



Evaluation and Modeling of Edge-Seal Materials for Photovoltaic Applications

M.D. Kempe, A.A. Dameron, T.J. Moricone, and
M.O. Reese

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EVALUATION AND MODELING OF EDGE-SEAL MATERIALS FOR PHOTOVOLTAIC APPLICATIONS

M.D. Kempe, A.A. Dameron, T.J. Moricone, M.O. Reese
National Renewable Energy Laboratory (NREL), Golden, CO, 80401, USA

ABSTRACT

Because of the sensitivity of some photovoltaic devices to moisture-induced corrosion, they are packaged using impermeable front- and back-sheets along with an edge seal to prevent moisture ingress. Evaluation of edge seal materials can be difficult because of the low permeation rates involved and/or non-Fickian behavior. Here, using a Ca film deposited on a glass substrate, we demonstrate the evaluation of edge seal materials in a manner that effectively duplicates their use in a photovoltaic application and compare the results with standard methods for measuring water vapor transport. We demonstrate how moisture permeation data from polymer films can be used to estimate moisture ingress rates and compare the results of these two methods. Encapsulant materials were also evaluated for comparison and to highlight the need for edge seals. Of the materials studied, desiccant filled polyisobutylene materials demonstrate by far the best potential to keep moisture out for a 20 to 30 y lifetime.

INTRODUCTION

Many types of photovoltaic (PV) technologies are sensitive to moisture [1-5]. The use of an impermeable front-sheet and back-sheet (e.g. a glass/glass laminate package) significantly reduces moisture ingress, but moisture may still diffuse in from the sides [6]. Therefore, to keep a module dry for an expected 30 y lifetime, the edges must be sealed against moisture. One way this is accomplished is through the addition of desiccant-filled polyisobutylene (PIB) around the outside ~15 mm perimeter between two pieces of glass (or other moisture barrier films). PIB uniquely provides a very low moisture- permeability and -diffusivity, as well as a low glass transition temperature [7, 8]. When laminated between two pieces of glass, a compliant material with a low glass transition is necessary to accommodate mechanical stress. Other edge seal materials (e.g. epoxies) can have very low diffusivities, but they are hard and brittle and could easily crack or delaminate in a large module.

The mechanics and logistics of measuring moisture penetration through a free-standing film of an edge seal material can be very difficult. This is especially true for PIB-based edge seal materials because they may flow, may use reactive desiccants, and may have extremely long breakthrough times. Furthermore, preparing free standing films of PIB is complicated by the need to keep them dry while forming a film and by the fact that they typically are compliant low glass transition (~75°C [9])

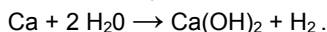
materials that may or may not cross-link prior to water exposure.

We demonstrate how a thin film of Ca deposited on a glass substrate laminated to another piece of glass can be used to evaluate edge seal materials. This method is advantageous because it allows both initial performance, and performance after thermal, mechanical and/or UV stress to be evaluated for a variety of encapsulant and edge seal materials. We use this method to evaluate several polymeric PV materials and compare them to PIBs. We compare these results with transient water vapor permeation measurements and show how these findings can be applied to estimate the moisture ingress rate of a module.

EXPERIMENTAL

Prior to use, all glass substrates were scrubbed using a 4F pumice slurry followed by scrubbing and rinsing using isopropanol and deionized water, then dried. Ca was deposited to a thickness of 100 nm on 3.18-mm-thick square glass plates with side dimensions of 51 mm, 76 mm, or 152 mm. Lamination of this plate to another piece of glass was accomplished by first drying the polymeric materials at an elevated temperature (~100°C to 150°C) in an argon-filled glove box followed by assembly using a heated press at ~100°C to 150°C (see Fig. 1). Two pieces of 0.25-mm-thick fluoropolymer-coated fiberglass sheets with a square hole in the center, were positioned between the Ca test sample glass plates as a spacer to help keep them parallel and separated at a distance of ca. 0.5 mm. With low-viscosity materials such as silicones, the square shape of the spacer was retained, but for higher-viscosity materials the spacer was deformed to produce a slightly rounded polymer region (see Figs. 2 and 4).

