Evaluation of encapsulant materials for PV applications

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ABSTRACT

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Market Watch Encapsulant materials used in PV modules serve multiple purposes. They physically hold components in place, provide electrical insulation, optically couple superstrate materials (e.g., glass) to PV cells, protect components from mechanical stress by mechanically de-coupling components via strain relief, and protect materials from corrosion. To do this, encapsulants must adhere well to all surfaces, remain compliant, and transmit light after exposure to temperature, humidity, and UV radiation histories. Encapsulant materials by themselves do not completely prevent water vapour ingress [1-3], but if they are well adhered, they will prevent the accumulation of liquid water providing protection against corrosion as well as electrical shock. Here, a brief review of some of the polymeric materials under consideration for PV applications is provided, with an explanation of some of their advantages and disadvantages.

Types of encapsulants

Many types of encapsulant resins have been considered for use in PV modules. When PV panels were first developed in the 1960s and 1970s, the dominant encapsulants were based on polydimethyl siloxane (PDMS) [4,5], chosen because of its exceptional natural stability against thermal- and ultraviolet light-induced stress. However, in an effort to reduce module costs, alternative materials were investigated and developed, leading to the emergence of ethylene vinyl acetate (EVA) as the dominant PV encapsulant.

Recently, there has been renewed interest in using alternative encapsulant materials. The common alternatives are shown in Fig. 1. Most of them, including ionomer, EVA, and polyvinyl butyral (PVB), have a backbone consisting of only carbon-carbon (C-C) bonds. Alternatively, thermoplastic polyurethane (TPU) formulations have nitrogen and oxygen incorporated into the backbone in the form of a urethane bond. All four of these structures incorporate an ester bond (R-COOR'), which is susceptible to hydrolysis. The presence of hydrolytically unstable bonds in the backbone is nevertheless of greater concern because depolymerization can facilitate significant reduction in viscosity, allowing creep and/or delamination to occur more easily [6]. If the side groups of PVB or EVA become cleaved, one would expect to see stronger hydrogen bonding between polymer chains and surfaces. This can lead to embrittlement of polymers; however, a substantially greater extent of hydrolysis (compared to breaking of the backbone bonds in TPUs) must occur for these effects to be significant.

In contrast, PDMS has a backbone consisting of alternating atoms of Si and O. Because the silicon atom is much larger than oxygen or carbon atoms, there is greater freedom of motion for rotation and bending of Si-C sidegroup and Si-O back-bone bonds for silicone-based polymers compared to hydrocarbon-based polymers. This enhanced mobility in PDMS results in polymers with extremely low glass transition temperatures and with lower mechanical modulii (so long as the



cross-link density is low). Additionally, the bond dissociation energy of Si-O is ~108kcal/mol compared to 83kcal/mol for C-C bonds, corresponding to photons with wavelengths of 263 and 343nm, respectively. The fact that no terrestrial solar radiation is present at 263nm relative to that ordinarily present at 343nm is one of the reasons for the exceptional UV stability of PDMS.

"The use of chemical crosslinks enables more effective use of primers to promote adhesion at surface interfaces."

Typically, ionomers, TPUs and PVBs are formulated as thermoplastic (noncross-linked) materials. For PVBs, plasticizers are also added to lower their mechanical modulii and to tailor their phase-transition temperatures. As is also summarized in [6], TPUs and PVBs typically have a glass transition around or below room temperature and are therefore in a rubbery state during much of their use, which makes them more susceptible to shear-induced flow. TPU and PVB are typically formulated to have a high viscosity at PV operating temperatures to reduce creep [6].

Ionomers are also typically thermoplastic, but often have a melt transition around 90° to 100°C. Below the melt temperature, polyethylene segments are aligned forming physical cross-links, the formation of which is reversible upon heating. The dramatic changes in viscosity upon heating through the melt transition, where viscosity can be decreased by orders of magnitude, must be considered for modules deployed in environments/ mounting configurations prone to reaching the melt temperature.



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Figure 2. Schematic of curing chemistry of PDMS-based encapsulants [7].

To overcome concerns with polymer creep/flow at elevated temperatures, EVA and PDMS materials are typically formulated to form chemical cross-links. For PDMS, a Pt-based catalyst combines vinyl groups (of vinyl-terminated PDMS) to silane groups of a poly(dimethylco-methylhydrogensiloxane) (see Fig. 2). This chemistry will proceed at room temperature, but is significantly accelerated at elevated temperature. Chemical cross-linking restricts material flow to only occur when mechanical stresses are large enough to break chemical bonds. Additionally, the use of chemical cross-links enables more effective use of primers to promote adhesion at surface interfaces.

