



Overview of Scientific Issues Involved in Selection of Polymers for PV Applications

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OVERVIEW OF SCIENTIFIC ISSUES INVOLVED IN SELECTION OF POLYMERS FOR PV APPLICATIONS

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ABSTRACT

Encapsulant materials used in photovoltaic (PV) modules serve multiple purposes. They physically hold components in place, provide electrical insulation, reduce moisture ingress, optically couple substrate 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. 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) [1, 2]. This was chosen because of its exceptional intrinsic stability against thermal- and ultraviolet (UV) light-induced stress [3]. 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. Many of them (see Fig. 1), including ionomer, EVA, polyvinyl butyral (PVB), and thermoplastic polyolefins (TPO), 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. The ester bond (R-COOR') is susceptible to hydrolysis; however, the presence of hydrolytically unstable bonds in the backbone (TPUs) is of greater concern because depolymerization can facilitate significant reduction in viscosity, allowing creep and/or delamination to occur more easily [4]. 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.

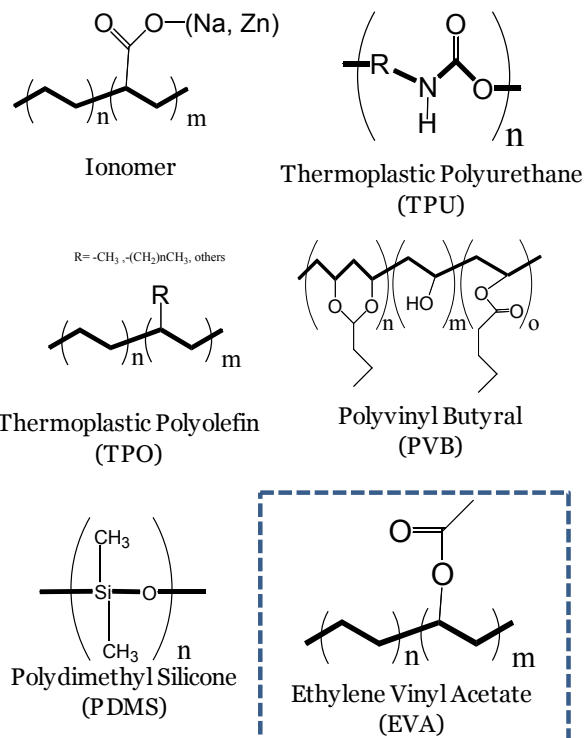


Figure 1 Structures of common PV encapsulant resins.

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 side-group 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 moduli (so long as the cross-link density is low). Additionally, the bond dissociation energy of Si-O is ~108 kcal/mol compared to 83 kcal/mol for C-C bonds, corresponding to photons with wavelengths of 263 and 343 nm, respectively. The fact that no terrestrial solar radiation is present at 263 nm relative to that ordinarily

present at 343 nm is one of the reasons for the exceptional UV stability of PDMS.

Typically, ionomers, TPUs, TPOs, and PVBs are formulated as thermoplastic (non-cross-linked) materials, though there is no inherent reason that they couldn't be made to form cross-links and/or chemically bond to surfaces. For PVBs, plasticizers are also added to lower their mechanical moduli and to tailor their phase-transition temperatures. As is also summarized in [4], 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, and susceptible to shear-induced flow. TPUs and PVBs are typically formulated to have a high viscosity at PV operating temperatures to prevent creep [4]. Ionomers and TPOs 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 whose formation is reversible upon heating.

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 polymethyl-co-dimethyl siloxane (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.

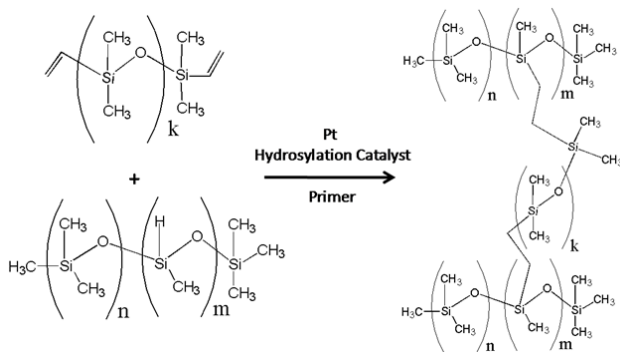


Figure 2. Schematic of curing chemistry of PDMS-based encapsulants [5].

