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Preprint

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*Presented at the 2012 IEEE Photovoltaic Specialists Conference
Austin, Texas
June 3–8, 2012*

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Conference Paper
NREL/CP-5200-54117
June 2012

Contract No. DE-AC36-08GO28308

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A Field Evaluation of the Potential for Creep in Thermoplastic Encapsulant Materials

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Abstract — There has been recent interest in the use of thermoplastic encapsulant materials in photovoltaic modules to replace chemically crosslinked materials, e.g., ethylene-vinyl acetate. The related motivations include the desire to: reduce lamination time or temperature; use less moisture-permeable materials; use materials with better corrosion characteristics or with improved electrical resistance. However, the use of any thermoplastic material in a high-temperature environment raises safety and performance concerns, as the standardized tests currently do not expose the modules to temperatures in excess of 85°C, though fielded modules may experience temperatures above 100°C. Here we constructed eight pairs of crystalline-silicon modules and eight pairs of glass/encapsulation/glass thin-film mock modules using different encapsulant materials of which only two were designed to chemically crosslink. One module set was exposed outdoors with insulation on the back side in Arizona in the summer, and an identical set was exposed in environmental chambers. High precision creep measurements (± 20 μm) and performance measurements indicate that despite many of these polymeric materials being in the melt state during outdoor deployment, very little creep was seen because of their high viscosity, temperature heterogeneity across the modules, and the formation of chemical crosslinks in many of the encapsulants as they aged. In the case of the crystalline silicon modules, the physical restraint of the backsheet reduced the creep further.

Index Terms — Encapsulant, Creep, Thermoplastic, Qualification Standards, Polymer.

I. INTRODUCTION

With the recent interest in thermoplastic photovoltaic (PV) encapsulants and adhesives, there has been an increased concern in the standards community regarding to the potential for viscoelastic creep of these materials. Currently, qualification and safety tests (IEC 61215, IEC 61646, IEC 61730, UL 1703) [1-4] stress modules up to a maximum temperature of only 85°C in the “damp heat,” “thermal cycling,” and “humidity freeze” tests. Additionally, small areas of a module may reach much higher temperatures during the “hot spot” test [5], but the localized nature of this test does not examine the condition inherent to the hottest module operating environments and mounting conditions. In

very hot environments, modules are known to reach temperatures in excess of 100°C [6, 7]. One could envision a material with a melting point near 85°C with a highly thermally activated drop in viscosity, resulting in significant creep at 100°C. To evaluate this potential scenario, we assembled modules with eight different encapsulant types using two different module constructions and exposed them outdoors in Mesa, Arizona for the summer of 2011. We also exposed a replicate module set to high temperatures in indoor environmental chambers. Here we present the results of these tests and discuss the implications for qualification testing, safety standards, and manufacturing practices.

II. EXPERIMENTAL

Encapsulant materials being used, or under investigation for use, in PV modules were obtained from industrial manufacturers. Under agreement with these manufacturers, we may disclose the general class of the polymeric resin and the physical properties we have measured (Table 1). For the poly(dimethylsiloxane) (PDMS) encapsulation, a different formulation was used for the thin-film mock modules than in the crystalline silicon modules, but both are similar sparsely crosslinked gels. The PDMS values in Table 1 apply to the thin-film mock modules. Notably, a non-curing poly(ethylene-vinyl acetate) (NC-EVA) was formulated identically to a standard EVA formulation but without the inclusion of a peroxide to promote curing during lamination.

The set of silicon modules were made using 42, 156-mm upgraded metallurgical silicon cells with a final average aperture area efficiency of 14.6%. The PDMS modules used 60, 156 mm, multicrystalline cells and were 13.9% efficient. The thin-film mock thin-film modules were constructed using two pieces of 3.18 mm thick, 61 cm by 122 cm glass. The rear surface of the back plate was painted black to simulate the optical absorption of a thin-film module. The inside of the front glass had a thin transparent conductive oxide (TCO) layer which was removed within 12.7 mm of the perimeter using laser ablation. The TCO was electrically connected to a ribbon going through a hole cut in the back plate. This

enabled the wet high pot test to be conducted to assess if creep would create a safety or performance concern. Thin-film mock modules were mounted by adhesively attaching fiberglass channel on the back, allowing the front piece of glass to move freely.

