Silicones For Photovoltaic Encapsulation

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ABSTRACT: Silicone materials are well known to be one of the most suitable materials for optical and opto-electronic applications, such as LED encapsulants and lenses. Silicones have also been noted as an ideal material for the encapsulation of PV cells. This is primarily due to their high transparency in the UV-Visible wavelengths, wide range of refractive indices, excellent tolerance to high optical flux and excellent thermal and environmental stability. Silicones can be formulated to a refractive index between 1.38 and 1.58 depending upon the chemical constituents attached to the silicon atom. Due to their low modulus and low glass transition temperature (-50 °C) they are very stress relieving in a wide temperature range. Also, when formulated with appropriate adhesion, they provide the required moisture protection needed for multiple applications. They have very good electrical properties and are well known as dielectric insulators. In many applications, their fire resistant properties are also important. These properties make them ideal candidates as encapsulants for photovoltaic modules. Internal evaluations at Dow Corning and with select external partners have shown that very efficient solar cells using silicones as the encapsulant can be assembled and show very good reliability. This paper will focus on the key properties of silicones both initial and after aging. Also discussed will be performance measurements on PV cells encapsulated with Dow Corning® brand silicones. Long-term durability in outdoor applications has been demonstrated.

Keywords: Silicone, Solar Cell Efficiency, Solar Cell Durability, Encapsulation

1 Introduction

Silicone polymers and resins have been formulated into multiple products that have a long history of successful use in a wide variety of applications and industries. Through chemical modifications of the polymer repeat unit, the optical, mechanical, and thermal properties of the polymers can be extensively varied and tuned to meet the requirements of specific applications. The inherent properties of silicones (1) such as very low ionic impurities, low moisture absorption, low dielectric constant and broad temperature utility make them excellent material choices for applications in many of the specialty markets such as automotive, healthcare, electronics and microelectronics. These properties, in conjunction with their excellent optical transparency over a wide spectrum and UV stability (2), make silicones highly suitable for meeting the materials requirements for encapsulation of photovoltaic cells and other opto-electronic applications. This review will focus on the unique properties of silicones that make them ideal products for the entire Photovoltaic (PV) module assembly market.

2 Photovoltaic Module and Assembly

The PV industry is growing rapidly as the demand for cleaner energy worldwide increases. As the industry expands it is critical that suitable material solutions are available to meet the numerous requirements including durability (3), performance, price, throughput and global availability. Silicones are an ideal product family to meet the needs in the PV module assembly market. Silicones are highly transparent in the UV-visible wavelength region which makes them ideal candidates for cell encapsulants. They can be formulated to have low modulus and be stress relieving while also having excellent adhesion (2) to the glass and PV cells and substrates. In addition, they can also be constructed into hard/resinous coatings that provide effective durable protection and abrasion resistant while maintaining optical clarity (2). Silicones can also be employed as PV junction box potting agents. For this application they need to have high reliability, long-lasting protection against environmental ingress and excellent electrical insulation of components (2). They can be modified to have a thermal conductivity in the range of 0.4-1.34 W/mK or higher if needed (4). Finally, silicones can be formulated into sealants for frame and junction box sealing. These sealants provide long-term bonding and protection against moisture and environmental attack (2).

3 Silicone Properties Critical for PV Industry

3.1 Silicone Chemical Functionality

Silicones can be considered a “molecular hybrid” between glass and organic linear polymers. As
shown in the figure below, if the Si atom is only bonded to oxygen atoms, the structure is an inorganic glass (called a Q-type Si). If one oxygen atom is substituted with an R group (i.e. methyl, ethyl, phenyl, etc.) a resin or silsesquioxane (T-type Si) material is formed. These silsesquioxanes are more flexible than the Q-type materials. Finally, if two oxygen atoms are replaced by organic groups a very flexible linear polymer (D-type Si) is obtained.

<table>
<thead>
<tr>
<th>0 (Q)</th>
<th>1 (T)</th>
<th>2 (D)</th>
<th>3 (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₄²⁻</td>
<td>R₁SiO₃/₂</td>
<td>R₂SiO₂/₂</td>
<td>R₃SiO¹/₂</td>
</tr>
</tbody>
</table>

Table 1 – Silicone Chemical Functionality

3.2 Silicone Mechanical Properties

The increased flexibility that is found with decreasing crosslinking results in a low glass transition (Tg) of the linear polymers. The Tg of linear polydimethylsiloxane (if all R groups are methyl units) is -120 °C. Due to the Tg, silicones also typically have a low and relatively flat modulus once formulated and cured over a large temperature range, especially when compared to organic polymers such as Ethylvinylacetate (EVA).