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, cross-linked 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 Figure 3 [6, 7]. The majority of the material is the EVA resin. Typically a 27 wt% to 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 may minimize shrinkage in subsequent laminations.

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 [8]. 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 [9]. The other two alkoxy groups may further react with other surface groups or with other trialkoxy silane groups, forming a three-dimensional 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 a benzotriazole or benzophenone. Early work on EVA formulations found an

interaction between benzophenone, lupersol 101 (peroxide), and a phenyl phosphonite that had a significant tendency to form chromophores [10]. 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 [11], but subsequent analysis demonstrated that solder joint breakage was the more significant problem [12].

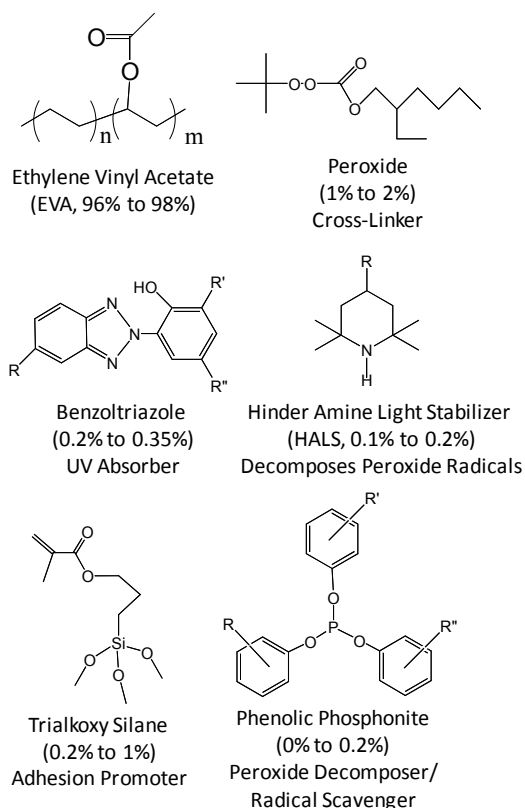


Figure 3. Example formulation of EVA for PV.

Finally, a hindered amine light 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 phosphonite, which is oxidized to produce phosphate and phenols.

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 3.2-mm-thick glass was measured to enable comparison

of different materials, as detailed in Table 1 [13]. From these and similar measurements of bare glass, the photon transmission through a glass superstrate and 0.45 mm of encapsulant to a hypothetical cell interface was estimated. The PDMS samples had the best transmittance, about 0.6% better than the best hydrocarbon-based 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. [14], using ray tracing models and considering multiple reflections, non-normal incidence, and reflections off the backsheet between cells, estimated this difference to be as high as 1.5%.

Encapsulant	AM 1.5 Solar Photon and x-Si QE Weighted Absorptivity	Transmission to Cells through 3.18 mm glass and 0.45 mm Encapsulant	Comments
	(1/mm)	%	
GE RTV615	0.000 ± 0.003	94.8 ± 0.3	PDMS, Addition Cure
Dow Corning Sylgard 184	0.002 ± 0.004	94.7 ± 0.3	PDMS, Addition Cure
Dow Corning 527	0.004 ± 0.003	94.7 ± 0.3	PDMS Gel, Addition Cure
Polyvinyl Butyral	0.011 ± 0.005	94.3 ± 0.4	
EVA	0.012 ± 0.005	94.3 ± 0.4	
Thermoplastic Polyurethane	0.024 ± 0.004	93.8 ± 0.3	
NREL Experimental	0.027 ± 0.006	93.7 ± 0.4	Poly α -Olefin Copolymer
Thermoplastic Ionomer #1	0.049 ± 0.007	92.7 ± 0.4	Copolymer of Ethylene and Methacrylic acid
DC 1199 SSL	0.064 ± 0.004	92.1 ± 0.3	PDMS, One Part Neutral Condensation Cure
DC 700	0.068 ± 0.004	92.0 ± 0.3	PDMS, Acetic Acid Condensation Cure
Thermoplastic Ionomer #2	0.149 ± 0.007	88.7 ± 0.4	Copolymer of Ethylene and Methacrylic acid

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

UV DURABILITY

Depending on its composition, glass may block much of the UV-B radiation, but typically blocks very little of the UV-A [11, 16]. Therefore the UV stability of the encapsulation material used in front of the cell is important. Figure 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 [17]. 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. Here, none of the five different PDMS silicone samples demonstrated any significant loss in transmittance after up to 6000 h of exposure. Under the same conditions, the four different EVA formulations showed very significant degradation after only 750 to 1700 h of exposure. This demonstrates the inherently greater stability of PDMS relative to EVA.

