DISCOLORATION OF EVA ENCAPSULANT IN PHOTOVOLTAIC CELLS

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1. Abstract

Crosslinked EVA sheet is a common encapsulant for photovoltaic cells which convert sunlight to electric power. In very hot regions with high solar radiation, the encapsulant often darkens over time, reducing the amount of solar energy converted to electricity. The cause of discoloration has been studied as to the extent due to changes in the polymer and to effects of the stabilizer and peroxide crosslinking additive systems. Laboratory aging studies have provided information on the effect of particular additives and combinations of additives. The work is sponsored by the U.S. Department of Energy through subcontract with the National Renewable Energy Laboratory of Midwest Research Institute.

2. Introduction

The objective of the program was to generate an understanding of discoloration, yellowing at first and ultimately browning, of crosslinked poly(ethylene vinylacetate) (EVA) which can accompany its use as an encapsulant in silicon-based photovoltaic (PV) modules when used in the field to generate electricity from terrestrial sunlight. The discoloration, which starts at the top of the EVA, affects the intensity of solar energy reaching the silicon cells, reducing the amount of solar energy converted to electricity. Discoloration is a problem particularly in regions of high solar radiation, such as southwestern US, and especially so if a mirror-enhanced design is used. The cause of discoloration has been studied as to the extent due to changes in the polymer and to effects of stabilizer and peroxide crosslinking additive systems. Laboratory aging studies have provided information on the effect of particular additives and combinations of additives. Overall, crosslinked EVA appears to be well suited for the encapsulation of solar cells, with the discoloration problem limited to very hot regions of the world.

A typical solar module contains about fifty individual cells each measuring ca. 4" x 5". Overall dimensions of a typical module are 12" to 24" wide by 48" long. The individual cells are linked electrically.

3. Theory of Discoloration and Experimental Approach

Pern and Czanderna[a] have proposed that the cause of discoloration in EVA encapsulated modules is the development of long sequences of conjugated double bonds resulting from loss of acetic acid from vinylacetate units in the copolymer. Equation (1) shows the loss of one mole of acetic acid.

$$(-CH_2-CH_2-)(CH_2-CH(OCOCH_3))-->-CH_2-CH_2-CH=CH- + CH_3COOH$$
(ethylene)   (vinyl acetate)   (acetic acid)
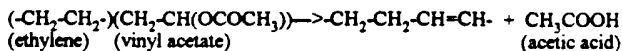
It has been proposed that as the process continues, conjugated double bonds are generated, i.e., alternating double and single bonds (-CH=CH-CH=CH-). A sequence of eight or more conjugated double bonds is required to absorb visible light, which is a known cause of discoloration of PVC[b]. The EVA used contains 33% VA by weight, which is about 15% VA on a molar basis. That means, on average, there is one VA unit for every six ethylene units(E_6VA).

Since reactivity ratios for ethylene and vinylacetate are unity for the high pressure polymerization of EVA, it is difficult to understand how chains of more than eight conjugated double bonds can be formed during weathering of PV module so as to be responsible for the high levels of discoloration experienced. EVA with 33% VA would not be expected to contain sufficient numbers of PVA blocks with more than eight monomer units to be the major source of discoloration in weathered EVA.

The present study focused initially on determining experimentally if long sequences of conjugated double bonds can be detected to confirm the conjugated double bond theory as the major cause of discoloration. Other possible contributors to color formation were considered to be changes in the stabilizing additives and peroxide crosslinking agent under the influence of heat, light, and oxygen (to the extent present). Figure 1 is a photograph of a typical single solar cell, showing the pattern of wires on the top of silicon for the purpose of conducting the electrical energy off to a storage battery. Between individual cells there are areas where there is no silicon, both at the perimeter of the rectangular cell, and at the four corners of each cell. Discoloration occurs only over part or all of the solar cell, and not between the cell, i.e. where there is no silicon.

Figure 2 shows schematically the arrangement of a solar cell in cross-section. EVA sheet thickness is ca. 18 mils. (0.018"). The space in the middle of the solar cell denotes the space between adjacent cells. In the spaces, top and bottom layers of EVA are fused together, and it is possible for air to diffuse into the EVA in those areas from the

[a] F.J. Pern and A.W. Czanderna, Solar Energy Materials and Solar Cells 25, 3-23 (1992).

