane applications like building sealants can see 80°C (176°F)–90°C (194°F) on dark colored Southern faces in warmer climates. Thus sealants used in high temperature applications require data that they are suitable for such use. This data must include the temperature it was tested, the length of time it was tested and the physical properties that were there at the end of the test. Heat is a major factor in sealant's life expectancy and most data sheets provide inadequate information on this topic. Thus the user of sealants is required to ask the manufacturer of sealants for heat stability data or do their own testing.

Low temperature flexibility is also an issue for many sealants. At low temperatures, the sealant can stiffen resulting in large forces at the bondline due to movement of the joint. Typically, the sealant does not fail, but the joint does, which is just as severe of a problem. When looking for low temperature data, it is important to get actual modulus of elasticity at low temperatures and compare that to the modulus at room temperature. Simple claims, such as low temperature flexibility, should be supported by these data. Even cold temperature adhesion testing will not always avoid problems, since bond fatigue is also a factor. It is the repeated strains that often cause the failures. Thus cold temperature joint data should include movement cycles (enough to mimic the application) or example of applications with similar movement, on similar surfaces, at similar temperatures.

Weatherability. One of the more destructive elements is exposure to sunlight; specifically, ultraviolet (uv) light. All sealants are affected by weathering, but there is much difference in the effect of weathering on different sealants. Most silicones are stable with respect to uv exposure. Urethanes and polysulfides show effects of uv exposure, but can be formulated with uv absorbers to provide reasonable lifetimes in most applications. However, there are exceptions in all classes of sealants and specifiers must be careful to look for test data that has proven a specific sealant's durability. The source of the test data is also important; data from an independent testing laboratory is generally apt to be more reliable.

A sealant's location on a building as well as the building's geographical location can greatly impact the sealant's durability. In the northern hemisphere, a sealant installed on the north side of a building has much less exposure to uv and high temperatures as compared to a sealant installed on the south side of a building, especially if the substrate is dark colored. This sheltered exposure can extend the useful life expectancy of sealants that are prone to degradation in outdoor weather. Conversely, sealants installed in southern states, eg, Florida, Arizona, Texas, and California, and on the south side of a building, have a high degree of exposure to harmful uv and high temperatures as compared to any of the northern states. Such a location can accelerate the decay of a sealant prone to uv degradation.

A sealant's durability is often estimated by accelerated testing that exposes the material to high temperatures, high humidity (condensation), and uv light. Because there is much debate on how to estimate actual lifetime from accelerated testing, the duration of accelerated test exposure varies with the test method and may range from hundreds to thousands of test hours. One study of weathering effects on the surface of sealants indicates that 2000 h of accelerated exposure is roughly equivalent to 2 years of full sunlight exposure in Florida with each of several different generic sealant types tested (5). Another study of the correlation of accelerated weathering to sealant modulus changes suggests eight weeks of accelerated weathering (1344 h) roughly corresponds to 1 year of weathering at Garston, England (6). In contrast, most official ASTM weathering tests for sealants at the turn of the twenty-first century require only 250 or 500 h in an accelerated weathering machine. Therefore, data cited by manufacturers as having passed ASTM accelerated weathering tests may have little meaning in the real world. For example, two weathering tests for highway sealants, ASTM D3406 and D3408, require only 160 h in an accelerated weathering machine. Meaningful data would require several thousands of hours in the weathering tests. These are essentially bad tests in that they give a false sense of security to the user. There are many such tests that give this type of wrong impression of durability to weathering. In actual use, sealants in these applications receive full sun exposure and much longer times in weathering machines are needed to obtain meaningful data. In general, silicones provide the best resistance to decay from water, temperature extremes, and uv light because the polymer is inherently stable. However, some urethanes and polysulfides can also successfully seal joints trouble-free for many years by incorporating sufficient uv and oxidation stabilizers. A key factor in a successful, long-life seal is for the specifier to determine the degree of exposure to harmful elements the sealant is expected to experience in its lifetime and demand test data that approximate that lifetime. Present technology suggests that durability studies looking to simulate outdoor conditions should include artificial weathering and this weathering should go from 5000 h to 20,000 h, depending on the expected use. Furthermore, it would be better if the tests included some joint movement during cure as well as during the artificial weathering of the specimens.

Adhesion Life. A second key factor in determining the durability of a sealant is the ability of the sealant to adhere to the substrate through its lifetime. A sealant may have excellent resistance to uv effects, but if it has poor adhesion performance and fails adhesively, it is of little use. The same can be said of a sealant with superior adhesion characteristics but poor resistance to uv. Either situation results in a short performance life.

A sealant's adhesion is commonly studied by 180° peel tests, eg, ASTM C794 or by tensile–adhesion joints tests, eg, ASTM C719. The adhesion test protocol should simulate actual field conditions as closely as possible. Sealants often have good adhesion to dry substrates, but this adhesion may be quickly destroyed by water. Because most sealants are exposed to water over their lifetime, adhesion testing should include exposure to water for some length of time. ASTM C719 is one of the better tests to determine a sealant's adhesion durability as it exposes sealants to 7 days of water immersion. The best test is to look for adhesion changes when there is joint movement in an accelerated weathering test.

The modulus of elasticity can also influence the adhesion lifetime. Some sealants may harden with age as a result of plasticizer loss or continued cross-linking. As a sealant hardens, the modulus increases and more stress is placed on the substrate–sealant adhesive bond. If modulus forces become too high, the bond may fail adhesively or the substrate may fail cohesively, eg, in concrete or asphalt. In either case, the result is a failed joint that will leak. The effect of modulus changes on adhesion can best be studied by using job site substrates when doing the above suggested weathering tests.

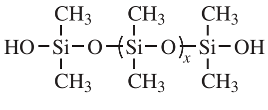
Another way to determine durability is to find successfully sealed, existing field installations. Sealant manufacturers often have case histories of successful installations. For the user or specifier of sealants, often it is more efficient to determine suitability by inspecting jobs with the various sealants in place rather than waiting for long term accelerated weathering tests. Note that this article somewhat emphasizes sealants in construction since this has such long-term and critical implications, but indeed sealants are used in appliances, autos, planes, electronic devices, and nearly everywhere. These other applications are much more controlled and each comes with their specific tests appropriate to their applications. In all sealant applications, adhesion performance can vary widely with sealant type, substrate type, and cleaning method. For this reason, it is important to understand the sealant's sensitivity to cleaning practices. Often with difficult-to-adhere substrates, a primer is used. Sealant manufacturers can provide recommendations as to which substrates require primers, what type of primers should be used, and how they should be applied.

