## Improved Photostability of NREL-Developed EVA Pottant Formulations for PV Module Encapsulation

F.J. Pern and S.H. Glick Presented at the 26th IEEE Photovoltaic Specialists Conference, September 29— October 3, 1997, Anaheim, California



National Renewable Energy Laboratory 1617 Cole Boulevard Golden, Colorado 80401-3393 A national laboratory of the U.S. Department of Energy Managed by Midwest Research Institute for the U.S. Department of Energy under contract No. DE-AC36-83CH10093

Prepared under Task No. PV706201

September 1997

# IMPROVED PHOTOSTABILITY OF NREL-DEVELOPED EVA POTTANT FORMULATIONS FOR PV MODULE ENCAPSULATION

F. J. Pern and S. H. Glick
Center for Performance Engineering and Reliability
National Renewable Energy Laboratory (NREL), 1617 Cole Blvd., Golden, CO 80401

### **ABSTRACT**

Several new formulations of ethylene vinyl acetate (EVA)-based encapsulant have been developed at NREL and have greatly improved photostability against UV-induced discoloration. The new EVA formulations use stabilizers and a curing agent entirely different from any of those used in existing formulations known to us. No discoloration was observed for the laminated and cured samples that were exposed to a ~5-sun UV light (300-400 nm) from a solar simulator at a black panel temperature (BPT) of  $44^{\circ}\pm2^{\circ}$ C for ~3250 h followed by at 85°C for ~850 h, an equivalent of approximately ~9.4 years for an average 6-h daily, 1-sun solar exposure in Golden, Colorado. Under the same conditions, substantial discoloration and premature delamination were observed for two commercial EVA formulations. Encapsulation with the new EVA formulations should extend the long-term stability for PV modules in the field, especially when coupled with UV-filtering, Ce-containing glass superstrates.

#### INTRODUCTION

Polymeric pottants made of EVA copolymer formulated with stabilizers have been widely used in the encapsulation of crystalline-silicon (c-Si) and some thin-film photovoltaic (*PV*) modules. The pottant provides the functions of (1) structural support, electrical and physical isolation, and thermal conduction for the solar cells and circuit components; (2) optical coupling between the solar cells and the glass superstrate; and (3) physical protection of the PV module from detrimental environmental factors. Chemical stabilization is often employed to enhance the durability of polymeric materials, especially for those used in outdoor environments. Long-term weathering stability of both the EVA and solar cell components is essential for extending the durability of PV modules to a 30-year service life as targeted by DOE's Solar 2000-A Collaborative Strategy [1]. However, commercial formula-tions of EVA pottants are subject to yellow-to-brown discoloration upon photochemical or photothermal degradation. In a critical review, Czanderna and Pern discussed the reliability issues of using EVA as a PV encapsulant [2].

Systematic studies have been conducted at NREL to determine the degradation and discoloration mechanisms for laminated and cured commercial EVA films and to quantify the effect of EVA discoloration on cell efficiency for EVA-encapsulated c-Si solar cells. The results have been reported [2-5] and compared with other results [2]. The extensive studies have resulted in a good understanding of the fundamentals about the EVA degradation mechanisms and the critical factors that can interactively and interrelatedly affect the rate and extent of EVA discoloration. This has enabled us to redesign the stabilization schemes to mitigate the chemical (and physical) factors, as reported recently [4,5]. This paper summarizes the major factors responsible for EVA browning and our approach to the development of the new NREL-EVA formulations and their greatly improved photostability.