[b] K.B. Abbas and E.M. Sorvik, J. App. Poly. Sci., 19, 2991-3006 (1975).

backing sheet. That is not possible in EVA fused to the top of the silicon. Whatever mechanism of discoloration is proposed, it must explain all these features of discoloration of modules, i.e., why discoloration has not occurred in certain areas as well as why it occurs above silicon.

The formulation of EVA encapsulant sheet studied, as manufactured by Springborn Laboratories, is as follows:

	parts by weight
EVA (33% VA)	100.0
Lupersol 101 Peroxide	1.5
Cyasorb UV 531	0.3
Tinuvin 770	0.1
Naugard P	0.2
	102.1

In addition to consideration of changes in the polymer that might contribute color, in particular conjugated double bonds, transformations of additives on exposure to heat, light and oxygen were also considered as possible causes of color development. Free radicals formed by the peroxide used for crosslinking have the potential to cause reactions that might cause color due to the additives. Quantitative analysis was performed for residual peroxide, Cyasorb UV 531, Tinuvin 770, BHT antioxidant present in EVA (300 - 400 ppm as received), and % VA in the polymers.

Aging experiments were performed at Springborn Laboratories in a Xenon Arc Weather-Ometer (XAW) with laboratory-prepared EVA films encapsulated between glass on both sides, and in some cases, glass on one side and permeable polymeric sheet on the back side. The laboratory aging studies looked at formulations in which the presence and levels of additives were controlled to evaluate the contribution of individual additives and combinations thereof, and of the polymer itself, to discoloration. The level of discoloration was measured as yellowness index.

4. Analytical Methods

1. Infrared spectroscopy-Nicolet 60 SX FTIR; Spectra Teck microIR (double bonds, oxidation effects, etc.)
2. Thermogravimetric analysis (TGA) -Dupont and TA Instruments TGA (percent vinylacetate)
3. Gas chromatography/FID detector-(peroxide content; samples (0.2-2.0 gm) were swollen in 100 ml methylene chloride; injections of solutions were made into the GC). GC column and conditions were as follows:
   Column - 100% methyl silicone, 15 m x 0.53 mm ID, 1.5μ film thickness, 15 psi
   Oven program - 40 to 160° at 20°/min
   Injection port - 100°
4. Thermal desorption gas chromatography/mass spectroscopy (GC/MS)-GC/MS was used for quantitative determination of BHT and to determine retention times of other additives so they could be determined by GC/FID. GC column and conditions were as follows:

Instrument - Hewlett/Packard 5890IIGC/5971A mass selective detector
   Column - SGE BPX-5, 25m x 0.2mm ID, 1.0μ film thickness.
   Sample - ca 0.2 mg
   Thermal desorption - 2'/350°C
   Oven program - 35 to 350° at 15°C/min
   Mass spectrometer - selected ion data collection using masses specific for Cyasorb UV531, Tinuvin 770 and BHT.
5. Thermal desorption gas chromatography/FID for determination of Cyasorb UV 531 and Tinuvin 770 - GC column and conditions were as follows: FID instead of MS detector permitted use of larger samples.
   Column - see 4 above
   Sample - ca 2 mg
   Thermal desorption - 2'/350°C
   Oven program - 40 to 300° at 15°/min

5. Analytical Results and Discussion

5.1 Double bond formation in the copolymer

5.1.1 % VA by TGA

Analyses were performed for EVA sheet representing a wide range of sheet exposure history, including uncured and unaged EVA. In all but one case, the % VA was within experimental error of the 33% value for unaged EVA. The exception was scrapings of degraded top surface of a highly degraded panel, which gave 35.2% VA. Even though acetic acid was detected by GC/MS, the amount formed was apparently too low to cause a significant reduction in VA content. Consequently, there appears to be little double bond formation from photolysis of VA. If there is little basis for double bond formation at any level, there is even less reason to expect conjugated double bond sequences of eight or more as required to develop color in the copolymer.

5.1.2 Infrared spectroscopy for double bonds

IR spectra of unaged EVA and highly discolored EVA were practically superimposable. In the region of the spectra where double bonds would have been expected to have absorbed, no perceptible absorption was seen. This result further supports the conclusion from the TGA analyses for % VA, i.e., no evidence for significant amounts of double bond formation in the degraded copolymer.