3. Sealant Types and Formulations

3.1. Silicones.

Commercially available silicone sealants are typically one of three curing types: moisture-reactive (curing) sealants, moisture-releasing (latex) sealants, and addition-curing sealants. Of these three types, moisture-curing silicones make up the vast majority of silicone sealants sold.

Moisture-Curing Silicones. The formulation of moisture-curing silicones includes a silicone polymer, filler, a moisture-reactive cross-linker, and sometimes a catalyst. The most common silicone polymer used in sealant formulations is an alternating silicon–oxygen backbone with methyl groups attached to the silicon, eg, the silicone polymer (**1**).



$$HO-\underset{CH_3}{\overset{CH_3}{Si}}-O\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_x\underset{CH_3}{\overset{CH_3}{Si}}-OH$$

(**1**)

Specialty silicone polymers with trifluoropropyl groups replacing half of the methyl groups are used to make solvent-resistant materials. Diphenyl substitution for the methyl groups on the polymer can lower the brittle point of a silicone sealant from -65 to $-110°C$ (7). Viscosity for silicone polymers can vary widely from $<100\,\mathrm{mPa\cdot s}$ ($=\mathrm{cP}$) to $>100{,}000\,\mathrm{mPa\cdot s}$ ($=\mathrm{cP}$). Most cure through a reactive end group. The end group can be one of several different functionalities, but is usually hydroxyl. The saturated backbone and high Si–O bond energy provides inherent stability to sunlight. Because of this stability, silicones, unlike other sealants, need no special uv absorbers. Silicone polymers also exhibit little change in physical properties with temperature as compared to organic systems. This results in sealants that are almost as easy to extrude in cold weather as in warm weather. It also means that the cured sealant shows less change in properties as a function of temperature as compared to other sealants. Another fundamental property of silicone polymers is the high vapor transmission rate. Because most one-part silicone sealants cure by reaction with water vapor, this high transmission rate allows for fast cure in depth as compared with one-part organic-based sealants.

Silicone polymer plasticizers have historically been used in many formulations. These plasticizers (qv) are of the same Si–O backbone as the functional polymers, but generally are terminated with trimethyl groups that are unreactive to the cure system. This nonreactivity means that, if improperly used, the plasticizer can migrate from the sealant and stain certain substrates. Staining has been a widely publicized flaw of silicone sealants, but the potential of a formulation to stain a substrate can be minimized or eliminated with proper formulation work. In general, this is accomplished by not using plasticizers for formulations developed for stain-sensitive substrates. Non-silicone sealants also use plasticizers that migrate. Thus for assurance that a sealant won't stain, testing for staining before a major installation is a good idea.

Silicone polymers when cured into elastomers by themselves are weak, gel-like materials. For this reason, fillers must be used to provide reinforcement. The type of fillers (qv) used in silicone sealants varies widely; two of the most common fillers are fumed silica and calcium carbonate. Fumed silica, a highly reinforcing filler, is usually added in amounts ranging from 6 to 20%. Silica is most often used when a high strength sealant is desired. Several silicas having different surface areas are available and surface treatment with silanes may be used as well.

For lower modulus sealants, either ground or precipitated calcium carbonates are commonly used. These fillers are much less reinforcing than silica and may take up 50 wt% or more of a formulation. The surface of calcium carbonate is often treated with fatty acids, eg, stearates, to provide improved compatibility and dispersion into the silicone. By using various filler types, loadings, and filler treatments, the rheological nature of the sealant can vary from nonsag to self-leveling with low or high extrusion rates, and tensile strengths can vary from 0.35 to 7 MPa (50 to 1000 psi).

The moisture-reactive cross-linkers used in silicones are of the form $R_n\mathrm{Si(OR')}_{4-n}$, where $n=0$ or 1 and R may be any organic group, eg, methyl, ethyl, or vinyl. The R′ groups also varies; acetoxy, alkoxy, oxime, and propenoxy are among the most typical. Common cross-linkers are listed in Table 1, and a typical formulation for a one-part silicone sealant is given in Table (2).

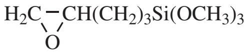
Some of the silicone cross-linkers are reactive enough on their own to cure a silicone sealant without the use of a catalyst. Most, however, require a catalyst, usually a tin carboxylate or an organotitanate.

The cure rate of a silicone sealant is dependent on the reactivity of the cross-linker, catalyst type, catalyst level, the diffusion of moisture into the sealant, and the diffusion of the leaving group out of the sealant. For one-part sealants, moisture diffusion is the controlling step and causes a cured skin to form on the exposed sealant surface and progress inward. The diffusion of moisture is highly dependent on the temperature and relative humidity conditions.

Most moisture-curing silicones have good general adhesion to a variety of substrates. However, adhesion can be markedly improved with different combinations of silanes. The more common silane adhesion promoters are categorized as amine functional, eg, 3-aminopropyltrimethoxysilane [13822-56-5] (**2**), 3-aminopropyltriethoxysilane [919-30-2], or *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane [1760-24-3]; as epoxy functional, eg, 3-glycidoxypropyltrimethoxysilane [2530-83-8] (**3**) and 2-3(3,4-epoxycyclohexyl)ethyltrimethoxysilane [3388-04-3] (**4**); as mercapto functional, eg, 3-mercaptopropyltrimethoxysilane [4420-74-0]; or as methacrylate functional, eg, 3-methacryloxypropyltrimethoxysilane [2530-85-0] (**5**).