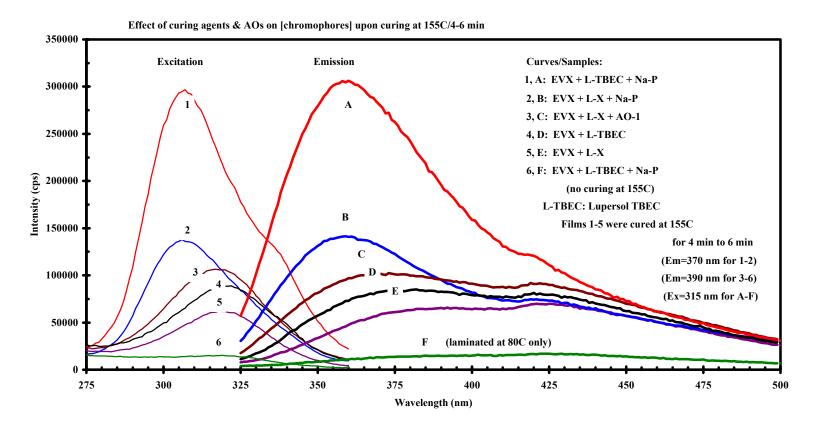
## **EXPERIMENTAL**

NREL-EVA films were made from high-purity cyclohexane solutions of Elvax 150<sup>TM</sup> (EVX) pellets (Du Pont) formulated with selected stabilizers, antioxidants, and curing agents at predetermined molar or weight percent concentrations. Details for preparing EVA laminate samples using a vacuum laminator with preset temperature-time-pressure programs, accelerated UV exposures, and spectroscopic characterization were reported previously [3-5].

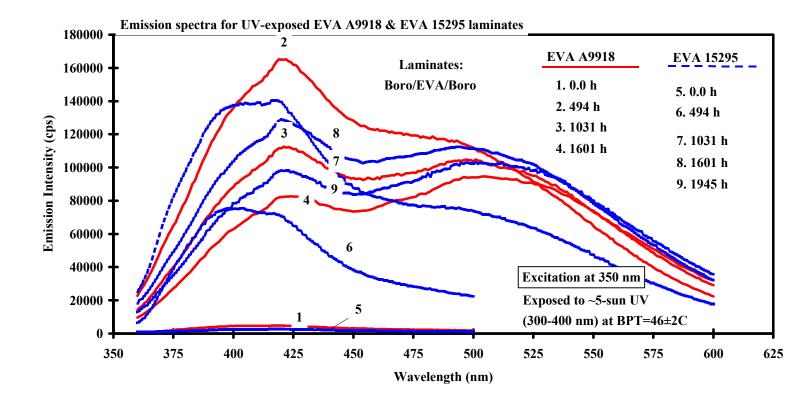
## **RESULTS AND DISCUSSION**

The components and their weight concentrations of the stabilizers and curing agents used in two commercial EVA formulations, A9918 and 15295, are given in Refs. 2-5. While polymeric crosslinking on the EVA by curing is required to provide sufficient mechanical strength for supporting the solar cell strings, the longer curing time needed for the EVA

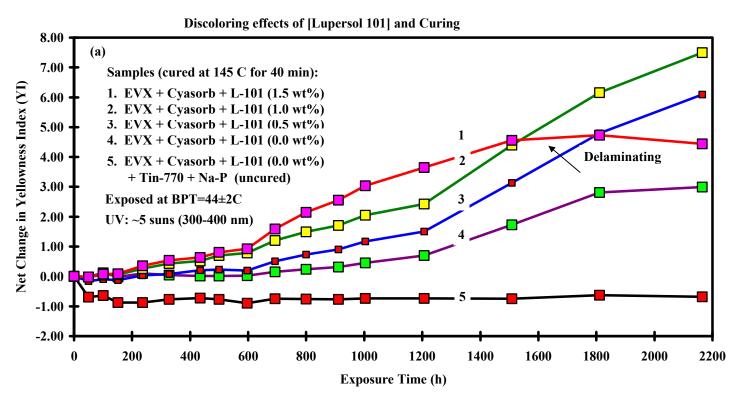
A9918 than for the EVA 15295, which is typically 40-45 min vs. 8-10 min at 145°-150°C, results in a greater concentration of curing-generated chromophores and residual curing peroxide [4,5]. Fluorescence analysis results indicate that the antioxidant Naugard P is a key element that greatly enhances the concentration of the UV-excitable chromophores produced by curing, as shown in Fig. 1 for 15295 EVA (compare curves 1 and 2 to curves 4-6). The results from previous studies further show that an increase in the concentration of the curing-generated chromophores results in an increase in the formation rate of discoloring polyenic conjugations and therefore a faster rate of EVA yellowing, as shown in Fig. 2. Additionally, longer curing times can possibly produce more acetic acid from deacetylation reactions of the EVA polymer; and the acetic acid can further increase the rate of EVA discoloration [2]. Therefore, A9918 EVA turns yellow-brown faster and to a greater extent than 15295 [2-5].