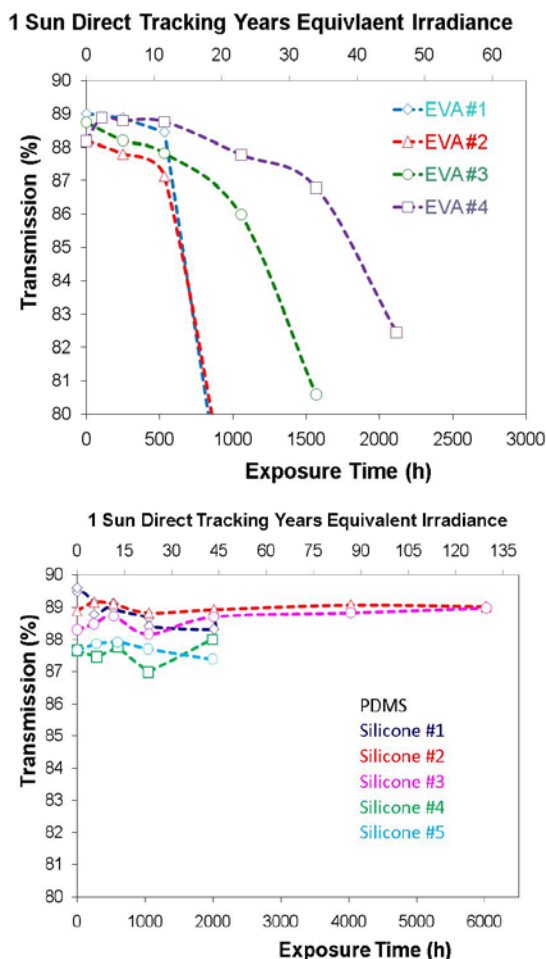


Figure 4. Solar and x-Si quantum efficiency-weighted transmittance of test samples exposed to 42 global-UV suns in a Xenon arc Weather-Ometer. Samples consist of 0.5-mm encapsulant laminated between two 2.5-cm-square, 3.18-mm-thick, low-Fe, non-Ce glass samples (i.e., highly UV transmissive glass). The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

Also important in Fig. 4 is 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. Similar experiments were also performed with PVB, TPU, and ionomer formulations [17]. Here 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.

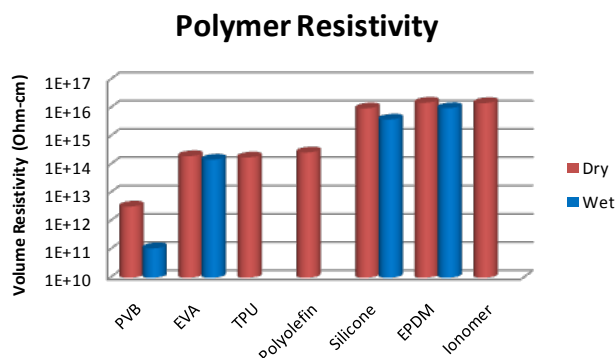


Figure 5. Volume resistivity measured using alternating DC polarity +/- 700V. "Wet" samples were immersed in water at 40°C.

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 [18, 19]. 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 [18], was most affected by saturation with water. Mon et al. [18, 19] found that, for PVB and EVA, temperature had a much greater affect 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.

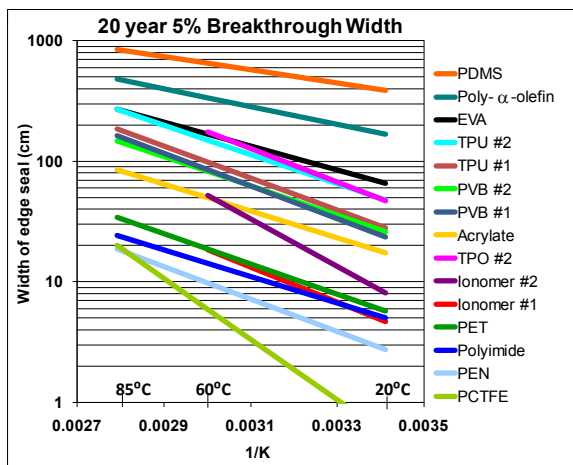


Figure 6. Width of edge seal made from different materials that would be necessary to keep moisture below 5% of equilibrium values at a given temperature[20].

