New Barrier Coating Materials for PV Module Backsheets

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New Barrier Coating Materials for PV Module Backsheets

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ABSTRACT

High moisture barrier high resistivity coatings on polyethylene terepthalate (PET) have been fabricated and characterized for use in PV module back sheet applications. These thin film barriers exhibit water vapor transmission rates (WVTR) as low as 0.1 g/m²-day at 37.8 °C and have shown excellent adhesion (> 10 N/mm) to both ethylene vinyl acetate (EVA) and PET even after filtered xenon arc lamp UV exposure. The WVTR and adhesion values for this construction are compared to and shown to be superior to candidate polymeric backsheet materials.

BACKGROUND

The PV community has shown interest in replacing the glass backsheet in PV module manufacturing with a lightweight, insulating, moisture barrier backsheet. It is necessary that the backsheet be insulating to prevent a conduction path from the back contacts to the grounded metal frame. The backsheet material must also prevent moisture ingress because this is the generally accepted mode of failure for devices that do not pass the IEEE 1262 qualification test [1]. IEEE 1262 is commonly referred to as the "damp heat test" and for part of the test PV devices are subjected to 85°C and 85% relative humidity (RH) for 1000 hours as per the specification.

Although insulating moisture barriers are routinely produced for the food packaging industry [2], the requirements for this industry are much less severe than what is believed to be necessary for PV modules to pass the damp heat test. For example, the food packaging industry desires materials that have a water vapor transmission rate $< 1 \text{ g/m}^2$ -day at ambient temperatures and humidity. Poly(vinylidene chloride) (PVDC) is a commercially available polymer that meets this criteria, but at 85°C this polymer is an extremely poor barrier and exhibits a water vapor transmission rate in excess of 300 g/m²-day [3]. As a substitute for using an expensive single polymer film such as PVDC, oxide coatings on inexpensive polymers such as polyethylene terepthalate (PET) and biaxially oriented polypropylene (BOPP) [4-6] have been investigated. However, these oxides are typically electron-beam evaporated onto the polymer. As a result, these solutions may be fine for ambient temperature applications, but are expected to be poor barriers at elevated temperatures because of their inherent columnar microstructure.

During service exposure, adhesive bonds between encapsulant and superstrate/substrate materials of PV modules can weaken, leading to delamination failure and/or moisture ingress. Thus any backsheet material must also exhibit excellent adhesion to the encapsulant material, which is typically a formulated ethylene vinyl acetate (EVA). Thin film coated polymer backsheets should be good barriers against moisture ingress, electrically insulating, UV stable, and highly adherent to EVA. The thin film should also be very adherent to the substrate.

EXPERIMENTAL

Insulating ($\rho \sim 10^{13}$ Ohms/square) thin films [7] of various compositions have been deposited on PET at room temperature by reactive pulsed DC magnetron sputtering from a single target. The target was precleaned prior to each deposition and the PET substrate (0.18 mm DuPont Mylar-D) was not sputter or glow discharge cleaned prior to thin film deposition. The target was 73.66 mm x 304.8 mm and sputtered at an applied power between 500 and 1000 W using an Advanced Energy MDX 2.5 kW source with a Sparc-V pulsing network. The pressure during the depositions ranged between 0.4 to 1.33 Pa (3 to 10 mTorr) and the target-to-substrate distance was nominally 90 mm. The water vapor transmission rates of these, as well as several commercially available candidate backsheet constructions, have been measured over a range of temperatures using a Mocon Permatran-W 3/31 instrument as per ASTM F1249-01 [8]. These candidate backsheets have also been vacuum laminated to EVA (STR Photocap 15295P) and a front glass superstrate (AFG Krystal Klear, 2 mm) to replicate backsheets in module constructions. Fig. 1 is a not-to-scale schematic of a "test module" construction used throughout accelerated testing. The test modules were then exposed to one of the these accelerated testing environments: i) filtered xenon arc lamp radiation in an Atlas XR-260 Weather-Ometer (light intensity ~1 sun, low temperature, low humidity); ii) filtered xenon arc lamp radiation in an Atlas Ci4000 Weather-Ometer (light intensity ~1 sun, high temperature, low humidity); or iii) damp heat (no light, high temperature, high humidity). To investigate any changes at the interfaces of the laminates as a function of accelerated testing exposure, peel tests were conducted on strips of the samples using an Instron 5500R as per ASTM D903-98 [9]. A representation of the pull test configuration for measuring peel strength is shown in Fig. 2.