**Figure 1.** Fluorescence excitation and emission spectra for Elvax 150 (EVX) films impregnated with a curing agent, Lupersol TBEC or "L-X", with or without an antioxidant Naugard P (Na-P) or "AO-1," and laminated between two 0.16 cm thick microslides. L-X and AO-1 are two of additives used in the NREL formulations. The spectra are not subtracted from those of microslides. Except for curves 6 and F, all samples were cured at 155°C for 4 to 6 min using a microprocessor-controlled laminator [4,5].

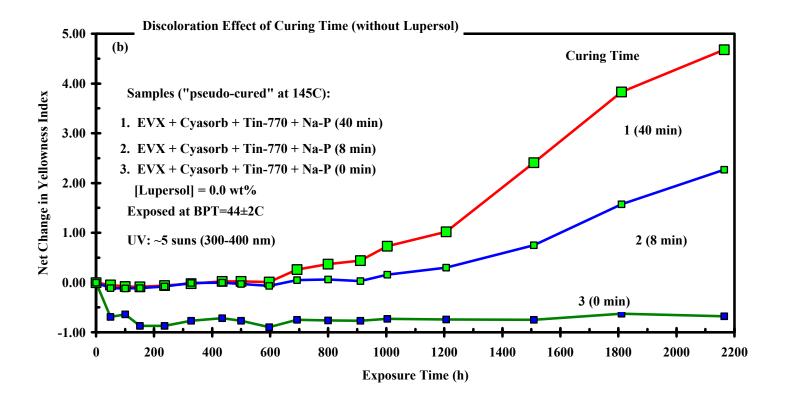


**Figure 2.** Fluorescence emission spectra as a function of exposure time obtained for samples of EVA A9918 and 15295 laminates, which were laminated and cured between two 5-cm x 5-cm x 0.32-cm borosilicate glass plates and exposed simultaneously to a  $\sim$ 5-sun UV light from an Oriel enhanced-UV solar simulator's 1-kW Xe light at a BPT=46°  $\pm$  2°C.



The UV absorber, Cyasorb UV 531, decomposes photochemically and its decomposition rate is directly related to the temporal evolution of discoloring polyenic chromophores. Typically, the loss rate of the UV absorber and the progress of EVA A9918 discoloration from light yellow to brown follow a sigmoidal pattern [3]. Figure 3 demonstrates the discoloring effects of (a) increased Lupersol 101 concentrations and (b) curing time in the presence of Cyasorb UV 531. These factors synergistically contribute to or induce the photooxidative reactions of EVA involving the formation and propagation of free radicals, and result in mixed formations of conjugated polyenes of various lengths [5,6].

In summary, the *chemical degradative factors* responsible for EVA browning include the (1) additives in the EVA formulations, (2) loss rate of the UV absorber, Cyasorb, (3) curing agent and curing conditions (temperature, pressure, and time), (4) concentration of curing-generated, UV-excitable chromophores, and (5) photobleaching reactions resulting from diffusion of air into the laminated films [3].