Ca samples were exposed to 85°C and 85% RH in a Blue-M FRS-361F (Thermal Product Solutions Corp.) environmental chamber. Because Ca reacts very quickly with water as compared to oxygen [10] and the solubility of oxygen in most polymers is very low, it is assumed that oxygen does not contribute significantly to the oxidation of Ca. That is, Ca metal reacts with moisture to produce a transparent hydroxide [10] as:



The change from a mirror-like film to a transparent film allows for easy determination of the distance of moisture penetration. Because the samples are very thin (0.5 to 0.8 mm polymer film) relative to the penetration depths, it is inferred that the edge of the metallic Ca indicates how far

moisture has penetrated the samples within ± 0.5 mm. This sample configuration is analogous to an edge seal used in PV applications (see Fig. 1B) and thus provides a method for readily evaluating edge seal materials as they would actually be implemented.

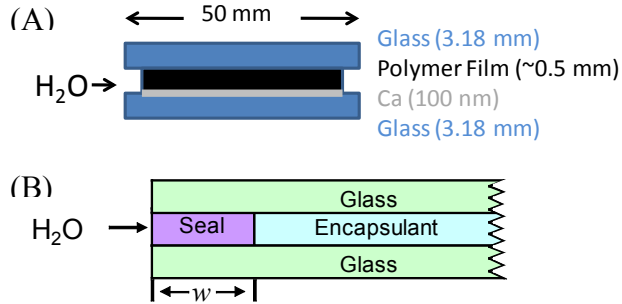


Figure 1. (A) Schematic (side-view in cross-section) of Ca edge seal test sample. (B) Schematic diagram of the edge of a module using a very low permeability edge seal.

Alternatively, the diffusivity of a material can be used to estimate moisture ingress depths. The use of two methods for estimating ingress provides greater depth of understanding and confidence in the results. For diffusivity measurements, the transient water vapor transmission of polymeric films was measured using a MOCON Permatran-W 3/31 [6]. This procedure involves drying out the film, introducing liquid water to one side, producing a saturated vapor, and monitoring the water vapor transmission rate (WVTR) as a function of time. If the material is Fickian, it can be fit to

$$WVTR = \frac{DC_{sat}}{l} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{\left(\frac{-Dn^2 \pi^2 t}{l^2} \right)} \right] \quad (1)$$

where D is the diffusivity, l is the sample thickness, t is elapsed time, and C_{sat} is the concentration of water at saturation.

RESULTS

Several PV encapsulant and edge seal materials were examined using Ca-film-based test specimens. Photographs of two examples are shown in Fig. 2 to demonstrate the extreme differences among encapsulant materials. Silicones based polymers [e.g. polydimethylsiloxane (PDMS)] have the highest diffusivities among polymeric materials [6, 11, 12]. Over the course of 4.5 h, moisture was able to completely consume the Ca to the center of this 50-mm-square sample. The penetration rate was so rapid that the thermal equilibration, occurring when samples were removed for measurement, adds uncertainty in the exposure time and temperature. Subsequent PDMS samples (Fig. 3) were

made using 152-mm-square glass and photographed through the test chamber window, avoiding removal from the environmental chamber, to determine moisture penetration distances (see Fig. 3).