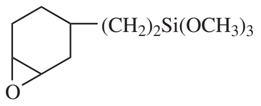
$_2HNCH_2CH_2CH_2Si(OCH_2CH_3)_3$

(**2**)

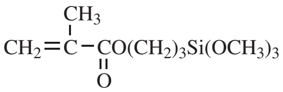


$H_2C{-}CH(CH_2)_3Si(OCH_3)_3$ (epoxide, O bridging both carbons)

(**3**)



(**4**)



$CH_2{=}C(CH_3){-}C({=}O)O(CH_2)_3Si(OCH_3)_3$

(**5**)

Each of these silanes consist of two functionalities: the moisture-reactive functionality (usually alkoxy), and the organic functionality. It is believed that this dual functionality allows the adhesion promoter to interact with both the substrate and the sealant. These silanes are also effective adhesion promoters for other nonsilicone-based sealants. Principal producers of these silanes are Dow Corning, Degussa, GE/OSI, and Wacker.

Moisture-Releasing (Latex) Silicones. A newer class of silicone sealants are known as the silicone latex sealants. These sealants are silicone-in-water emulsions that cure by evaporation of the emulsifying water. They should not be confused with siliconized acrylic sealants, which contain <2% silicone and have all the characteristics of acrylic sealants. The silicone latex polymer is prepared by first emulsifying a low molecular weight silicone polymer in water and then polymerizing it to the desired molecular weight. Inherent to emulsion polymerization is the ability to produce high molecular weight polymers at a low emulsion viscosity. Next, a silicone cross-linker is added with a condensation catalyst. The cross-linker, the structure of which is similar to those described previously, must diffuse through the water phase and into the siloxane phase where it can react with the silicone polymer. The water pH must be carefully controlled to prevent the cross-linker from reacting with water before it reaches the silicone phase. Fillers and freeze–thaw additives are also typically added to silicone latex sealants (8).

Addition-Curing Silicones. Addition-curing silicones in general are two-part systems that cure by the platinum-catalyzed reaction of a silicone hydride with typically a vinyl group attached to silicon. Because no by-products are generated by the cure, there are few volatiles and no shrink in thick sections. The cure can take place at room temperature or be accelerated by heat. Addition-curing silicones have little inherent adhesion and proprietary adhesion promoters or primers are often used to give adequate adhesion to substrates. The typical catalyst is a platinum compound and the level used in these systems ranges from 5 to 500 parts per million (ppm) of a platinum. Because this level is so small, these systems are easily poisoned by things that react with or complex with platinum.

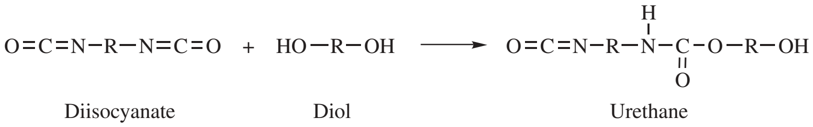
Reactive Hot Melt Silicones. The concept of reactive hot melt is similar to conventional hot melt technology: the sealant is applied as a viscous liquid at elevated temperature (80–200°C) and its viscosity builds up rapidly by cooling down. This aspect leads to improved productivity in numerous industrial assembly applications. Hot melts use less energy per unit of production than solvent or water-based sealing systems and are more environmental friendly than solvent-based systems. They are characterized by the absence of any solvent; they do not require mixing of two parts and give immediate green strength. Contrary to standard hot melts for which the process is reversible, reactive hot melts further react, usually by reaction with atmospheric moisture, leading to the formation of a thermoset sealant. These sealants can provide highly efficient bonding operations in OEM assembly applications by decreasing cycle time due to the rapid green strength development.

Moisture curable silicone hot melt sealants are made from mixtures of silanol terminated silicone polymers and silicone resins with glass transition temperature above room temperature (9). These hot melt sealants are typically applied ~120°C and have open times between 10 and 20 min. They are made moisture curable by the introduction of $Si{-}OCH_3$ groups and presence of a condensation catalyst. They cure in a few days to a flexible weather-resistant silicone elastomer with outstanding durability and ultraviolet (uv) resistance.

Due to their silicone nature, these sealants have a very low surface tension and therefore are prone to correctly wet even low energy surfaces, eg, polyethylene or polypropylene. They also show excellent movement capability and are therefore perfectly adapted for plastic bonding or bonding plastic to materials with much lower coefficients of thermal elongations, eg, metals and glass. Their unique stress–strain behavior makes them suitable for use in many demanding applications.

Silicone reactive hot melts are heavily promoted in the fenestration industry where they claim to provide better thermal behavior and sound proof properties, and improved mechanical properties due to the frame-glass composite structure.

3.2. Urethanes. Urethane sealants are particularily noted for toughness and find some of its more prominent uses in areas where toughness and abrasion resistance are a concern. The basis for urethane chemistry is the reaction of an isocyanate group with a component containing an active hydrogen.



$$O{=}C{=}N{-}R{-}N{=}C{=}O \; + \; HO{-}R{-}OH \longrightarrow O{=}C{=}N{-}R{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}R{-}OH$$

The first step in formulating a urethane sealant is to prepare what is commonly called the prepolymer, typically by reaction of a hydroxy-terminated polyether with a stoichiometric amount of a diisocyanate. Each hydroxy group reacts with one end of every diisocyanate molecule.

Although polyethers are the main building blocks of the prepolymer, other materials, eg, polyesters, polythioethers, and polybutadienes are also used. The choice of the starting polymer provides certain characteristics to the resulting urethane sealant; especially important are polymer size and branching. Most urethanes use blends of polymers to achieve desired properties. With proper additives, polyether-based urethanes provide good general weathering properties and abrasion resistance. Some urethanes claim a heat stability to 135°C, but typical urethanes have a stated use temperature maximum of 50, 60, 70, or 80°C. Typical urethane sealants have a high temperature limit of 135°C, and a maximum use temperature of 70 or 80°C. Polyester-based sealants have good fuel and weather resistance, but poor low temperature flexibility and poor resistance to water. In contrast, polybutadiene-based urethanes have good resistance to water, but have poor weather resistance and a limited temperature range. Polythioethers provide chemical resistance in elastomeric materials that cannot be achieved in polyether urethanes (10).