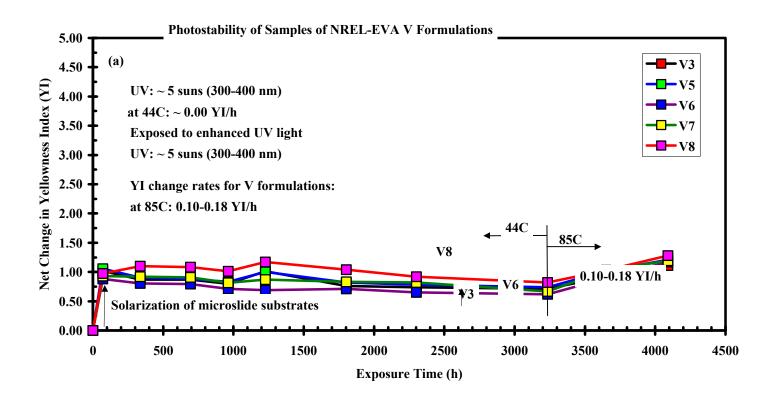
**Figure 3.** Net change in the yellowness index (YI) measured as a function of UV exposure time for (a) a set of EVX film samples (1-4) that contained a fixed concentration of Cyasorb UV 531 and increasing concentrations of Lupersol 101, and cured at 145°C for 40 min. Sample 5 was uncured; and (b) a set of EVX film samples containing Cyasorb and Naugard P that were cured for 40, 8, and 0 min, respectively.

Details of the degradation and discoloration mechanisms have been described and elaborated elsewhere [3-6]. In addition, we observed that the curing peroxide Lupersol 101 seems to decompose gradually in cyclohexane solutions during storage, which can reduce the shelf life of the extruded A9918 EVA sheets. Also, the curing peroxide Lupersol TBEC tends to produce bubbling in EVA 15295 if the processing conditions (i.e., temperature, time, and pressure) are not well controlled during the encapsulation process.

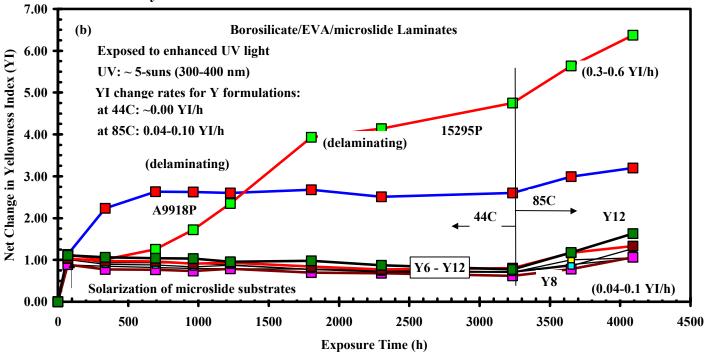
To produce EVA formulations that can have greater photothermal stability against browning problems, we addressed *simultaneously* all the above-mentioned degradative factors. Essentially, we selected and tested a number of stabilizers, antioxidants, and curing agents that are (1) able to reduce the formation of curing-generated UV-excitable chromophores, (2) more stable against hydrolysis by moisture, (3) more effective to scavenge (neutralize) the degradative free radicals that can be produced in the course of photooxidative reactions, (4) more stable for a longer

shelf life, and (5) fast in curing while not producing bubbles. We also addressed the photothermal instability of the UV absorber, Cyasorb UV 531. Consequently, we have developed several new formulations that have been *simultaneously* able (1) to reduce by ~2.2 times the concentration of curing-generated chromophores as shown in Fig. 1, (2) to achieve a curing in 4-6 min at 155°C at a reduced pressure, (3) to leave little to no curing peroxide residue in the EVA laminates, (4) to produce the desired degree of cross-linking (~80% gel content), (5) to eliminate or greatly reduce the bubbling problems, (6) to improve the stability of the antioxidants against moisture and thermal decomposition and, more importantly, (7) to improve greatly the photostability against UV-induced discoloration.