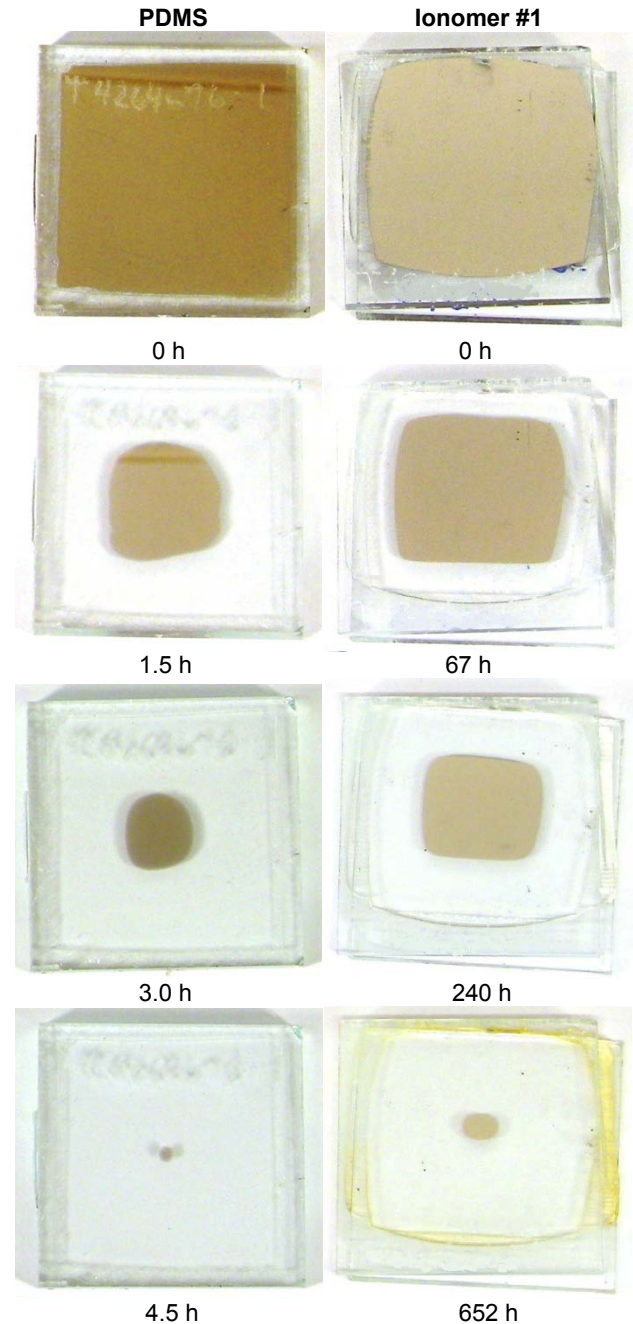


Figure 2. Photographs of Ca test samples of PDMS and an ionomer #1 after exposure to 85°C and 85% RH. Samples are 50 mm on each side.

An ionomer [thermoplastic poly(ethylene-co-methacrylate) with Na^+ , and Zn^{2+} counter ions] with an extremely low diffusivity is shown alongside the PDMS to demonstrate

the other extreme for encapsulant materials. It takes ~100 times longer for moisture to penetrate this ionomer, which is typically utilized as an encapsulation material whereas PDMS is commonly used as a sealant or a potting material for junction boxes. In this capacity, PDMS serves to exclude liquid moisture (as long as it remains well adhered), but it does not prevent ingress of dissolved water vapor.

The movement of a dissolved substance is governed by the diffusivity, D , and concentration, C , as

$$\frac{\partial C}{\partial t} = \nabla(D\nabla C) \quad (2)$$

If temperature is held constant, the time scale for a one-dimensional, diffusion controlled process is expected to scale as the square of the characteristic distance, X , such that

$$X = K\sqrt{t} \quad (3)$$

where K is a proportionality constant [13, 14]. This relationship is expected to hold for both Fickian and non-Fickian materials where diffusivity is a function of concentration. Comparing the performance of PDMS and the ionomer in Fig. 2, PDMS is estimated to be about 10,000 times more diffusive as the ionomer.