For the thin-film mock modules, the creep (displacement of the front glass relative to the back glass) was measured using a high precision depth gauge, that incremented $\pm 1\mu\text{m}$. This gauge was mounted to a flat plate to ensure that it was positioned perpendicular to the side of the module, and in the plane of the glass. With this set-up, creep measurement reproducibility was better than $\pm 20\mu\text{m}$.

Table 1. Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) determined phase transitions. DMA glass transitions (T_g) were determined as the peak in the phase angle, and the DMA melting transitions (T_m) were determined when the phase angle was 45° except for the crosslinked PDMS and EVA where an inflection point in the modulus was used.

Encapsulant Material Type		DSC Determined Transitions			DMA Determined	
		T_g (°C)	T_m (°C)	T_f (°C)	T_g (°C)	T_m (°C)
Commercial PV EVA resin	EVA	-31	55	45	-30	47
Commercial PV EVA Resin with all components but the peroxide	NC-EVA	-31	65	45	-28	69
Polyvinyl Butyral	PVB	15	NA	NA	17	NA
Aliphatic Thermoplastic Polyurethane	TPU	2	NA	NA	3	NA
Pt Catalyzed, Addition Cure Polydimethyl Siloxane Gel	PDMS	-160	-40	-80		
Thermoplastic Polyolefin #1	TPO-1	-43	93	81	-35	105
Thermoplastic Polyolefin #3	TPO-3	-44	61	55	-41	79
Thermoplastic Polyolefin #4	TPO-4	-34	106	99	-21	115

Modules were deployed in Mesa, Arizona from May until September 2011 on a rack tilted at 33° latitude tilt and a 255° azimuth so they would more directly face the sun at the hottest part of the day. Additionally, a single NC-EVA thin-film mock module was exposed in Golden, Colorado at a 180° azimuth and 40° tilt [8]. For both the thin-film and silicon module types, insulation was placed on the backside to simulate a close-roof installation (resulting in maximum measured temperatures between 102 and 104°C in Mesa,

Arizona). The temperature of the modules was monitored by placing thermocouples on the backside of each module underneath the insulation. One thermocouple was placed in the center of each module and the other about 7.5 cm diagonally from one corner of the module.

Following field deployment, the formation of polymer chain crosslinks on the Arizona-fielded NC-EVA thin-film mock module was evaluated using size exclusion chromatography (SEC) in conjunction with multi angle laser light scattering (MALLS, Waters Corporation GPCV 2000 instrument) and viscometric detection (using a capillary viscometer detector CV from Waters). Samples were cut using a ceramic saw blade enabling samples to be taken at different distances from the edge. Polymer was removed from the glass by extraction for 72 h in a solution of tetrahydrofuran (THF); however, this left behind approximately 60% of the EVA as an insoluble fraction. The residual glass-EVA specimens were soaked in trichlorobenzene (TCB) overnight at 150°C to solubilize the remaining EVA. Samples of “virgin” (unexposed) NC-EVA film were dissolved in THF and TCB at room temperature and 150°C , respectively, to serve as controls. Solutions were made with approximately 1 mg/ml.

III. RESULTS

A. Outdoor Testing

Of the outdoor exposed modules, only the thin-film mock modules constructed using NC-EVA experienced significant creepage, moving 3.0 ± 0.2 mm over the course of the summer, Fig. 1. Despite this, the NC-EVA module still passed the wet high-pot test. A more detailed indoor measurement after the exposure, (Fig. 2) indicated that the TPO-3 module crept 0.090 ± 0.036 mm and the TPO-1 module crept 0.032 ± 0.024 mm (Fig. 2). Even though most of these thermoplastic encapsulants reached either the melt or rubbery state during exposure, no significant movement was observed.