Polyethers are available in a wide range of molecular weights, from ~400 to >6000. Diols and triols are most common, but higher functionalities are also available. Common diisocyanates employed are toluenediisocyanate [1321-38-6] (TDI) or 4,4′-methylenediphenyldiisocyanate [101-68-8] (MDI) with toxicity issues leading toward more use of MDI. Aromatic diisocyanates are most common, but aliphatic diisocyanates are also used. Although more expensive than aromatic isocyanates, aliphatic isocyanates have better color and uv stability. They are used in applications where added stability is needed and where price can support the extra cost. The other unreacted isocyanate end of the prepolymer is still reactive to active hydrogens and is the basis for two-part urethanes. The first part consists of the urethane prepolymer and the second part contains a polyether. By mixing the two parts together, reactions occur between the isocyanate prepolymer and the polyether, resulting in a network having elastomeric properties. Most urethane sealants are of these two- or even three-component types that are mixed on-site.

One-part urethane sealants (Table 3) are more complicated to formulate on account of an undesirable side reaction between the prepolymer's isocyanate end and water vapor that generates carbon dioxide. If this occurs, the sealant may develop voids or bubbles. One way to avoid this reaction is to block the isocyanate end with phenol and use a diketamine to initiate cure. Once exposed to moisture, the diketamine forms a diamine and a ketone. The diamine reacts with the isocyanate end on the prepolymer, creating a cross-link (12). Other blocking agents, eg, ethyl malonate, are also used (13). Catalysts commonly used in urethane formulations are tin carboxylates and bismuth salts. Mercury salt catalysts were popular in early formulations, but have been replaced by tin and bismuth compounds.

The fillers used in urethane formulations are similar to those used in silicones; calcium carbonate, talc, clays, and silica are among the most common. On account of the undesirable reaction of isocyanates with water, fillers used in urethane formulations must be dry.

Urethane sealants have good inherent adhesion to most substrates, but silane adhesion promoters are often used to improve this adhesion. Epoxy-, amino-, and mercapto-functional silanes are the most common because of their dual reactive nature. The silane end can react with surface hydroxyls; the epoxy, amino, or mercapto end can react with the isocyanate.

Urethanes have many uses and most urethanes are readily paintable. Note well the sealants in moving joints will be stretching more than the paint film and thus even if painted the paint can become cracked and checked and occasionally loose adhesion. The high plasticizer content can sometimes cause bleeding and staining, just as with some of the silicones. As with silicones, suitability for a given appplication must be tested, with each specific sealant, and each color of each sealant. The need to test each color is especially true with the testing for urethanes for durability to weathering, since some pigments have good (uv) blocking qualities and give a uv stability that sealant in other colors, without those pigments, do not have. Typically, but not always, the most stable urethane colors are black and white. However the white can become a tan since the degradation products are highly colored and even small amouts of degradation will effect the sealant's color.

Reactive Hot Melt Polyurethanes. Polyurethane (PU) hot melts are well known in the adhesive market: they are usually based on thermoplastic polyurethanes which have either a glass temperature or a melting point in the 80–200°C region. These polymers lead to very high modulus structural adhesives that cannot be classified as sealants.

Recently, moisture curable hot–warm melt sealants based on polyurethanes have been developed with application temperatures between 80 and 140°C. Manufacturers include National Starch, HB Fuller, and Sika. These products acquire high green strength by cooling down and further cure to a thermoset that resists melting after a few days. Open times for reactive PU hot melts is typically between 10 s and a few minutes depending on the application.

Moisture curable PU prepolymers are combined with thermoplastic raw materials, eg, EVA or PiB. Other components include tackifier resins and waxes. Tackifiers are used to improve adhesion and provide pressure sensitive characteristics. Waxes, eg, natural paraffins and microcrystalline waxes, are used to reduce the melt viscosity and to promote wetting on the substrate. Oil, plasticizers, fillers, pigments, antioxidants, uv absorbers, adhesion promoters and catalyst are also used in hot melt PU compounding. Most recent developments combine the use of Si-modified polyurethanes and hot melt behavior.

These sealants combine the advantages of “silicone-type” curing and hot melt behavior.

Polyurethane reactive hot melts are generally sold into the fenestration and automotive industies, and for mobile home and truck component assembly, and for sealing and insulating electrical appliances.

3.3. Si-Hybrid Sealants. In order to combine good adhesion on various substrates and properties typical of organic-based sealants, eg, paintability and nonstaining character, organic polymers functionalized with Si-alkoxy groups have been developed. Sealants based on these polymers have similar cure chemistry to standard silicone based sealants; beside the polymer, the formulation contains fillers (preferably calcium carbonate or silica), plasticizers, rheology modifier, silane adhesion promoters, organotin or organotitanium catalysts, silane adhesion promoters, water scavengers, antioxidants, uv, and light stabilizers.

Silyl-Terminated Polyethers. Sealants based on silyl-terminated polyethers (MS polymer based sealants) have been commercialized in Japan since the early eighties. Their market share increased gradually mainly versus acrylic and polysulphide based sealants. Since 1997, they dominate the Japanese market (35%) followed by Silicone (25%) and Polyurethane (25%) based sealants. Market share has stabilized since then. In Europe and the United States, silicones continue to dominate the market, but Sealants based on silyl-terminated polyethers are penetrating the market since the late nineties with a higher growth rate than conventional sealants.

Silyl-terminated polyethers are obtained from allyl end blocked polypropylene-oxide polymers that are further reacted with dimethoxysilane using hydrosilylation. These polymers are formulated with plasticizers (phthalates or aliphatic oils), fillers (typically calcium carbonates, silica, or talc) and other additives, eg, catalysts, adhesion promoters, drying agents, uv stabilizers, HALS, antioxidants to obtain sealants that cure in the presence of moisture.

There are currently two sources for this silyl-terminated polyether: MS polymer (Kaneka) and Excestar (Asahi Glass Company).

Sealants based on MS polymer are generally considered to be versatile. Key properties include good adhesion, paintability, and nonstaining performance. They usually show a lower dependency of extrusion rate with temperature than polyurethane sealants but still more temperature sensitive than silicone sealants. Surface tackiness is also generally higher than silicone based sealants. As with polyurethane sealants, MS polymer-based sealants usually show poor resistance to weathering (uv and water), especially when used to bond glass: they usually do not pass ISO 11600 norm for glazing and are not normally used in glazing. They can be formulated both as one or two-part sealants. Sealants with 100% modulus’ between 0.3 and 1.0 MPa and elongations up to 1000% (dumbbell) can be produced.