In Fig. 3 we show the moisture penetration distance from the edge of the polymer as a function of time. X was determined as the average of all four sides. With longer exposures one or more sides occasionally were eliminated from the average because of bubbles in the encapsulant and/or delamination. These distances were measured from the center of the 5- to 15-cm sides. When the penetration depth is equal to about 25% of the sample side width (i.e., about 1.2 cm for the 5-cm square samples), the two-dimensional nature of the samples begins to be important and deviations from Eq. 3 become apparent as the remaining Ca film takes on a more rounded shape. Furthermore, at distances around 0.1 cm the fact that the Ca film did not always extend to the edge of the polymer films affected the ability to measure very small moisture penetration distances producing large scatter in the data. Similarly, the edge of the polymer was not perfectly straight and square, so there was some uncertainty as to where to measure the penetration edge from. However, for the range of 0.1 cm to 25% of the edge length, the penetration distance was proportional to $t^{1/2}$. Here one can see the dramatic differences between the materials. The PIB formulas have withstood thousands of hours of exposure to 85°C and 85% RH whereas the Ca was completely consumed in 4 h for the silicone sample.

Two different edge seal formulations based on PIB were investigated using the Ca film method to see how they perform in damp heat (85°C/85% RH). Figure 4 shows that

PIB #1 had some problems with delamination after a few hundred hours, while PIB #2 survived much longer without delamination issues. Delamination and bubble formation are both potentially catastrophic to the edge seal application. The Ca test method highlights how such defects allow for very rapid moisture ingress. When delamination occurs on the glass with the Ca film, a sharp oxidation edge is seen (Fig. 4, PIB #1, 652 h). When delamination occurs on the glass without Ca, the moisture must penetrate the sample on that side and move through the material under test, which produced a more diffuse oxidation edge. These photos indicate that delamination occurred on both pieces of glass and is not solely attributable to poor adhesion to Ca.

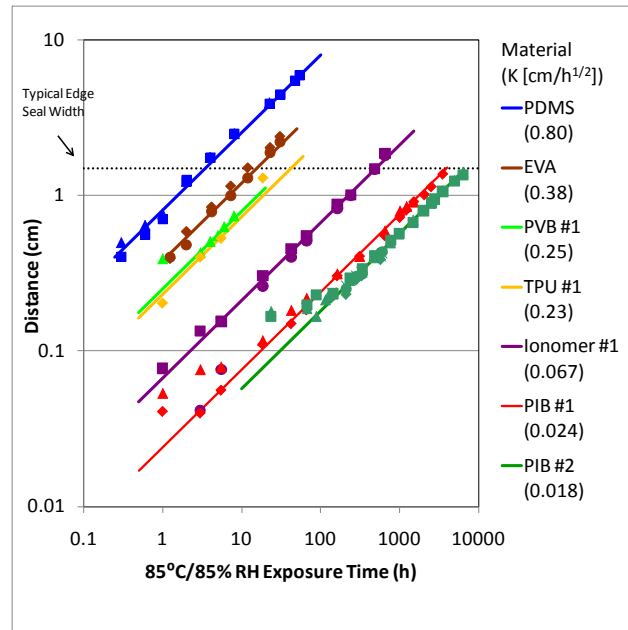


Figure 3. Plot of moisture penetration distance for Ca samples exposed to 85°C and 85% RH. Lines are fits to Eq. 3 with the constant K indicated in the legend. PDMS is a Pt catalyzed addition cure polydimethylsiloxane. EVA is a PV formulated ethylene-co-vinyl acetate with ~33 wt% vinyl-acetate. PVB is poly(vinyl butyral). TPU is an aliphatic thermoplastic polyurethane. Ionomer #1 is a thermoplastic poly(ethylene-co-methacrylate) with Na, and Zn counter ions. PIB #1 is a thixotropic polyisobutylene edge seal filled with molecular sieves. PIB #2 is a pseudoplastic silane and polyisobutylene copolymer edge seal filled with a reactive desiccant.

In PIB #2 (Fig. 4) some Ca degradation is seen in central spots at 2,780 and 4,970 h. Because these samples are only 0.5-mm thick and there is a 2- or 3- mm width of Ca film between the spots and the leading edge of moisture ingress, it is not possible that delamination on the opposite side and subsequent moisture ingress could have created these spots. Furthermore, upon oxidation, the polymer under these spots has a darker appearance than the polymer revealed by reaction of Ca with water on the

perimeter. When the moisture ingress boundary does reach these spots, it does not rapidly advance as it did when PIB #1 delaminated in the bottom right corner (Fig. 4, PIB #1). This indicates that delamination has not occurred just over these spots. This demonstrates that after a long period of time a component of PIB #2 can react with Ca. Also notable is the symmetry of the spot pattern in Fig. 4 and in a duplicate PIB #2 sample (not shown). We postulate that this symmetry suggests that these features originate with sample processing, possibly associated with the high shear stress involved with our lamination procedure.