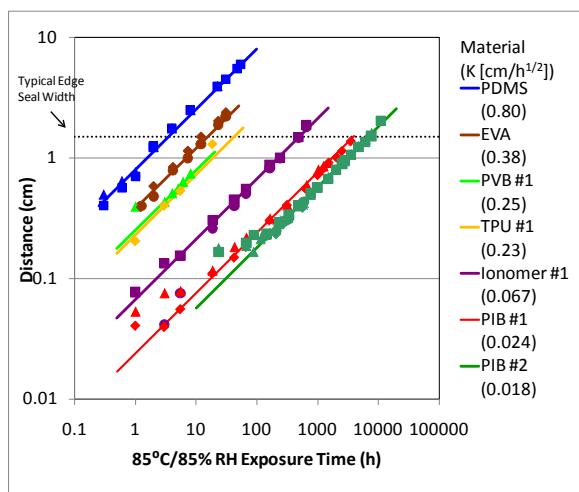


Figure 7. Penetration depth of moisture between glass plates laminated with different materials as measured by the oxidation of a 100 nm film of Ca [20].

MOISTURE INGRESS PREVENTION

Typical transparent encapsulant materials by themselves do not completely prevent water vapor ingress [20-22], but if they are well adhered, they will prevent the accumulation of liquid water providing protection against corrosion as well as electrical shock. Thus good adhesion is more important than low permeation as most module

constructions will equilibrate with moisture in a time frame on the order of less than a year [22].

Even for a module construction with an impermeable backsheet (e.g. glass) water will still diffuse in from the edges. Figure 6 shows estimates of how far moisture can penetrate different PV polymeric materials as a function of temperature. Of the encapsulant materials, Ionomer #1 has the lowest diffusivity and even if it was installed in a cold climate with an average effective temperature of 20°C, moisture would still penetrate to a depth of 4 or 5 cm over the course of 20 years. Depending on the sensitivity of a PV material, this may not be sufficient [21].

In another set of experiments encapsulant materials and edge seal materials composed of polyisobutylene (PIB) filled with desiccants were laminated between two pieces of glass one of which had a 100 nm film of Ca metal deposited on the surface [20]. As moisture permeates the polymer, the Ca metal is oxidized to transparent CaO giving a simple visual indicator of the extent of moisture ingress. As shown in Fig. 7, these PIB based edge seal materials are an order of magnitude better than Ionomer #. This should enable them to restrict moisture ingress to less than a cm over the lifetime of a module. If a PV material is very sensitive to moisture, a desiccant filled PIB edge seal material is needed to prevent moisture ingress.

CONCLUSIONS

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.

With the development of thin film based PV technologies, concerns with moisture ingress are important. Some effort has focused on flexible barriers with permeation rates less than 10^{-4} g/m²/day [22], but even with an impermeable front- and back-sheet moisture vapor will penetrate a module unless extremely low permeability materials are used such as desiccant filled PIBs.

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 or price reductions), and one must balance initial cost and performance with the unknowns of long-term service life.