Silyl-Terminated Polyisobutylene. Silyl-end blocked polyisobutylene (SiPiB) constitutes another class of Si-hybrid polymer. These polymers are obtained by hydrosilylation of telechelic allyl-terminated polyisobutylene leading to Si-alkoxy terminated polymers (14). These polymers will cross-link in the presence of water–moisture. The biggest commercial source for this polymer is the

Epion from Kaneka. Formulated sealants based on this polymer are currently only commercialized in Japan.

Because of the extremely low vapor permeability of polyisobutylene, sealants based on Si-alkoxy modified PiB can only be formulated as two-part sealants. Sealants based on SiPiB show very low vapor transmission, good resistance to weathering, good adhesion to various substrates, and no staining.

Silyl-Terminated Polyurethanes. In order to extend the performance of polyurethane sealants, silyl modified polyurethanes (SPU) have been developed (SPUR from GE/OSI or Desmoseal from Bayer). Such polymers are obtained by reaction of isocyanate terminated polyethers/polyesters with aminosilanes leading to alkoxysilyl terminated polymers. In the presence of a suitable catalyst (organotin based in general), atmospheric moisture reacts with silane end-groups to form a three-dimensional (3D) structure with SiOSi linkages. As with MS polymers, to produce single component sealants based on SPU, it is essential to eliminate moisture either by drying the fillers or by addition of a water scavenger.

A wide-variety of polymers can be obtained by using different isocyanates (aliphatic or aromatic), different polyether (EO/PO) or polyester types and MWs' that can lead to either high or low modulus sealants.

Sealants based on Si-modified polyurethanes have several advantages over conventional PU based sealants (15).

- Isocyanate-free in the application, leading to less environmental impact.
- No bubbling (bubbling in conventional PU sealants occurs through reaction of isocyanate with water, leading to the formation of carbon dioxide).
- Increased uv stability, better resistance to weathering and better adhesion to a wider variety of substrates (due to the possibility to broaden the additives that can be used in the formulation: uv stabilizers, adhesion promoters).
- Better shelf-life stability (less sensitive to water).

These sealants, however, still suffer from the high dependency of extrusion rate with temperature.

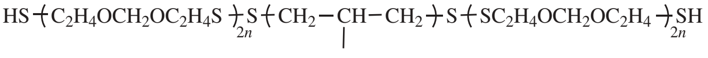
There are several producers of SPU based sealants or SPU polymers, including Sika, Bayer, Henkel, GE/OSI, Bostik, May National, HB Fuller, Rohm & Haas, and Den Braven.

Recently a new set of SPU polymers have been obtained by reacting polyether terminated polyurethanes with isocyanatopropylalkoxysilanes (SPUR + from GE) (16). These polymers have fewer polyurethane hard segments that reduces the possibility for hydrogen bonding, leading to lower polymer viscosities at equivalent molecular weight, and therefore lower modulus sealants. Contrary to the standard SPU technology, these polymers can be produced in the absence of plasticizers that gives producers more latitude to optimize the sealant formulation. These polymers are also claimed to improve tack free time, deep section cure performances and yellowing issues.

Silicon Modified Polyacrylates. In order to reduce the gap between silicones and MS polymer based sealants, a novel telechelic acrylate polymer obtained by atom transfer radical polymerization (ATRP) has been developed by Kaneka (17). This polymer differs from Si-modified acrylates obtained by radical polymerization (18), by the position of the Si-methoxy functionalities at the chain ends compared to side chain grafting and the narrower molecular weight distribution. Sealant formulations based on this polymer have shown excellent resistance to weathering (19) combined with good adhesion on many substrates, good paintability and nonstaining characteristics. Adhesion on glass was shown to be unaffected after 10,000 h uv irradiation (super Xenon Weather meter; 180 W/m^2 (300–400 nm), Black panel temp.: 63°C, water spray 18 min in 2 h). Sealants based on this polymer claim to pass the ISO 11600 25LM/HM norm for glazing applications.

Sealants based on the Si-modified acrylate polymer used in conjunction with self-cleaning glass did not show contamination on the glass after several months of outdoor exposure. However, since this technology is still quite new, there is not much field data available at this time confirm performance is real world applications.

3.4. Polysulfides. Polysulfide sealants were the first high performance synthetic elastomeric sealants produced in the United States. The basic polymers are mercaptan-terminated (HS–R–SH), with molecular weights ranging from 1000 to ~8000. Cross-link concentrations range from 0.5 to 2.0 mol%. Curing occurs through the mercaptan groups by oxidation and results in an S–S linkage. In addition to the terminal SH groups, pendent SH groups are located along the polymer chain and contribute to cross-linking. A typical polysulfide polymer may be represented as follows:



$$HS\!-\!\!(C_2H_4OCH_2OC_2H_4S)_{2n}\!-\!S\!-\!(CH_2-\underset{|}{C}H-CH_2)\!-\!S\!-\!(SC_2H_4OCH_2OC_2H_4)_{2n}\!-\!SH$$

The value of n is ~6 for Morton International Polymer LP-3, 24 for LP-32.

Polysulfide polymers provide inherent resistance to fuel and quite good resistance to alkali. In contrast to the silicone polymers, they have low gas permeability. Although low gas permeability is an asset in certain applications, eg, single-seal insulating glass, it also causes slow cure for one-part moisture-activated sealants where the moisture must diffuse through the sealant to initiate cure. Because of the slow cure of the one-part sealant, the most common form of polysulfides is the two-part mix-on-site sealants.

Two of the more recently developed polysulfide polymers are the mercaptan-terminated polyoxypropylene urethane polymer and the polythioether polymer. The urethane-backbone-based polymer is used in many sealant formulations for insulating glass applications. The thioether backbone contains sulfur, but no S–S bonds, which are the weakest part of the conventional polysulfide polymer. This polymer improves the thermal stability and reduces the gas–liquid permeability.

Early formulations typically used lead dioxide as the oxidative curing agent. More recently, curing agents, eg, manganese dioxide and sodium perborate monohydrate have been used (Table 4). Different curing agents have different effects on the properties of the polysulfide sealant. Therefore, the choice of curing agent depends on the sealant application. Early polysulfides used polychlorinated biphenyls (PCBs) as plasticizers, but these have been completely replaced with phthalate esters or other plasticizers (qv).