Noting the absence of creep beyond day 110 in AZ, a general reduced creep rate when the maximum temperature is lower during the first 60 days or so, and noting that the Colorado deployed module barely crept and that it rarely reached temperatures above 90°C , this indicates that creep is possible for uncured EVA when the maximum module temperature approaches around 90°C , Fig. 1. Because the modules were mounted individually, as opposed to a close-packed installation (i.e. they were mounted allowing air flow between modules), the temperature was between 10 and 15°C cooler at the edges of the modules during the hottest part of the day. The temperature differential appeared in both the thin-film mock and the crystalline Si modules, but the presence of an Al frame in the crystalline silicon modules is expected to make it harder, but not impossible, to realize an installation configuration that would reduce this temperature heterogeneity significantly. It is this temperature differential

that helps to significantly reduce the creep despite the fact that most of the module is well above its melting point of around 65 to 69°C.

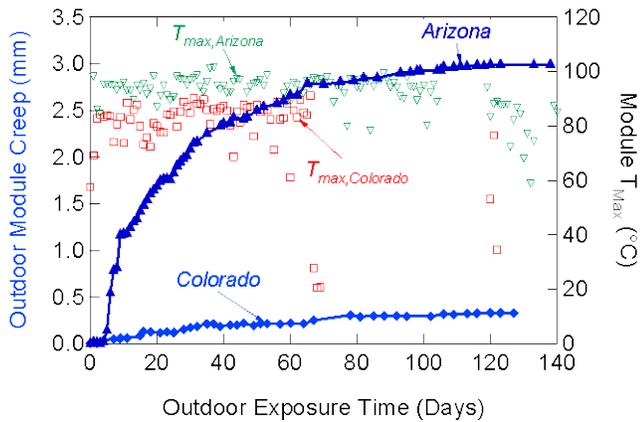


Fig. 1. Measurement of thin-film mock module creep during outdoor exposure. The module displacement, daily maximum module temperature, and daily maximum ambient temperature for the NC-EVA modules deployed in AZ and CO.

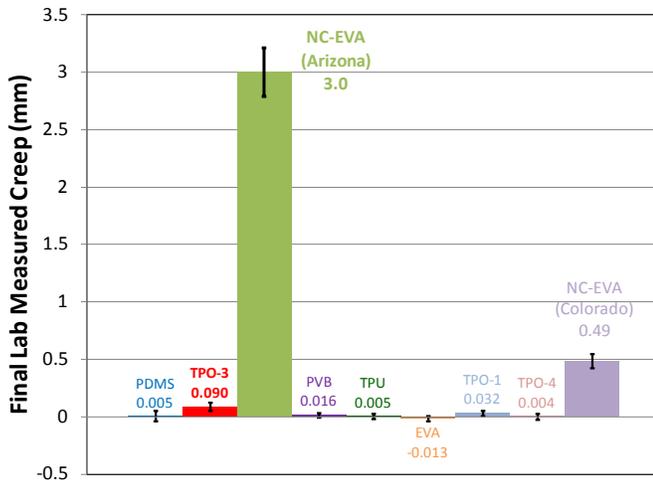


Fig. 2. Measurement of thin-film mock module creep after field deployment in AZ or CO.

Over the first 30 days, creep was faster in the Arizona module, but slowed down mid-summer despite the fact that the temperature did not fall significantly. Typical EVA formulations are known to crosslink as they age in the field [9]. This reduction in creep rate suggests that even without the peroxide additive, NC-EVA is crosslinking at these high temperatures.