5.1.3 Color formation in EVA without additives

Laboratory-aged panels did not develop significant amounts of color after aging twelve weeks in a XAW. Under the same conditions crosslinked EVA containing all the additives of the standard formulation discolored significantly. This experimental evidence also does not support formation of double bonds in copolymer as long sequences as the main cause of discoloration. The XAW exposures suggest that discoloration may be due mainly to

transformations of additives caused by photolysis in the presence of peroxide.

5.2 Stabilizing Additives Concentrations by Thermal Desorption GC/MS and GC/FID

Both discolored field-aged and discolored laboratory-aged panels containing full formulation showed substantial losses of BHT, Cyasorb UV531 and Tinuvin 770. Less discolored panels experienced lower losses of stabilizing additives. The low concentrations indicate poor protection from UV radiation. Additive concentration is higher and there is no discoloration between cells, i.e., where there is no silicon. Higher temperature over the silicon than where there is no silicon may contribute to greater degradation.

5.2.1 Effect of peroxide on color and stabilizing additives concentration

XAW laboratory-aged panels with glass on both sides of EVA in which additive levels and combinations were studied showed a marked effect of peroxide causing color and lowering of stabilizer concentrations (Cyasorb UV 531 and Tinuvin 770). Cyasorb UV 531 concentration was practically unchanged after ten weeks exposure in the absence of peroxide, and dropped 40% when peroxide had been included in the formulation. Similarly, Tinuvin 770 concentration dropped 61% when peroxide had been included. Clearly peroxide causes reactions of Cyasorb UV 531 and Tinuvin 770 which reduce the concentration and cause color formation, in the case of Cyasorb UV531. Tinuvin 770 did not discolor in the presence or absence of peroxide when Cyasorb UV531 was absent.

5.3 Changes in Peroxide due to Crosslinking and UV Exposure

As shown in Table 1, crosslinked sheet before exposure to UV had a considerable level of undecomposed peroxide, ca. 30% of the formulation level. That suggests that reactions between peroxide and stabilizing additives that can take place either in the presence or absence of UV can occur because there is ample peroxide content. The level of peroxide content dropped quickly on exposure to UV, from about 0.37% before exposure to 0.03% after two weeks exposure.

5.4 Undiscolored Areas in Discolored Field-Aged Modules and Laboratory-Aged Panels with polymeric sheet backing

Most of the discolored weathered panels in this investigation exhibited colorless diamond-shaped regions where four silicon cells met (Fig. 1). In addition, the EVA in the perimeters of the individual silicon cells was lighter colored than the EVA above the silicon. A few discolored panels contained silicon cells with small cracks over which the encapsulant was virtually colorless. Micro FTIR of these regions of colorless EVA showed the presence of

absorption bands due to hydrogen-bonded hydroxyl at about 3580 cm^{-1}. Discolored regions of EVA encapsulant exhibited little, if any, absorption in this region (Figure 3). Cyasorb UV 531 content was depleted to the same extent in the colorless crack area and colored area away from the crack.

Hydroxyl absorption in the IR indicates oxygen had migrated into the solar cells and oxidized the EVA during many-year exposure in the field. Apparently the backing was permeable to oxygen, which diffused into the rear of the modules and migrated through regions without the silicon cell barriers. It is proposed the perimeters of the silicon cells and the diamond-shaped regions where four cells meet were light-colored due to photo-oxidative bleaching of colored additive reaction products.

In the case of laboratory prepared and aged samples which developed color with glass on both sides of EVA, the same formulations did not discolor when polymeric backing sheet was used, which allowed access of oxygen to the encapsulant. Here too, "photo-oxidative bleaching" appears to have taken place.

6. Conclusions

1. Discoloration of EVA encapsulant in photovoltaic modules does not appear to be related to long chains of conjugated unsaturation.

2. Unreacted Lupersol 101 peroxide remaining after curing exhibited a significant effect on the concentrations of stabilizing additives.

3. Transformation products of BHT, Cyasorb UV 531, and Nonyl Phenol (from reactions of Naugard P), arising from reactions with alkoxy radicals from the photolysis of Lupersol 101, might play an important role in the discoloration of EVA encapsulant. Investigations with laboratory aged panels showed correlation between color development and stabilizing additives/Lupersol 101 interactions.