Common fillers used in polysulfide formulations are ground calcium carbonate, precipitated calcium carbonate, carbon blacks, and clays. The pH of the ingredients used in the formulation can impact the cure rate either positively or negatively. Organic amines are used to increase the cure rate, and acids to decrease the cure rate. Small-particle-size calcium carbonate is often coated with organic treating agents, eg, stearic acid, to improve the dispersing properties. However, such an acid treating agent can slow the cure rate. Very slow cure rates can cause damage to the sealant and often these type sealants will take a compression or extension set in long-term outdoor exposures.

Adhesion promoting silanes are often added to improve adhesion to various substrates. As is the case with urethane sealants, silanes with a dual-reactive nature are typically used. Examples of such silanes are mercapto- and epoxy-functional silanes. Organic titanates may also be used (20).

3.5. Acrylics.

There are two principal classes of acrylic sealants: latex acrylics and solvent-release acrylics.

Latex Acrylics. High molecular weight latex acrylic polymers are prepared by emulsion polymerization of alkyl esters of acrylic acid. Monomer, water, surfactants, and an initiator are mixed and polymerized until the acrylic monomer is depleted. Two types of monomers are used to vary polymer properties. High T_g monomers, eg, methyl methacrylate and vinyl chloride improve durability and hydrophobicity, whereas polar-functional monomers, eg, hydroxyethyl acrylate are used to improve adhesion. The maximum level of solids for the acrylic latex polymer is $\sim$60%. In typical formulations (Tables 5 and 6), above this point the viscosity increases rapidly and the emulsion stability is poor. In relatively low solids (high water) content formulations, rather severe shrinkage occurs during cure. This can introduce stress and may be one of the reasons most latex acrylics are of lower performance and lower movement ability. The surfactants used are of special concern to sealant formulations because they can interfere with adhesion if improperly used. One approach to solve this problem is to incorporate the surfactant into the polymer backbone during polymerization. This approach, which places the surfactant in an ideal location to stabilize the emulsion, does not allow the surfactant to migrate through the aqueous phase and interfere with adhesion because the surfactant is connected to the backbone (21). The emulsion polymers are compounded into sealants by adding fillers, plasticizers, freeze–thaw stabilizers, thickeners, and adhesion promoters. As is true of the silicone latex sealants, the acrylic latex sealants are easy to apply and clean with water. One common characteristic of many, if not all, latex acrylics is they harden with time in the weather. The user of latex acrylics needs to have a manufacturer's letter certifying the long term performance because there are so many latex acrylics sealants of such wide quality range.

As suggested earlier, there are a wide variety of silicone sealants (performance variations) and an even wider variation in performance of the urethanes but the variations in performance of the various latex acrylic sealants is vast and thus there are few "typical" properties. Each must be tested for suitability and longevity in an application.

Solvent-Releasing Acrylics. Another class of acrylic sealants are the solvent-releasing acrylics. Acrylic monomers are polymerized in a solvent. The molecular weight of the polymer is lower than in the latex acrylics because of the inherently higher viscosity of the medium. However, the percentage of solids is ~80 versus the 60% common to latex acrylics. The natural adhesion of most of the solvent-releasing acrylics produces some of the best unprimed adhesion in the sealant industry. However, slow, continual cure generally produces large compression sets and limits their use to low movement applications. Also, the relatively high amounts of solvent and traces of acrylic monomer in these formulations limits their use to outdoor applications, usually in construction.

3.6. Butyls. Butyl-based materials are sold in the form of preformed tapes, thermoplastic hot melts, and one-part solvent-releasing sealants. Butyl polymers are made by the copolymerization of 97–98 mol% isobutylene with 2–3% isoprene. Another butyl-based polymer, polyisobutylene, is produced by the polymerization of isobutylene. Both polymers are available in a wide range of viscosities. These polymers are low cost and have the lowest moisture vapor transmission rates of the common sealant types. Formulations of butyl-based sealants also include plasticizer, filler, and tackifier resins. Polybutenes are common plasticizers for butyl sealants. They are made from the polymerization of a mainly isobutylene feedstock and are available in several different viscosities. Butyl sealants are often filled with carbon black, but other fillers such as talc and calcium carbonate are also used, especially for lighter colored sealants. Tackifier resins, eg, the pentaerythritol ester of rosin, are added to provide tack or adhesion to various substrates. Solvents, eg, mineral spirits, are used for the one-part solvent-releasing formulations (Table 7). As the solvent leaves the typical one-part butyl, the sealant hardens and loses its elastomeric ability. This limits the use of solvents to low movement applications where durability is not of high concern. The hot melts, on the other hand, are quite plastic in nature and cracks tend to self-heal. Hot melts usually have good longevity in special applications, eg, the primary seal in insulating glass (Table 8).

Reactive Hot Melt Butyls. Polyisobutlylene reactive hot melts do not have a strong presence on the market. In the early 2000, Delchem launched a reactive hot melt butyl IG sealant in order to improve the mechanical and adhesion properties of butyl hot melt used as primary seal in insulating glass units (IGU).

4. Manufacture and Processing

Almost all sealants contain a mixture of a powdered filler incorporated into a viscous liquid, which results in a viscous liquid sealant having a paste-like consistency. Batch mixers such as Ross Mixers and other planetary types are common to the industry. Also, continuous compounding of sealants can be accomplished using compounders such as the Werner-Pfleiderer (WP) Compounder. Mixers can be broadly classified into low and high shear mixers (see Mixing and Blending). In general, low shear mixers are able to disperse low surface area fillers, eg, ground calcium carbonate (average particle size of 1 μm), into the sealant polymers quite well. However, high surface area fillers, eg, the high surface area fumed silicas (surface area >200 m^2/g), usually require higher shear rate mixers, eg, the WP Compounder or sigma-blade batch mixers. High surface area fillers incorporated into sealants on a low shear mixer may result in material having a grainy appearance as the mixer is not able to disperse the small particles of filler sufficiently.