Thus, a cross-linked system will be chemically bonded to surfaces, whereas thermoplastic systems must rely on a combination of ionic, hydrogen, and/or van der Waals forces for adhesion. When water reaches an interface between the polymer and an inorganic material, the polar water molecules will compete with the less polar polymer at adhesion sites. If the polymer is displaced by the water, delamination will occur. In contrast, with a chemically bonded encapsulant, chemical bonds must be broken in addition to the physical bonds, making it easier for chemically bonded, crosslinked encapsulants to be formulated for durable interfacial adhesion.

PDMS-based materials are inherently UV and thermally stable, but hydrocarbon-based materials (EVA, TPU, PVB, and ionomer) require stabilizers to be durable. An EVA formulation is not just simply EVA resin, but a complex mixture of components. A typical EVA formulation is shown in Fig. 3 [8,9]. The majority of the material is the EVA resin. Typically, a 33 wt% vinyl acetate EVA is used to balance its characteristics, which include: a low glass transition, low modulus, low crystallinity/highly light transmittance resin, and a convenient melting temperature (45°C to 65°C), enabling easy melting for processing. EVA resins are also designed with molecular weight distributions and branching characteristics to facilitate extrusion into a film, which will minimize shrinkage in subsequent laminations.

"A trialkoxy silane is used to promote adhesion between EVA and inorganic surfaces."

About 1 to 2 wt% of an EVA film is a thermally-activated peroxide used for cross-linking at elevated temperatures during lamination. The peroxide decomposes to produce radicals, which react with the polymer using non-specific chemical pathways to form cross-links. At temperatures above 140°C, a typical peroxide such as tertbutyl-2-ethylhexyl-

peroxycarbonate (TBEC) will decompose sufficiently to facilitate the cure within two minutes [10]. The time required to heat the polymer in a module to this temperature range is therefore the most significant factor limiting the speed of lamination.

A trialkoxy silane is used to promote adhesion between EVA and inorganic surfaces. The silane end tends to be attracted to polar surface hydroxyl groups and is able to react with them, creating methanol as a leaving group and forming a covalent chemical bond in place of the hydroxyl group [11]. The other two alkoxy groups may react further with other surface groups or with other trialkoxy silane groups, forming a threedimensional network that ensures good adhesion. This interfacial structure also helps to passivate inorganic surfaces against corrosion by limiting the movement of corrosion by-products away from the interface.

The effects of UV radiation are mitigated by the inclusion of a UV absorber such as benzotriazole. Early EVA formulations used benzophenonebased UV absorbers. However, it was later determined that an interaction between benzophenone, lupersol 101 (peroxide), and a phenyl phosphonite had a significant tendency to form chromophores, imparting a yellow colour to EVA upon outdoor exposure [12]. These early formulations resulted in extreme degradation of the historically sizable installation of PV panels at Carrizo plains. Initially, the loss in power of the modules was attributed primarily to EVA discoloration [13], but subsequent analysis demonstrated that solder joint breakage was the more significant problem [14].

Finally, a hindered amine light



Figure 3. Example formulation of EVA for PV.

Transmission to Cells through 3.18 mm glass and 0.45 mm Encap Encapsulant Comments GE RTV615 94.5±0.3 PDMS, Addition Cure 94.4 ± 0.3 Dow Corning Sylgard 184 PDMS, Addition Cure Dow Corning 527 94.4 ± 0.3 PDMS, Addition Cure Polyvinyl Butral 93.9 ± 0.4 93.9 ± 0.4 EVA 93.4 ± 0.4 NREL Experimental Poly-a-olefin 93.3 ± 0.3 Thermoolastic Polyurethane Thermoplastic lonomer #1 92.3 ± 0.4 Copolymer of Ethylene and Methacrylic acid DC 700 91.7 ± 0.3 PDMS. Acetic Acid Condensation Cure Th noplastic lonomer #2 88.4 ± 0.4 Copolymer of Ethylene and Methacrylic acid

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Table 1. Solar photon (300 to 1100nm) weighted average optical density determined from transmittance measurements through polymer samples of various thickness (1.5 to 5.5mm) laminated between two pieces of 3.18mm-thick, Ce-doped, low-Fe glass [15].

stabilizer (HALS) and possibly a phenolic phosphonite may be added as antioxidants. The HALS acts to decompose peroxide radicals that may form due to thermal or UV exposure. In this process, the HALS is not consumed as opposed to the phenolic phosponite, which is oxidized to produce phosphate and phenols. These phenols are able to further react with radicals and thus have additional antioxidative effects.