Fig. 1. A schematic of the test module construction used throughout the accelerated testing environments. PV devices are normally located between the glass and EVA.

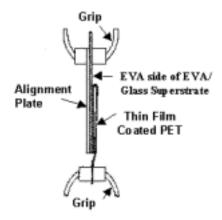


Fig. 2. Peel strength measurement set-up adapted from ASTM D903-98 [8].

Table 1. WVTR for polymer laminates at 37.8 $^{\circ}$ C and 85 $^{\circ}$ Relative Humidity.

Material	Thickness (mm)	WVTR (g/m²-d)
Tedlar®/Al/Tedlar® (TAT)	0.10	0.02-0.04
NREL Coated PET	0.18	0.10-0.20
Tedlar®/PET/EVA (TPE)	0.20	3.0
PET	0.10	3.4
EVA	0.4-0.5	27-33

RESULTS AND DISCUSSION

In order for a backsheet to be used as a replacement for glass, it must meet the previous requirements of being insulating and preventing moisture from reaching the back contact, plus not delaminate or crack after lamination and be weatherable. All samples discussed here have been stressed and measured with respect to these criteria.

Water Vapor Transmission Rates (WVTR)

Table 1 contains the measured water vapor transmission rate of bare PET, EVA, a representative NREL coated PET, and several commercially available candidate backsheet materials at 37.8°C and 85% RH. The coated PET exhibits a dramatic improvement over the uncoated polymer. The representative sample has two significant advantages: it does not contain a conductive

layer such as aluminum in the commercial Tedlar[®]-Aluminum-Tedlar[®] (TAT) construction nor does it contain a fluoropolymer (Tedlar[®]) which would need to be modified to improve the adhesion to EVA. The candidate construction may also be cheaper to manufacture than a fluoropolymer based construction.

Adhesion under Accelerated Testing

Table 2 shows the measured interfacial adhesion between candidate backsheets and EVA as a function of UV exposure in an Atlas XR-260 Weather-Ometer® at ~1 sun intensity, 35°C, and ambient humidity. The uncoated PET weakly adheres to EVA and could be peeled by hand from the EVA/glass superstrate after 2 weeks of exposure. Similarly, the interfacial adhesion strength of TPE (Tedlar®-PET-EVA) degraded by 30% during this time. The adhesion of the coated PET sample is significantly improved over TPE and is so high that for the t=0 measurement, the PET failed in tension when pulled at a high rate. The peel rate was reduced but to avoid further film failure, testing was stopped after 8 N/mm was reached. After 1 week of exposure, this upper boundary was pushed further and the test was stopped at 10 N/mm because the PET exhibited plastic deformation under those stresses. After 2 weeks of exposure, failure was observed at the glass/EVA interface and not the EVA/thin film coated PET interface.

Table 2. Peel strengths (N/mm) for candidate backsheet materials as a function of UV exposure in an Atlas XR-260 Weather-Ometer® (~1 sun, 35°C, and ambient humidity). * Denotes failure at glass superstrate/EVA interface.

Material	t=0	t=1 week	t=2 weeks
Uncoated PET	1-1.7		~0.8
NREL Coated PET	>8	>10	6.5-8*
TPE	~6	-	~4.2

Although these coated PET samples exhibited good adhesion, weatherability, and low water vapor transmission rates, they exhibited cracking during and/or after lamination. An example of the cracking can be seen in Fig. 3a. Fig. 3b is a photomicrograph of a non-cracked sample with a similar water vapor transmission rate for the same construction and lamination procedure as for Fig. 3a. The cracking was attributed to stress in the films and deposition parameters were adjusted to lessen the stress. As can be seen in Fig. 4, cracking was not observed at compressive stresses less than $\sim 5 \times 10^9 \ dynes/cm^2$.