Processing conditions can have a dramatic effect on sealant rheology, cure time, and physical properties. Typical processing variables are mixer speed (rpm), time, temperature, and vacuum. Order of ingredient addition is also important. For one-part moisture-curing silicones, it is important to keep the raw materials dry and to minimize exposure of the finished sealant to moist air. Failure to do so can result in the formation of small cured gels in the sealant. Dry raw materials are also critical when manufacturing one-part urethanes and polysulfides. The isocyanate end of the prepolymer is very reactive with moisture and can lead to gassing from carbon dioxide formation. The catalysts used to cure one-part polysulfides are moisture-sensitive and must be protected from moisture during manufacture. Three methods used to dry urethane and polysulfide raw materials are azeotropic distillation with toluene, vacuum drying, and addition of a desiccant to the formulation. Stoichiometry of the urethane prepolymers is critical for achieving the desired sealant properties. Specifically, this means closely controlling the ratio of isocyanate to hydroxyl.

Temperature also plays an important role. The ordered reactivity of the diisocyanate may change if the temperature is too high, resulting in both ends of the diisocyanate reacting with the polyether's hydroxyl groups. Latex sealant compounding has a special requirement of its own. The processing equipment must achieve specific particle size, specific particle size distribution, and specific molecular size within the particle. High shear equipment is usually required to produce stable emulsions. Incorrect processing conditions can produce a variety of bad effects, including the ability to break a smooth emulsion, which results in a two-phase mixture of water and large curds.

5. Economic Aspects

Since the introduction of the first polysulfide sealants in the 1950s, the sealant market had grown by 1992 into a $1.4 billion industry [$3.6 billion in 2002 (source ASC 2002)]. Sealant use is generally divided into four categories: transportation, construction, consumer, and industrial. Table 9 lists the market segment value of each use as of 1992 and Table 10 the market share of the various material types. Continued growth is expected, especially for silicones, urethanes, and acrylics. Table 11 lists suppliers of sealants.

6. Specifications

Numerous specifications exist for sealants. One of the more important specifications for construction sealants is ASTM C920. This specification is based on experience with high performance sealants in the structural sealing and glazing applications. Among the most confusing specifications are the highway/pavement sealant specifications. Each U.S. state Department of Transportation

(DOT) lists specifications for pavement sealants, almost all of which are less stringent than ASTM C920; The International Standards Organization has a specification for construction sealants ISO 11600. This has some similarities to ASTM C920. For construction applications these are the most important specifications. The confusing issue is that different chemical types of highway sealants have different performance specifications for the same application. Performance specifications as opposed to material specifications for the highway products, have not been developed and is perhaps the single biggest cause for the short, effective lifetimes of highway sealants. Almost all other applications for sealants have performance specifications. It is possible for the highway entities to adopt the durability aspects of C920 and add a long term weathering component as well. For military applications, many military specifications apply and must be adhered to. These are typically performance specifications. In industrial applications, typically each industry has developed its own specifications to meet a specific application. For example, automobile manufacturers have a series of specifications relating to the use of sealants in cars and trucks. Aircraft sealants are another example of specifications developed for an application. An excellent reference for the numerous specifications is available (26). In addition to specifications, other testing codes may be important, depending on the application. For fire or electrical applications, testing approved by the Underwriters Laboratory (UL) is necessary. For sealants that are used in food processing, U.S. Food and Drug Administration (FDA) testing is needed.

7. Health and Safety Factors

7.1. Sealant Manufacturing. Most sealants use mineral-based fillers that may contain small amounts of crystalline silica. If crystalline silica is present, dust control is important to prevent inhalation of these particles during the manufacturing. Crystalline silica is a known cause of silicosis, a debilitating disease of the lung. Another common safety concern in sealant manufacturing is the use of flammable materials. Not all sealants use flammable ingredients, but for those that do, proper inerting and grounding are needed to prevent potential explosions.

For silicone manufacturing, handling of cross-linkers and catalysts in 100% pure form requires knowledge of any unusual hazard. These materials may be skin irritants, flammable, or capable of reacting with moisture to release one of the leaving groups in Table 1. Urethane sealant manufacturing requires special precautions during the production of the prepolymers. Some isocyanates used to make the prepolymer are known skin irritants and can cause dermal sensitization by direct contact. Inhalation of the vapors of some isocyanates can sensitize the pulmonary tissues of certain people and may cause serious asthmatic symptoms (11). Acrylic monomers used to make emulsion polymers for acrylic sealants have varying degrees of toxicity and may require special safety and handling procedures. Acrylic sensitivity is not uncommon. Also, some surfactants and freeze–thaw stabilizers may be skin irritants.

7.2. Sealant Application. The moisture-reacting silicones cure by reaction of the cross-linker with atmospheric moisture and release of the leaving groups listed in Table 1. In general, these sealants should be used in areas that have good ventilation. The leaving groups are released in small amounts, but they can accumulate in a confined or unventilated area. Acetoxy-curing silicones release small amounts of acetic acid. Oxime-curing silicones release methyl ethyl ketoxime that can be a potential skin sensitizer. Although relatively small amounts of these materials are released, it is a good idea in general to avoid skin contact. Latex acrylic sealants may be minor skin irritants on account of the surfactants from the polymerization step. Urethane sealants may also be skin irritants; skin contact should therefore be avoided. Polysulfide sealants have a characteristic odor, probably resulting from small amounts of low molecular weight, sulfur-containing components. Although the odor is somewhat objectionable, the polymers are not known to be skin or eye irritants. Primers and cleaners historically have been mainly neutral organic solvent-based, but many are being formulated to minimize or eliminate solvent. However, a careful review of the material safety data sheet is fundamental before use of any sealant.

8. Uses

Each class of sealants has certain attributes inherent to the polymer on which it is based. These attributes often define the sealant's applications and limitations. Table 12 summarizes each type of sealant's key attributes, principal markets, and limitations.

Future developments are likely to feature the production of more silicone sealants that do not pick up dirt, more latex acrylic sealants that have high performance properties, urethanes that have improved uv stability, and high performance polysulfides that are made in the United States.