4. IR evidence indicates light colored areas of modules recovered from the field have experienced oxidation. This suggests the backing is permeable to oxygen which diffuses into the rear of the modules and migrates through regions without the silicon cell barriers. Regions reached by oxygen might be "photo-oxidatively bleached". Colorless regions in the vicinity of cracks in silicon are part of this same phenomenon, that is, the crack provides access of oxygen to the discolored EVA above the silicon.

5. It is postulated that some of the discoloration of field-aged panels might be related to heating caused by the electrical current generated by the panels. The heating would be expected to be greatest within the interior of the panels. The temperature of the solar cell is determined in

part by the dissipation of heat at the edges which may account in part for the lesser degrees of discoloration at the edges. "Photo-oxidative bleaching" is expected to also contribute to the lesser discoloration at the edges.

TABLE 1: CONCENTRATIONS OF LUPERSOL 101 PEROXIDE AT VARIOUS STAGES

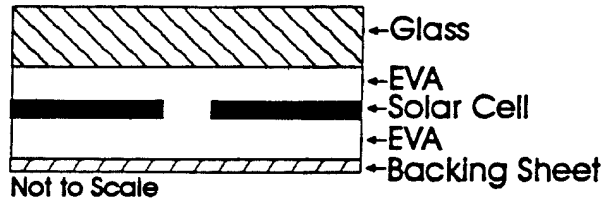| STAGE	CONC.(%)
Formulation charge to production lot	1.5
Extruded sheet, production lot	1.15
Lab-prepared glass/EVA/glass laminate	0.37
XAW-exposed laminate, 2 weeks	0.03
XAW-exposed laminate, 12 weeks	0.00

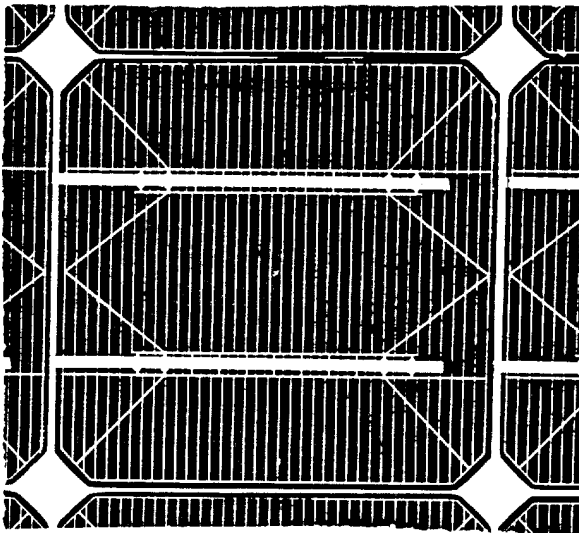Figure 2 - Cross-section diagram of solar cells.

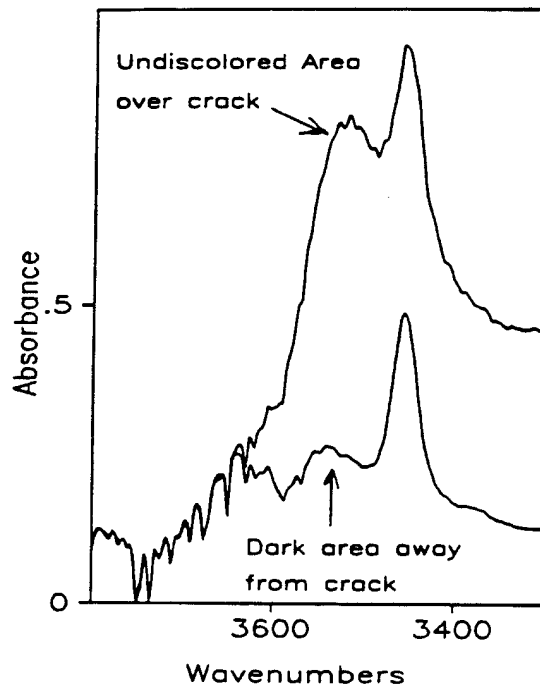Figure 1 -   Photograph of a single solar cell.

Figure 3 -   Infrared spectra of hydroxyl region for field aged solar module EVA at an undiscolored crack and in discolored area away from crack.