The results shown in Fig. 4 illustrate the improved photostability for some samples of our V and Y EVA formulations, as compared to the two commercial formulations. All of the samples were UV-exposed simultaneously. From measured net changes in the yellowness index ( $\Delta YI$ ), the samples of the V and Y formulations that are laminated/cured between a borosilicate superstrate and a soda lime microslide substrate show no UV-induced discoloration (rate =  $\sim 0.00 \Delta Y l/h$ ) after exposing to the  $\sim 5$ -sun UV light (300-400 nm) for  $\sim 3250 h$  at a BPT=44°  $\pm 2$ °C. which is roughly equivalent to 7.4 years for an average 6-h daily solar exposure in Golden, Colorado at the same BPT. Subsequently, the samples were placed inside a custom-built, aluminum sample chamber with heating foils and the UV exposure was continued at an elevated BPT=85° ± 1°C for an additional ~850 h, a rough equivalent of ~2 more years. Under such harsh exposure conditions, a discoloration rate of 0.10-0.18 \( \Delta YI/h \) was measured for the samples of V formulations and 0.04-0.10 ΔYI/h for the samples of Y formulations. Furthermore, only a few samples of the V and Y formulations showed a minor degree of edge delamination at a much later stage of UV exposure (probably after 2500 h) at 44°C, compared to the visible delamination seen earlier in A9918 at <800 h. The sample of 15295 EVA probably also delaminated after >1800 h, as suggested by the YI data curve. The premature delamination of A9918 EVA upon UV exposure at a BPT=44°C in the ambient resulted in photobleaching reactions that prevented further discoloration of the sample, and a relatively constant  $\Delta YI$  was thus obtained. Interestingly, the visible delamination around the edges of samples, including the A9918 EVA sample, disappeared after the samples were heated at 85°C for some time. The "self-sealing" effect is attributed to softening and flowing of the EVA at elevated temperatures.



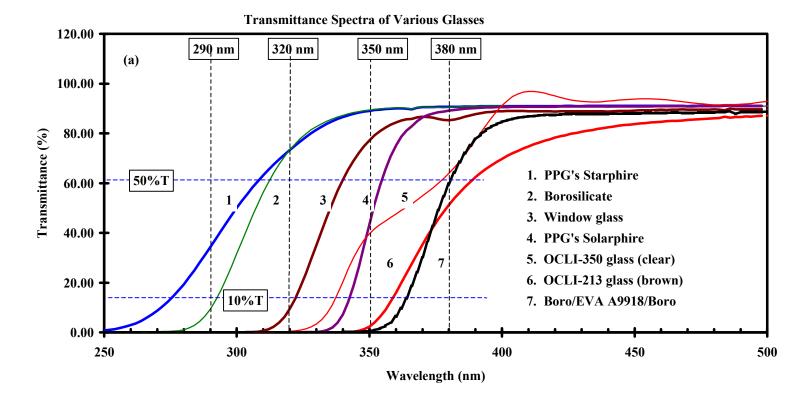


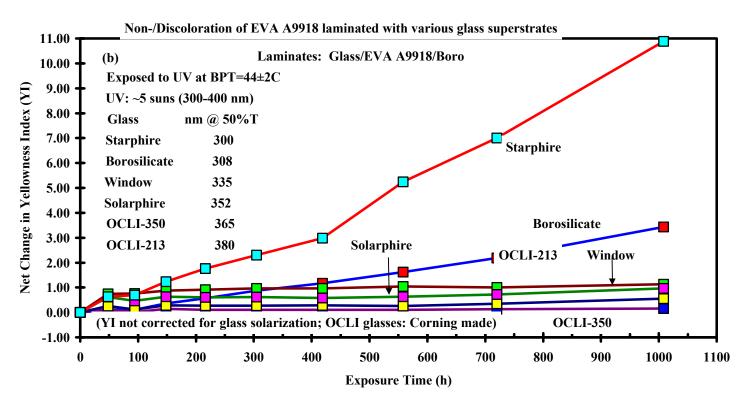


**Figure 4.** Net changes in the YI as a function of exposure time for two sets of NREL-EVA formulations: (a) V formulations with varying concentrations of an antioxidant and (b) Y formulations compared to discoloring samples of A9918 and 15295 EVA. All of the samples were laminated and cured between a 1/8"-thick borosilicate glass superstrate and a 0.16-cm-thick soda lime microslide. Exposures to the ~5-sun UV light through the borosilicate superstrate were conducted simultaneously for all samples at a BPT=44°  $\pm$  2°C for ~3250 h in the ambient followed by at a BPT=85°  $\pm$  1°C for ~850 h inside a heated custom-built, aluminum chamber covered with a quartz plate window.