Polymer light transmittance

PV encapsulants optically couple PV cells to a transparent superstrate such as glass; therefore, high transmittance is desirable. Hemispherical transmittance of light through encapsulant samples laminated between two pieces of

3.2mm-thick glass was measured to enable comparison of different materials, as detailed in Table 1 [15]. From these and similar measurements of bare glass, the photon transmission through a glass superstrate and 0.45mm of encapsulant to a hypothetical cell was estimated. Of the materials measured, the PDMS samples had the best transmittance, about 0.6% better than the best hydrocarbonbased materials. Part of this difference is attributable to the absence of UV absorbers in PDMS. This analysis considered only normal transmittance. A more thorough analysis by McIntosh et al. [16] using ray tracing models and considering multiple reflections, nonnormal incidence, and reflections off the backsheet between cells, estimated

this difference to be as high as 1.5%. Of the materials currently being considered for PV applications, PDMS has the best transmittance.

UV durability

Depending on its composition, glass may block much of the UV-B radiation, but typically blocks very little of the UV-A [13,17]. Therefore the UV stability of the encapsulation material used in front of the cell is important. Fig. 4 shows the results of a highly accelerated stress test designed to investigate the possible use of non-silicone-based encapsulants in medium-concentration PV applications [18]. Sample encapsulants were laminated between two pieces of low-Fe, UV-transmitting glass while monitoring the solar/quantum efficiency-weighted transmittance. They were exposed to 42 UV suns at a temperature between 80° and 95°C. In this scenario, none of the five different PDMS silicone samples demonstrated any significant loss in transmittance after up to 6000 hours of exposure. Under the same conditions, the four different EVA formulations showed very significant degradation after only 750 to 1700 hours of exposure, demonstrating the inherently greater stability of PDMS relative to EVA.

Fig. 4 also illustrates the great variation in performance of the EVA formulations provided by different manufacturers. This is attributable to changes in either the type or the amount of the different additives described in Fig. 3. Considering the extreme conditions of this test, these formulations performed quite well.



Figure 4. Solar and x-Si quantum efficiency-weighted transmittance of test samples exposed to 42 global-UV suns in a Xenon arc Weather-Ometer. Samples consist of 0.5mm encapsulant laminated between two 2.5cm-square, 3.18mm-thick, low-Fe, non-Ce glass samples (i.e., highly UV transmissive glass). Prior to sample discoloration, sample temperatures were maintained from 80° to 95°C during aging. The top axis corresponds to the amount of UV radition that would be seen with a system tracking the sun and utilizing only the direct spectrum.



Similar experiments were also performed with PVB, TPU, and ionomer formulations [18]. In this experiment, PVB performed exceptionally poorly, TPU was comparable to EVA, and the ionomer was more durable than EVA. It must also be kept in mind that this test addressed only light transmittance, which is only one of several important characteristics such as adhesion.

Resistivity

The resistivity of encapsulants is relevant to electrical insulation, although the backsheet properties are a greater determining factor for a module. More importantly, relatively low resistance in encapsulant materials has been linked to electrochemical corrosion [20,21]. The volume resistivity of several candidate encapsulant materials is shown in Fig. 5. Measurements were performed using the DC alternating polarity method with some of the samples preconditioned by soaking them in water at 40°C. For most materials, saturation with water versus dry measurement did not significantly impact resistivity. PVB, which can absorb as much as 8%water at this temperature [19], was most affected by saturation with water. Mon et al. [19,20] found that, for PVB and EVA, temperature had a much greater effect on resistivity than absorbed water. The EVA, TPU, and poly- α -olefin examined demonstrated resistivities about 100 times greater than PVB, and the silicone, ionomer, and EPDM were about 10,000 times more resistive than PVB. Mon et al. were also able to find good correlation between degradation induced by electrochemical corrosion and total leakage from cells to the frame in amorphous-Si-based PV modules. There is a great range in the value of resistivity among polymers, which can be a significant determining factor for electrochemical corrosion processes.

Conclusions

This work discussed many of the attributes to be considered when selecting a polymer as a PV encapsulant and how different polymers are designed to meet these needs. An encapsulant provides optical coupling of PV cells and protection against environmental stress. Polymers must perform these functions under prolonged periods of high temperature, humidity, and UV radiation. The base polymer structure is the first thing to consider as it dominates subsequent properties. However, encapsulant films of the same base polymer have varying amounts and types of stabilization additives, resulting in different durabilities among manufacturers.

While some discussion was presented relative to maintenance of transmission after accelerated stress, getting good correlation of lab results with field results is very challenging. This is particularly true when one considers retention of adhesion strength, where there is a great variety of interfaces that are easily affected by trace amounts





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of surface contaminants. Ultimately, to have good service life prediction, long-term durability studies comparing indoor to outdoor tests are necessary to provide good confidence in the choice of encapsulant.

EVA is currently the dominant encapsulant chosen for PV applications, not because it has the best combination of properties, but because it is an economical option with an established history of acceptable durability. Getting new products into the market is challenging because there is not room for dramatic improvements (e.g., transmittance), and one must balance initial cost and performance with the unknowns of long-term service life.

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ΡV

Modules

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About the Author



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