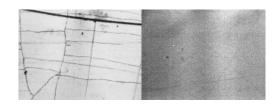


Fig. 3. Optical microscope photograph (40x magnification) of samples that cracked (a, left) and did not crack (b, right) during lamination to EVA and a glass superstrate.

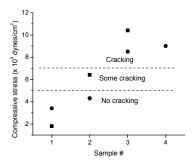


Fig. 4. Correlation between compressive stresses and cracking for several inorganic thin film systems on PET.

Samples that did not exhibit cracking after/during lamination were stressed by either UV exposure or damp heat. UV exposure was conducted in an Atlas Ci4000 Xenon Weather-Ometer® (~1 sun intensity, 65°C sample temperature, and 10% RH) and damp heat samples were placed in a controlled temperature/humidity chamber (no light, 85°C, 85% RH). The adhesion values of these samples as a function of exposure time in the Ci4000 and the damp heat chamber are shown in Tables 3 and 4 respectively. Peel strengths of the EVA/thin film coating interface have increased for most of the samples with exposure in the Ci4000 whereas they have remained almost constant with damp heat exposure. However, the adhesion value of sample 102-5 has decreased after 400 hours of exposure in the Ci4000, but has increased with damp heat exposure. Conversely, the adhesion of sample 102-6 has increased with Ci4000 exposure and decreased slightly with damp heat exposure.

Table 3. Peel strength (N/mm) at the EVA/coating interface as a function of exposure time in an Atlas Ci4000 Xenon Weather-Ometer® (light intensity ~1 sun, 65°C, and 10% RH). * Denotes sample underwent a transition in failure to the glass/EVA interface.

Sample	0 hours	400 hours
102-5	11.7	8*
102-6	12.1	13.4*
102-29	12.0	
102-30	9.4	10.8
102-31	11.2	15.6*

Table 4. Peel strength (N/mm) of the EVA/coating interface as a function of damp heat exposure time (no light, 85°C sample temperature, and 85% RH). ** Denotes same transition in failure as Table 3.

Sample	0 hours	7 hours	15.5 hours
102-5	11.7	13.4**	
102-6	12.1	11.4**	11.3**
102-29	12.0	12.0	
102-30	9.4		9.4**
102-31	11.2	11.4	11.2**

The results suggest that the interfacial adhesion strength of the EVA/coating interface appears to be quite stable under several accelerated testing environments.

Initially, peel strength values of ~11–12 N/mm between the coated PET backsheet and EVA encapsulant are measured. After exposure to either damp heat for short periods of time or lower humidity environments for longer periods of time, these peel strengths can be reattained if the sample is allowed to return to ambient temperature and dry out for a period of time before pull tests are reconducted. However, these peel strengths are usually short-lived before the peel fracture transitions to the glass /EVA interface. Thus the glass/EVA interface appears to be the weakest interface and is more affected by the accelerated testing environments. In particular, it is believed that this interface is degraded by water vapor.

For a module with a very good backsheet, the dominant path of moisture ingress is in from the edges and through the EVA due to the very large water vapor transmission rate of EVA, even at 37.8°C (see Table 1). Once inside the EVA, water vapor rapidly diffuses throughout the EVA and reaches its equilibrium value at the glass/EVA interface, as well as the EVA/coating interface, as it progresses in from the edges. Of these two interfaces, the peel strength data in Table 5 suggests the water vapor preferentially weakens the glass/EVA interface. A comparison of the peel strength data in Tables 3, 4 and 5 shows that when a sample undergoes a change in failure from the EVA/coating interface to the glass/EVA interface, there is at least a 30% reduction in the peel strength. Furthermore, as shown in Table 5, the interfacial adhesion strength of the glass/EVA interface appears to decrease with increasing exposure to damp heat. This is in contrast to the nearly identical peel strength of the EVA/coating interface with damp heat exposure listed in Table 4.