## **CONCLUSIONS**

In conclusion, we have developed several new formulations of EVA-based pottants at NREL that show highly improved photostability against UV-induced discoloration and better processibility. These pottants are readily usable by the PV industry with existing module encapsulation equipment and methods. The EVA encapsulants made of these new formulations should provide improved weathering stability and an extended service life for PV modules. The module service life can be further extended if cerium oxide-containing (ceria-doped) glass superstrates are used to effectively remove the UV  $\leq$  350 nm to reduce greatly the UV-induced browning effect on commercial EVA formulations, as demonstrated in Fig. 5 for the A9918 EVA from our previous study [3,7].





**Fig. 5.** (a) Transmittance spectra of various glass plates and (b) effectiveness of protection of the glasses for the commercial EVA formulations, A9918 and 15295 EVA.

#### **ACKNOWLEDGMENTS**

The authors are grateful for the project support by A. W. Czanderna, R. DeBlasio, and R. Hulstrom of the Center for Performance Engineering and Reliability. The following companies are gratefully acknowledged for providing samples of the stabilizers (Ciba-Geigy), polymer pellets (Du Pont), extruded EVA films (Springborn Laboratories, Richmond Technology), and Ce-containing glass plates (PPG, OCLI). This work was performed with support of the U.S. Department of Energy under Contract No. DE-AC36-83CH10093.

#### REFERENCES

- 1. "Solar 2000 -- A Collaborative Strategy," Vol. II (Appendices), Office of Solar Energy Conversion, Department of Energy, Washington, D.C., Feb., 1992.
- 2. A.W. Czanderna and F.J. Pern, "Encapsulation of PV Modules using Ethylene Vinyl Acetate Copolymer as a Pottant: A Critical Review," *Solar Energy Materials and Solar Cells*, **43** (1996), 101-183.
- 3. F.J. Pern, "Factors That Affect the EVA Encapsulant Discoloration Rate Upon Accelerated Exposure," *Solar Energy Materials and Solar Cells*, **41/42** (1996), 587-615.
- 4. F.J. Pern, "Development of New EVA Formulations for Improved Performance at NREL," AIP Conf. Proc. No. 394 for the 14th NREL/Sandia National PV Program Review Meeting, C.E. Witt, M. Al-Jassim, and J.M. Gee ed., American Institute of Physics (AIP), Woodbury, NY, 1997, pp. 795-810.
- 5. F.J. Pern, "Ethylene-Vinyl Acetate (EVA) Encapsulants for Photovoltaic Modules: Degradation and Discolor-ation Mechanisms and Formulation Modifications for Improved Photostability," Proc. of 19th Annual International Conference on Advances in the Stabilization and Degradation of Polymers, Luzern, Switzerland, June 9-11, 1997, Institute of Materials Science, State University of New York, pp. 189-208.
- F. J. Pern, "Luminescence and Absorption Characteri-zation of The Structural Effects of Thermal Processing and Weathering Degradation on Ethylene Vinyl Acetate (EVA) Encapsulant for PV Modules," *Polym. Deg. and Stab.*, 41 (1993), 125-139.
- F.J. Pern, "Comparsion of The Photostability for Two Common EVA Formulations: EVA A9918 and EVA 15295", Proc. of 6th PV Performance and Reliability Workshop, Sept. 21-23, 1994, Lakewood, CO, pp. 329-347. (NREL/CP-411-7414).