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Table 1. **Common One-Part Silicone Cross-Linkers and Their Leaving Groups**

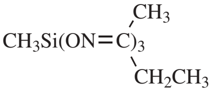
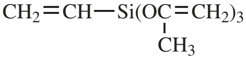
Cure system	Cross-linker	CAS Registry Number	Leaving group
alkoxy	$CH_3Si(OCH_3)_3$	[1185-55-3]	methanol
acetoxy	$CH_3Si(OOCCH_3)_3$	[4253-34-3]	acetic acid
oxime	 $CH_3Si(ON{=}\overset{CH_3}{\underset{CH_2CH_3}{C}})_3$	[22984-54-9]	methylethyl ketoxime
propenoxy	 $CH_2{=}CH{-}Si(O\underset{CH_3}{C}{=}CH_2)_3$	[15332-99-7]	acetone

Table 2. **Typical One-Part Silicone Sealant Formulation**

Component	High modulus sealant, %	Low modulus sealant, %
silicone polymer	70–85	40–60
silicone plasticizer	0–5	0–20
fumed silica	6–12	
calcium carbonate		40–60
cross-linker	3–8	3–8
silane adhesion promoter(s)	0–1	0–1
catalyst (if needed)	<1.5	<1.5

Table 3. **Typical One-Part Urethane Sealant Formulation**[a]

Ingredient	Wt %
diisocyanate prepolymer	30–35
filler	30–45
plasticizer	15–35
uv absorber	1–3
antioxidant	1–2
dehydrating agent	1–3
adhesion promoters	1–3
thixotrope	2–3
solvent	3–5
coloring paste	2–3

[a] Ref. 11.

Table 4. **Typical One-Part Manganese Dioxide-Cured Polysulfide Formulation**[a]

Ingredient	Wt %
polysulfide polymer(s)	30
calcium carbonate (coated)	30
phthalate plasticizer	25
titanium dioxide	8
molecular sieve	0.5
adhesion promoter	1.5
fumed silica	0.5
manganese dioxide (active)	2.0
barium oxide paste (75% active)	1.5
stearic acid	0.2

[a] Ref. 20.

Table 5. **One-Part Pigmented Siliconized Acrylic Latex Sealant**[a]

Ingredient	Wt %
acrylic latex polymer (polymer and water)	30
calcium carbonate	56
plasticizer	8
mineral spirits	1.7
propylene glycol	1
titanium dioxide	1
ammonium hydroxide (14%)	<1
preservative package	<1
nonionic surfactant	<1
inorganic dispersants	<1
organic dispersants	<1
defoamer	<1
associative thickener	<1
silane adhesion promoter	<1

[a] Ref. 21.

Table 6. **One-Part Clear Acrylic Latex Sealant Formulation**[a]

Ingredient	Wt %
acrylic latex polymer (polymer and water)	78.7
plasticizer	11.2
fumed silica	2.2
nonionic surfactant	1.7
amino silane	0.8
ammonium hydroxide	0.7
other	4.7

[a] Ref. 22.

Table 7. **One-Part Solvent-Releasing Butyl Sealant Formulation**[a]

Ingredient	Wt%
butyl polymer	22
talc	31
calcium carbonate	21
polybutene plasticizer	10
mineral spirits	6
tackifier (terpene phenolic resin)	4
rutile titanium dioxide (pigment and uv protection)	3
thixotrope (fumed silica)	2
other	<1

[a] Ref. 23.

Table 8. **Hot-Melt Polyisobutylene Formulation**[a]

Ingredient	Wt%
polyisobutylene polymer	25
resin	30
amorphous polypropylene resin	20
low density polyethylene	15
carbon black	10

[a] Ref. 23.

Table 9. **2003 U.S. Sealant and Adhesive Consumption by End-Use Application**[a]

Market segment	Value, $\$ \times 10^6$	2003	2008 (projected)
transportation	520	865	960
construction	415	1850	2050
consumer	350	460	510
industrial	140	680	820
total	*1425*		

[a] Ref. 24.

Table 10. **U.S. Consumption by Sealant Type**[a,b]

Product type	2003 Value, $\$ \times 10^6$
silicone	570
butyl rubbers	55
acrylics	128
polyurethanes	288
polysulfides	38
Si-hybrids	37
other	124

[a] Does not include adhesives.
[b] Ref. 25.

Table 11. **Suppliers of Sealants**

Sealant	Supplier
silicones	Dow Corning, General Electric, Wacker Silicones, Bayer, Shin-Etsu, Henkel, Sika, Tremco
polyurethanes	Essex Speciality Products, Mameco International, Pecora Chemical, Courtaulds Aerospace Inc., Sika, Tremco, ChemRex, Dow Chemical, National Starch
polysulfides	Morton International, ChemRex, Pecora, Courtaulds Aerospace Inc., Chemseal
acrylics	DAP, 3M, Tremco, Rohm and Haas (polymers), RPM
butyls (hot melt)	H. B. Fuller, Tremco, Exxon (polymers)
Si-Hybrids	General Electric, Sonneborn, Den Braven, Kaneka (polymers)

Table 12. **Summary of Sealants**

Sealants	Key attribute	Principal market	Limitation
silicone	excellent uv stability, fast cure on account of high moisture vapor transmission, good high temperature stability, good low temperature flexibility	structural glazing, weatherproofing, insulating glass (secondary seal), pavement, consumer, premium housing	some not abrasion-resistant, some not recommended for below-grade or continuous water immersion, generally not paintable, some pick up dirt
urethane	tough, abrasion-resistant, good adhesion to many substrates, good chemical resistance	weatherproofing, automotive, parking structures, insulating glass	80°C (175°F) temperature limit, limited uv stability, most not used for typical glazing, some have limited stability in water, not suitable for structural glazing
polysulfide	excellent chemical resistance, low gas permeability	insulating glass, aircraft sealants, fuel-resistant applications, below-grade applications	slow cure for one-part sealants, limited uv stability, not suitable for structural glazing
acrylic	good uv stability, easy to apply and clean (latex), low cost, good adhesion	residential housing, consumer	low movement capability, limited low temperature flexibility
butyl	low gas permeability, low cost, paintable	insulating glass (primary seal), automotive, low cost housing	low movement capability, limited durability
Si-Hybrids	good adhesion, good resistance to weathering, paintable	weatherproofing	not used for structural glazing