Table 5. Peel strength (N/mm) of the glass super-strate/EVA interface as a function of exposure time in damp heat and the Ci4000.

Sample	7 hours damp heat	15.5 hours damp heat	400 hours Ci4000
102-5	9.2	7.5	6
102-6	7.5	6.5	8.1
102-30		6	
102-31		8	9.2

EVA contains adhesion-promoting silane coupling agents that undergo condensation reactions at the silica glass surface during lamination. For this reaction, there is also a reverse hydrolysis reaction. A simple example of this surface equilibrium reaction is:

$$RR'R"Si(OH) + HO-Si_{(s)} \Leftrightarrow H_2O + RR'R"Si-O-Si_{(s)} \quad (1)$$

where (s) denotes a silicon atom of the glass surface that is connected to the bulk. The above reaction may be an oversimplification of the exact groups and the number of surface bonds that the silane coupling agent may form because this molecule may contain anywhere from one to three alkoxyl groups and some silicon surface atoms may contain two or more hydroxyl groups.

If there is sufficient concentration of water in the near surface/interface vicinity, the equilibrium is shifted toward the reverse reaction and the interface will increasingly favor surface hydrolysis. Once hydrolyzed, the number of bridging -Si-O-Si_(s) surface groups is reduced and the glass/EVA interfacial adhesion is reduced correspondingly. Equilibrium will depend on the solubility of water vapor in EVA and the number of surface bonds formed between the silicon containing molecule and the glass surface. It becomes rather straightforward to propose an explanation for the transitioning of the peel strength failure from the EVA/thin film interface to the glass/EVA interface based on this condensation-hydrolysis equilibrium.

When a sample is placed in damp heat, the WVTR through the EVA is ~50-100x higher than at room temperature and water vapor more easily permeates the EVA. Upon removing from damp heat, the outside of the sample and EVA cools rapidly and there is a corresponding drop in the WVTR. Thus the rate at which water vapor diffuses out of the EVA is much slower than the rate at which it diffuses into the EVA because of this increased water vapor barrier at the edges. This barrier creates a water vapor concentration gradient in the EVA since the water vapor in the near edge vicinity of the EVA can escape because of the short escape depth while that from the bulk is impeded. It is proposed that where the peel fracture changes from the EVA/thin film coating interface to the glass/EVA interface there is a corresponding shift in the EVA adhesion promoting equilibrium surface reaction from condensation (low water vapor concentration) to hydrolysis (higher water concentration). The distance before the transition should be a function of the drying time and temperature. Thus the amount of water vapor that diffuses into the EVA is crucial for determining the overall stability of the glass/EVA interface. However, this also suggests that the EVA/coating interface either favors condensation reactions and is more difficult to hydrolyze or that there is a different type of adhesive bonding/reaction taking place.

Tables 3 and 5 also show that samples exposed in the Ci4000 chamber for 400 hours have exhibited similar failure patterns and peel strength degradation at the glass superstrate/EVA interface. The degradation in adhesion is still suggested to be moisture ingress through the EVA and attacking of the glass superstrate/EVA interface. However, during this exposure, UV-induced embrittlement of the thin film coated PET backsheet material also occurs. This results in occasional tensile failure and/or tearing of the PET during peel tests making data analysis more difficult.

SUMMARY

NREL fabricated insulating films on PET show promising properties as a backsheet replacement for glass. Initial investigations have produced films that cracked during lamination. Subsequent films, exhibiting similar

water vapor barrier properties, have been produced that do not crack during lamination. These coatings exhibit very good moisture barrier properties and have good adhesion to EVA even after UV or damp heat exposure. A simple model to explain the complex peel strength failure mechanism is presented and moisture ingress through the EVA appears to be the problem.

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