B. Indoor Testing

The modules were also examined indoors in a step stress experiment. Modules were mounted vertically with the

crystalline Si modules simply resting on their frames and the thin-film mock modules mounted vertically using adhesive on their backside allowing the front glass to move (Fig. 3). More creep is seen in indoor testing relative to outdoor experiments at lower temperatures where the cool perimeter of the outdoor modules limits motion. The NC-EVA began creeping detectably at 75°C in the thin-film mock module construction, and at 80°C in the crystalline Si construction. Similarly, the TPO-3 and TPO-1 thin-film mock modules began to creep detectably at 90 and 105°C respectively. Furthermore, the slope of the creep vs. temperature curve for TPO-3 does not continue to increase rapidly beyond 95°C suggesting that it is chemically crosslinking at temperatures above 90°C. At even higher temperatures, above 120°C, the amount of creep in each cycle begins to plateau for TPO-3. Similar behavior is also seen for TPO-1, TPO-4, and PVB. The only thermoplastic material that did not appear to crosslink as it aged was the TPU. In this case, after exposure at 130°C, the module plates were displaced by more than 1 cm where they contacted the chamber floor. Additionally, a large number of bubbles began to appear within the module starting at 105°C and becoming present throughout the module after exposure to 110°C.

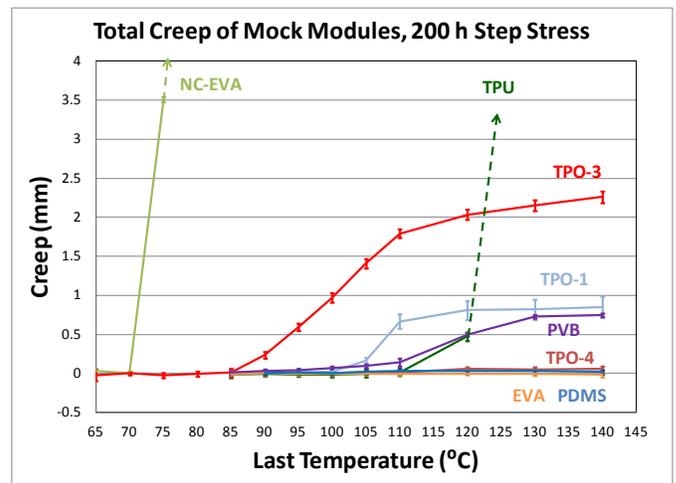


Fig. 3. Relative displacement of glass sheets in the thin-film mock modules after step-stress tests, of a duration of 200 hours each.

C. Molecular Weight Changes

The crosslinking of the NC-EVA in the fielded module was verified using SEC in conjunction with MALLS and viscometry detection. Three samples were removed from the modules. One cut from the edge of the module, one about 2 cm in from the edge, and another about 4 cm in. Figure 4 shows that the THF-insoluble, TCB-solubilized sample taken from the edge of the NC-EVA module deployed in Arizona has a lower molecular weight distribution than the unaged TCB-solubilized control sample, indicating that chain scission

has dominated over polymer crosslinking. In contrast, the samples taken at distances of 2 cm and 4 cm in from the edge have a higher molecular weight than the control indicating that crosslinking dominates over chain scission. However, all the aged samples do show changes in intrinsic viscosity relative to the control indicating some degradation causing changes in the degree of branching of the polymer chains.

This result is supported by numerous observations of fielded modules where discoloration of EVA is observed in the center area of a cell, yet greater oxygen incorporation is seen around the cell perimeter [10]. Similarly, it has been observed that the gel content in the more highly yellowed EVA at the center of the cell is higher than EVA at the perimeter in aged samples [9]. Thus yellowing and crosslinking are correlated to lower oxygen incorporation and oxidative bleaching and lower crosslink densities are correlated to higher oxygen incorporation.