Figure 1 – Modulus variation with temperature change of silicones and EVA

The modulus in linear silicones can be quite low due to low crosslink density and in this form silicones often function to relieve stress to due CTE mismatch between two components in many applications. Similarly, the modulus is higher in branched, tack free resin systems; they can be as high as 10 MPa at room temperature. It is also important to note that the branching vs. linear nature of the silicon polymer also impacts the coefficient of thermal expansion (CTE), as Tg decreases, the CTE increases. Along with a wide range in modulus is a variation in other mechanical properties such as tensile strength and elongation depending upon many formulation variables. For example, often reinforcing fillers are added to enhance mechanical properties. In addition, silicones wide temperature of use range results in many of their properties remaining virtually unchanged from -40 °C to 150 °C (2).

In a PV module where a hot spot could approach 150 °C, it’s important that there be no degradation in properties upon exposure to temperature spikes and the typical operation temperatures. Silicones are known for very high temperature stability and retention of properties upon exposure to high temperatures for extended periods. Previous studies have shown little change in transparency and mechanical properties when exposed to temperatures >150 °C for extended times (2) for a number of Dow Corning silicones that are applicable to the PV assembly market. A sample of this study is presented in Figure 2.

Figure 2 – Thermal stability of silicones in extended exposure at high temperatures.

3.3 Silicone Corrosion Protection

While silicones are very permeable to gas and liquid vapors, they are also very hydrophobic. These two attributes result in silicones having very low moisture pick-up in damp heat environmental exposure or total water immersion. In one example a silicone elastomer was measured to have < 0.05 wt % gain of water upon exposure to 85%RH/85 °C conditions (2). This is significantly less than measured for typical organic polymers. Another key component in the performance of silicone in corrosion protection from environmental exposure is adhesion. The silicones can be formulated to have strong adhesive bonds to multiple substrates. When strong adhesive bonds are formed the moisture will not have a path to wick into moisture sensitive components and cause corrosion or other degradation mechanisms. The ability for silicones to transmit water vapor rather than absorb it prevents moisture from being trapped at an interface. The Dow Corning® PV-6100 Encapsulant Series have been formulated to excel in adhesion to metal components and even to materials such as PET. The data shown in Figure 3 shows 100% cohesive failure to PET at continuous exposure to 85°C/85%RH for 6 weeks with no loss in peel strength.
3.4 Silicone Electrical Insulation Properties

Silicones are very well known for their excellent dielectric strength and high volume resistivity. There are many applications were silicones are used as electrical insulators. They are non-conductive because of their chemical nature, and when compounded with the proper fillers and additives, they can be made to meet a wide range of electrical insulating applications.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric strength, Volts/mil</th>
<th>Thickness, mils</th>
<th>Break-through voltage, kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV-6100 Series</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sample A</td>
<td>1290</td>
<td>16 (0.29)</td>
<td>12.9</td>
</tr>
<tr>
<td>sample B</td>
<td>789</td>
<td>21 (0.53)</td>
<td>16.6</td>
</tr>
<tr>
<td>EVA</td>
<td>907</td>
<td>17 (0.43)</td>
<td>15.4</td>
</tr>
</tbody>
</table>

In addition, because of the low equilibrium moisture content they remain non-conductive even in high humidity conditions.

Silicones are also known as one of the most flame resistant polymers. Certain Silastic® silicone rubber products inherently possess a profile of fire hazard characteristics which makes them useful for applications where good flame retardation and minimum fire hazard is desired. Silicones can be compounded and fabricated to meet many specifications, including: UL-94, V-1 or V-0. Silicones have a low flammability rating and they typically do not support or promote a flame and do not produce toxic combustion by-product (2).

Finally, silicones can be formulated with a variety of thermally conductive fillers and have been used successfully in thermal management applications. This is typically an important property for PV junction box pottants for diode temperature control.

3.5 Silicone Durability

Many applications and markets have exposed silicones to outdoor weather conditions. For example construction sealants have proven silicones to withstand UV and other outdoor conditions (2). These durable materials are virtually unaffected by ultraviolet light or ozone and have been successfully tested in many accelerated aging tests (2). Dow Corning silicones have also been put in PV modules as the cell encapsulant and have withstood 25 years of sun exposure and are still performing satisfactorily (5). A recent study of modules built in 1982 and used in an array at the BP Solar facility in Frederick, Maryland USA has shown minimal loss of power after 25 years. A module rated at 55 watts in 1982 as shown in the picture of the junction box in Figure 4 was tested at 52 watts in June 2008 the IV data is shown in Figure 5. The Isc measured on the module was essentially the same as the initial measurement and visually other than being quite dirty the module looks very good. It does not due the module justice, but a picture of the module is presented here as evidence of the good condition.

Silicones offer the best long-term resistance to...
environmental extremes. In extended environmental aging studies silicone has shown very good response to protection of cells well beyond the typical testing required by IEC and UL standards.