Both PIB #1 and PIB #2 are pseudoplastic (i.e. lower viscosity at higher shear rates), but PIB #1 is also thixotropic (i.e. a time-dependent viscosity). In these studies, PIB #1 was found to flow less than PIB #2. During the processing in a manufacturing setting, lower flow (correlated with thixotropic behavior) can be beneficial because it will limit the severity of edge pinch [15] making a glass/glass package more durable. However, PIB #2 had a lower viscosity making it more easily dispensed in a liquid rather than tape form.

PIB #1 lacks additives that would enable it to chemically bond to surfaces, or to form cross-links. PIB #2, however, does cross-link and chemically bond to surfaces. Because of this, any tensile stresses in PIB #1 may cause it to tear and/or delaminate more easily than PIB #2.

An alternative way to evaluate the effectiveness of a material as an edge seal is to consider the transient WVTR through a film as governed by Eq. 1. If one assumes that the diffusivity of the encapsulant is much greater than the diffusivity of the edge seal, then as soon as moisture penetrates the edge seal it will readily disperse, allowing the water concentration on the inside of the edge seal to be negligibly low. With this, one can use Eq. 1, substituting film thickness for edge seal width (w), to model diffusion through an edge seal with Fickian properties. If one defines a breakthrough time, $\tau_{b,5\%}$ as the time required for the WVTR to reach 5% of its steady state value, then

$$\tau_{b,5\%} = \frac{1}{(K_{b,5\%})^2} w^2 = \frac{1}{18.3D} w^2 \quad (4)$$

where $K_{b,5\%}$ is the proportionality constant for a Fickian material analogous to K in Eq. 3. For non-Fickian materials, $K_{b,5\%}$, can be determined directly from the transient WVTR (MOCON) data at the point where the WVTR reaches 5% of its steady state value. Evaluation of many potential PV materials (not including PIB) was made using this method. Here diffusivity was measured as a function of temperature, fit to an Arrhenius curve, and used to compute the penetration depth as shown in Fig. 5. Most of these materials are compliant materials, suitable for lamination between two rigid plates, but some of the best materials [PET, Polyimide, poly(ethylene naphthate

(PEN), and poly(chlorotrifluoroethylene) (PCTFE)] are too brittle to function as an edge seal. The least permeable material here, PCTFE, would have a $K_{b,5\%}$ of 0.048 ($\text{cm/h}^{1/2}$), which is higher than the values of K for the PIBs of 0.024 ($\text{cm/h}^{1/2}$) and 0.018 ($\text{cm/h}^{1/2}$) (Table 1).