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REFERENCES

- [1] D. C. Corporation, "Develop Silicone Encapsulation Systems for Terrestrial Silicon Solar Arrays," *DOE/JPL/954995-80/6*, December, 1979 1979.
- [2] M. A. Green, "Silicon photovoltaic modules: A brief history of the first 50 years," *Progress in Photovoltaics*, vol. 13, pp. 447-455, Aug 2005.
- [3] M. D. Kempe, "Accelerated UV Test Methods for Encapsulants of Photovoltaic Modules," *33rd IEEE Photovoltaic Specialist Conference Program*, 2008.
- [4] D. Miller, M. D. Kempe, S. H. Glick, and S. Kurtz, "Creep in Photovoltaic Modules: Examining the Stability of Polymeric Materials and Components," Honolulu, HI, 2010, pp. 6 pp.-6 pp.
- [5] F. de Buyl, "Silicone sealants and structural adhesives," *International Journal of Adhesion and Adhesives*, vol. 21, pp. 411-422, Oct 2001.
- [6] P. Klemchuk, M. Ezrin, G. Lavigne, W. Holley, J. Galica, and S. Agro, "Investigation of the degradation and stabilization of EVA-based encapsulant in field-aged solar energy modules," *Polymer Degradation and Stability*, vol. 55, pp. 347-365, 1997.
- [7] F. J. Pern, "Composition and Method for Encapsulating Photovoltaic Devices," *Patent# 6,093,757*, 2000.
- [8] E. F. Cuddihy, A. Gupta, C. D. Coulbert, R. H. Liang, A. Gupta, P. Willis, and B. Baum, "Applications of Ethylene Vinyl Acetate as an Encapsulation Material for Terrestrial Photovoltaic Modules," *DOE/JPL/1012-87 (DE83013509)*, 1983.
- [9] E. F. Cuddihy, C. D. Coulbert, A. Gupta, and R. Liang, "Electricity from Photovoltaic Solar Cells, Flat-Plate Solar Array Project Final Report, Volume VII: Module Encapsulation," *DOE/JPL-1012-125*, 1986.
- [10] W. W. Holley and S. C. Agro, "Advanced EVA-Based Encapsulants, Final Report January 1993-June 1997," *NREL/SR-520-25296*, 1998.
- [11] C. F. Gay and E. Berman, "PERFORMANCE OF LARGE PHOTOVOLTAIC SYSTEMS," *Chemtech*, vol. 20, pp. 182-186, Mar 1990.
- [12] J. H. Wohlgemuth and R. C. Petersen, "Reliability of EVA modules," Louisville, KY., 1993, pp. 1090-1094.
- [13] M. D. Kempe, "Ultraviolet light test and evaluation methods for encapsulants of photovoltaic modules," *Solar Energy Materials and Solar Cells*, vol. 94, pp. 246-253, February 2010.
- [14] K. R. McIntosh, J. N. Cotsell, J. S. Cumpston, A. W. Norris, N. E. Powell, and B. M. Ketola, "An optical comparison of silicone and EVA encapsulants for conventional silicon PV modules: a ray-tracing study," Philadelphia, PA., 2009, pp. 000544-000549.
- [15] M. D. Kempe, "Ultraviolet light test and evaluation methods for encapsulants of photovoltaic modules," *Solar Energy Materials and Solar Cells*, vol. 94, pp. 246-253, February.
- [16] M. D. Kempe, T. Moricone, and M. Kilkenny, "Effects of cerium removal from glass on photovoltaic module performance and stability," *Proceedings of the SPIE - The International Society for Optical Engineering*, vol. 7412, pp. 74120Q (12 pp.)-74120Q (12 pp.), 2009 2009.
- [17] M. D. Kempe, M. Kilkenny, T. J. Moricone, and J. Z. Zhang, "Accelerated stress testing of hydrocarbon-based encapsulants for medium-concentration CPV applications," Philadelphia, PA., 2009, pp. 6 pp.-6 pp.
- [18] G. Mon, L. Wen, and R. Ross, Jr., "Encapsulant free-surfaces and interfaces: critical parameters in controlling cell corrosion [photovoltaic modules]," New Orleans, LA., 1987, pp. 1215-1221.
- [19] G. R. Mon and R. G. Ross, Jr., "Electrochemical degradation of amorphous-silicon photovoltaic modules," Las Vegas, NV., 1985, pp. 1142-1149.
- [20] M. D. Kempe, A. A. Dameron, T. J. Moricone, and M. O. Reese, "Evaluation and modeling of edge-seal materials for photovoltaic applications," Honolulu, HI., pp. 000256-000261.
- [21] D. J. Coyle, H. A. Blaydes, J. E. Pickett, R. S. Northey, and J. O. Gardner, "Degradation kinetics of CIGS solar cells," *Proceedings of the 2009 34th IEEE Photovoltaic Specialists Conference (PVSC 2009)*, pp. 001943-7, 2009.
- [22] M. D. Kempe, "Modeling of rates of moisture ingress into photovoltaic modules," *Solar Energy Materials and Solar Cells*, vol. 90, pp. 2720-2738, 2006.