Figure 6 – Multicrystalline cell Pmax response to extended environmental aging

3.6 Silicone Cure Systems

Silicones can be formulated to a variety of cure systems. The most common cure system for materials used in electronics applications is the addition cure of Si-H to Si-Vinyl. This reaction is typically catalyzed by platinum and can be accelerated with heat. This type of cure system can be formulated as a one–part or two–part product and it is a neutral cure system that releases no cure by-products. This cure system has the advantage of being able to cure at a variety of temperatures and can be formulated to be very fast curing; this can be very beneficial for high through-put assembly. The other type of cure system is condensation (moisture) cure with is typically employed in Sealant systems can be formulated with a neutral cure system with no acidic by-products. They also typically have excellent adhesion and mechanical properties. However the cure rates are typically much slower. The graph shown in Figure 7 shows the cure profile of the developmental Dow Corning® PV-6100 Encapsulant Series as measured by a parallel plate rheometer. The initiation of cure takes place at ~70 C and is essentially complete within 1 minute.

Figure 7 – Cure profile of developmental Dow Corning® PV-6100 Encapsulant Series

3.6 Silicone Optical Properties

Silicones also have unique optical properties. The refractive index of silicone polymers can vary from 1.38 to 1.58 (6), depending on the nature of the R groups and RI tuning can be critical for some optical applications. Silicone polymers are also highly transparent in the UV-Visible wavelengths. In the figure below the % Transmission of a 2.6 mm thick cured PDMS elastomer is shown, high transparency is seen down to 250 nm as compared to the cut off of 400 nm for EVA (2).

Figure 8 – Percent Transmission comparative measurements of silicone and EVA by UV-Vis Spectrometer

In addition, the % transmission measurement of silicone as compared to EVA was repeated at NREL (Figure 9) with similar results. The major difference is the type of glass that actually cuts off the amount of transmission below 350 nm for silicone.

Figure 9 – Percent Transmission comparative measurement of silicone and EVA by Hemispherical Transmittance
Because silicones are essentially transparent to UV wavelengths, they are inherently UV stable and require no additional additives to protect against UV degradation such as those used in other organic encapsulant formulations. This property allows cells more efficient by utilizing the UV light to be converted into electrons rather than be absorbed by UV stabilizers. The effect on PV cells can be seen in Figures 10 and 11 by comparatively measuring the External Quantum Efficiency of cells encapsulated with silicone and EVA.

![Figure 10 - % Quantum Efficiency comparison of Front Contact Mono-crystalline PV cells encapsulated with Dow Corning® PV-6100 Encapsulant Series and EVA.](image)

![Figure 11 - % Quantum Efficiency comparison of Back Contact Mono-crystalline PV cells encapsulated with Dow Corning® PV-6100 Encapsulant Series and EVA.](image)

Additionally, ray-racing simulations of SunPower-type cells show a similar result of 1.5% gain in Isc when encapsulated with silicone rather than EVA. The results are presented in Figures 13 and 14 in terms of the optical loss mechanisms, plotting Isc as a function of wavelength under the AM1-5g spectrum. The figures show that the difference between the encapsulants is almost entirely due to absorption of short-wavelength photons by the EVA. This study will be described in detail in a future publication.

![Figure 12 - % Change Isc comparison of SunPower (7) PV cells encapsulated with Dow Corning® PV-6100 Encapsulant Series and EVA.](image)

![Figure 13 – Ray tracing simulation of EVA Encapsulated PV Cell](image)

![Figure 14 – Ray tracing simulation of Silicone Encapsulated PV Cell](image)

The efficiency improvement has also been measured directly when comparing SunPower cells encapsulated with Silicone and EVA. The figure below shows the relative % change when comparing SunPower cells encapsulated with Dow Corning® PV-6100 series and EVA. As shown in Figure 12, on average silicone encapsulation delivers 1.5% higher Isc values than that of EVA. This effect remains true even when using Antireflective (AR) coatings on the glass.

4 Conclusions

Silicones are a very unique family of materials that cover a wide range of properties. They can be
formulated in a multitude of products depending upon the application needs and requirements. Silicones are proven in numerous industries with wide range of performance criteria, some of these are automotive, construction, and electronics. Several properties of silicones make them an ideal fit to the needs of the PV module and assembly market. This includes mechanical properties that remain almost constant over a wide range of temperatures, and remain stable even after long periods of exposure at high temperatures. UV stability, low equilibrium moisture content, electrical insulation, and flame resistance are inherent due to the chemical nature of silicones. In addition, properly formulated silicone formulations can exhibit very fast cure rates, high level of adhesion to many and hard to stick to substrates, and optical transparency. These all contribute to a high durability in outdoor exposure, and higher efficiency due to more effective use of the light from the solar spectrum.

5 References

(2) Internal Dow Corning data
(3) Polymer Material Science Engineering, #56, 1987, pg 469-75
(4) Electronics Brochure on “Thermally Conductive adhesives”
(5) PV modules with Sylgard® 184 Silicone Elastomer have been on roof tops of BP Solar and Georgetown University for 25 yrs
(7) SunPower Corporation makes no warranties, express, implied or otherwise, regarding the sufficiency, accuracy or completeness for any data it has provided herein.