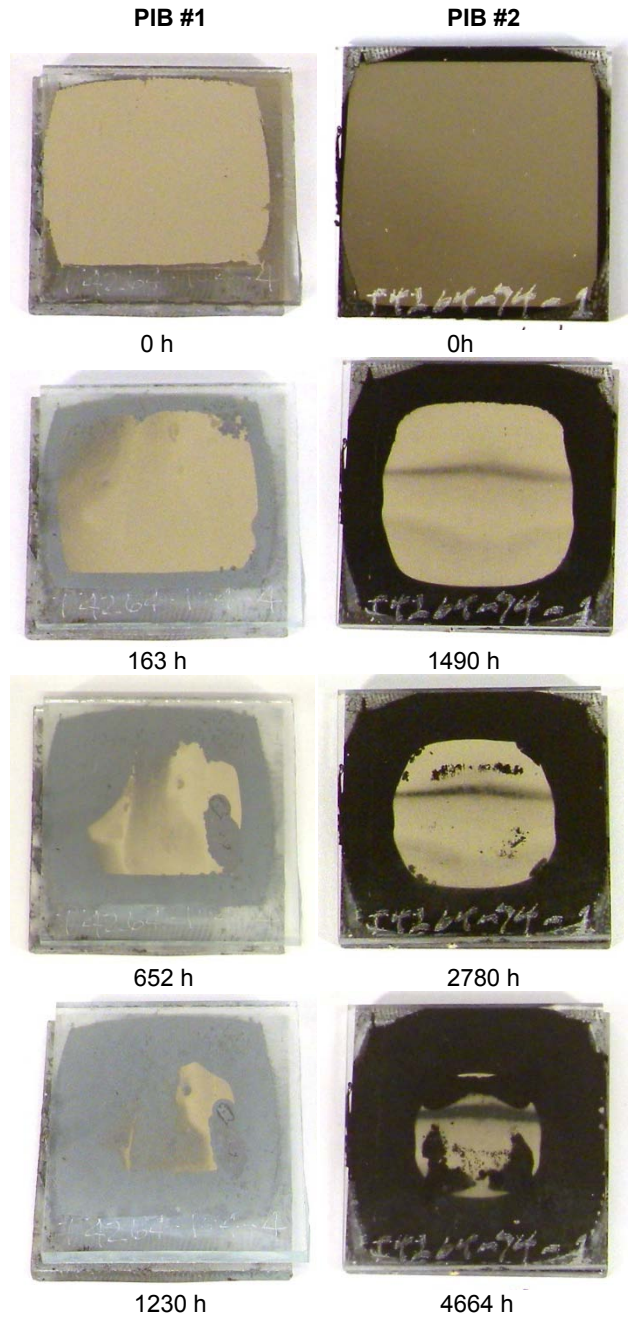


Figure 4 Ca test samples after 85°C/85% RH exposure. Samples are 50 mm by 50 mm.

These two constants, K and $K_{b,5\%}$, are governed by different parameters. K is a measure of penetration depth upon reaction with a known amount of Ca and is thus dependent on the solubility of water. In contrast, $K_{b,5\%}$ is

only dependent on the diffusivity, and indicates the time scale to respond to changes in the external environment as a function of depth. For desiccant-filled materials, such as the PIB formulas tested, the desiccant acts in a manner similar to the Ca film (most notably for the case of a reactive desiccant where it is similarly consumed). Here, the moisture penetration depth as a function of time is dependent on both temperature and humidity; thus to accurately model these materials, moisture ingress data as a function of temperature and humidity are needed. Because of these factors, K and $K_{b,5\%}$ give slightly different values in Table 1. However, they enable an approximate comparison for evaluating moisture ingress from the module edges.

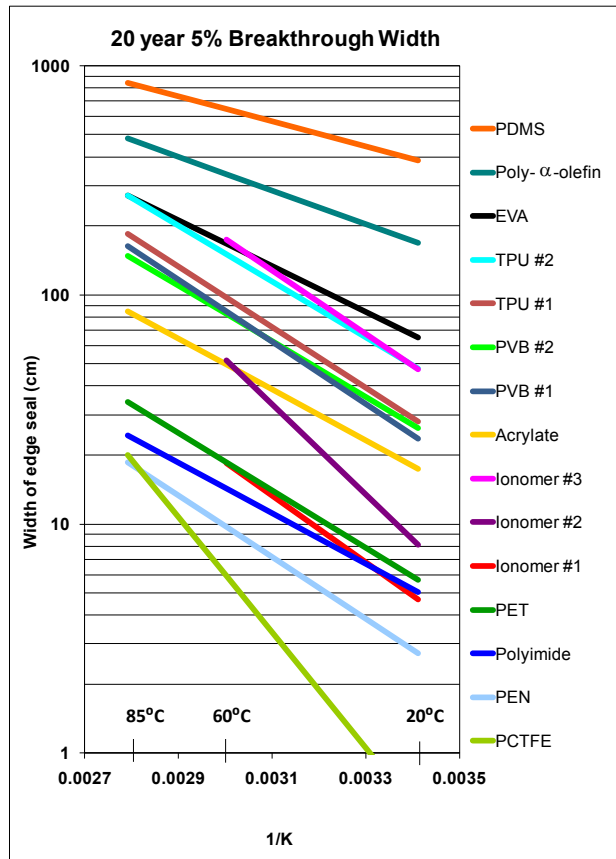


Figure 5 Calculated breakthrough distance (w) for PV materials using transient WVTR Mocon data according to Eq. 4 as a function of inverse temperature.

All three of the ionomer materials tested showed approximately Fickian behavior below about 60°C. At 85°C Ionomers #2 and #3 were measurable, but did not fit Eq. 1 well. However, Ionomer #1 was not only non-Fickian, but at 85°C it absorbed a very large amount of water, deformed significantly, and never achieved a steady state WVTR. Upon removal of the film from the Mocon fixture, it was completely opaque as a result of the extreme supersaturation of water, which caused the precipitation droplets within the polymer. After several

days of storage in ambient conditions, the water diffused out and the film became transparent again. This behavior is distinctly different from the results shown in Figs. 2 and 3 where the Ca film method did not show the same effects of moisture saturation. This example illustrates the utility of the Ca film method for determining moisture ingress for edge seal materials.

Material	K	$K_{b,5\%}$
	(cm/h ^{1/2})	(cm/h ^{1/2})
	Ca Film 85°C/85% RH	Eq. 3, Mocon 85°C
PDMS	0.8	2.0
Poly-α-olefin		1.1
EVA	0.38	0.65
TPU #1	0.23	0.44
TPU #2		0.65
PVB #1	0.25	0.39
PVB #2		0.35
Acrylate		0.20
Ionomer #3		0.44
Ionomer #2		0.25
Ionomer #1	0.067	
PET		0.081
Polyimide		0.058
PEN		0.044
PCTFE		0.048
PIB #1	0.024	
PIB #2	0.018	

Table 1. Comparison of moisture penetration constants for different methods. Ionomers #3 and #2 were non-Fickian so $K_{b,5\%}$ was determined directly from the Mocon WVTR data; all other materials were determined according to Eq. 3.

Of the candidate encapsulant materials tested, Ionomer #1 showed the lowest effective diffusivity and the greatest potential for keeping water vapor out. However, as shown in Fig. 5, even if a module was constructed with impermeable front- and back-sheets, and the module temperature was kept at 20°C for a 20-year lifetime, moisture would still penetrate to a depth of about 5 cm. If a PV material is sensitive to moisture, this could cause catastrophic failure. Alternatively one could consider using such a material in conjunction with a PIB based edge seal. In this case, if there was a localized failure of the edge seal, the affected area of the module would be greatly reduced.

A straight line was obtained in Fig. 3 for both PIB formulations indicating that these materials are very

thermally stable with respect to the diffusivity of water in the polymer as well as the effectiveness of the desiccant. Exposure to 3500 h and 6400 h of 85°C without significant performance degradation is more than enough thermal stress to assure confident in its thermal stability for a 20- to 30 year lifetime [16].

CONCLUSION

Using a 100-nm layer Ca on glass, we have developed a method for evaluating edge seal materials. Assuming no delamination or bubbles, at 85°C and 85% RH a 15-mm wide edge seal was estimated to keep moisture out for about 6,900 h. In contrast, the best encapsulant material tested here (ionomer #1) would allow moisture penetration to a depth of 5 cm in 20 y even if kept at 20°C. When one considers that the diffusivity of polymers at the average exposure temperature seen by a typical module is about five to ten times lower than at 85°C, that the molecular sieve desiccant is less effective at high temperature, that the solubility of water in polymers at 85°C is two to three times greater, and that the relative humidity will be much less (~20 to 50% RH) than 85%, one could estimate about 17 to 127 times better performance in common field locations relative to 85°C and 85% RH. The aforementioned edge-seal material is therefore estimated to be capable of keeping moisture out of a module keeping them for 20- to 30-year service life.

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