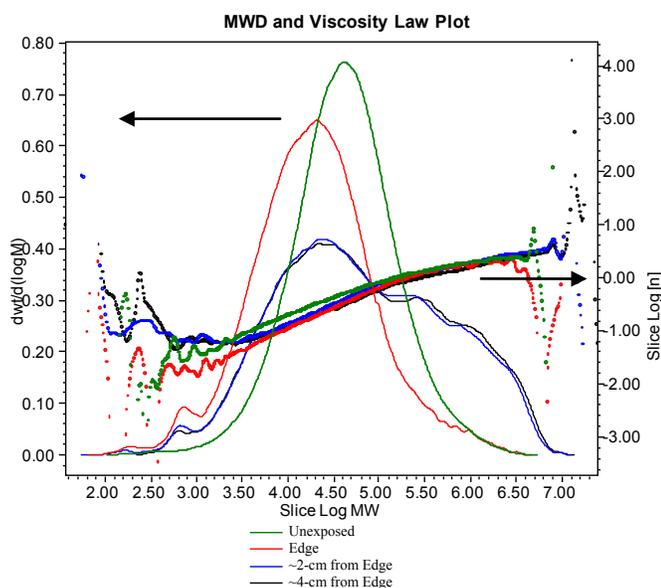


Fig. 4. SEC-MALLS and viscometry results from the NC-EVA thin-film mock module after exposure in Arizona. Samples dissolved in trichlorobenzene (TCB) by extraction at 150°C overnight. Molecular weight (MW) is in units of [g/mol]. Left axis, weight fraction in slice, thinner lines. Right Axis, intrinsic viscosity [dl/g] in slice, thicker lines.

For the THF soluble fraction, very little difference in the molecular weight distribution was seen between the EVA samples extracted from the fielded modules as compared to the unstressed EVA, Table 2. THF was only able to dissolve about 40% of the polymer. Therefore, it appears that any degradation causing chain scission or crosslinking renders EVA significantly less soluble in THF.

Sample		Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	PDI	MP (g/mol)
THF Soluble Fraction	Unexposed	20,400	97,800	448,000	4.8	42,800
	Edge	19,900	89,100	379,000	4.5	40,300
	~2-cm from Edge	19,900	84,600	326,000	4.2	37,900
	~4-cm from Edge	21,300	104,000	437,000	4.9	40,900
TCB Soluble Fraction	Unexposed	15,600	97,800	512,000	6.3	44,400
	Edge	5,540	66,800	632,000	12	21,100
	~2-cm from Edge	8,720	394,000	2,220,000	45	25,000
	~4-cm from Edge	10,600	382,800	2,050,000	36	22,000

IV DISCUSSION

A. Oxidation and Crosslinking

There are many different chemical pathways possible for producing crosslinking in polymer chains. For the NC-EVA, the fact that the formation of crosslinks varies with position in the sample indicates that some chemical species must be entering or leaving the module package affecting the kinetics. Going in from the edge, there are gradients in temperature, water content, and in oxygen content. The temperature gradient from the edge to the center is at most around 20°C at the hottest part of the day (as indicated by infrared imaging). This would not be expected to create large differences in the reaction kinetics by itself over a 2 cm distance. The diffusivity of water in EVA has an activation energy of about 38 kJ/mol (0.40 eV) [11], which was used to estimate an Arrhenius activation energy-weighted effective module temperature of 50°C for the corner and 60°C for the center thermocouples [12, 13]. At 50°C, the diffusivity of water in EVA is 1.6×10^{-6} cm²/s. For the deployment time of 140 days, the characteristic penetration depth (x) was around 4.1 cm [11]. Alternatively, for a distance of 2 cm, the characteristic ($x = \sqrt{Dt}$) time is 29 days.

Marias et al. [14], compared the permeation characteristics of H₂O and O₂ in 33 wt% VA EVA at 25°C and found it to selectively permeate water 350 times faster, at the same vapor pressures, principally because of differences in solubility. Using 10% RH in Arizona at 25°C for the water content, the partial pressure of water is about 0.24 cm-Hg as compared to 21% oxygen with 16 cm-Hg, this means water permeates EVA about 5.2X faster than oxygen. This makes it more likely that O₂ is the limiting reagent enabling the shift from crosslinking dominated reactions to chain scission dominated reactions. However, more research is necessary to verify the kinetic pathways to confirm which component is limiting the reaction.

The reduction in creep rate of field exposed modules and the formation of crosslinks as shown by SEC-MALLS, indicate that in anaerobic and anhydrous conditions when exposed to heat and UV light, EVA will crosslink even without the addition of peroxide-based crosslinkers to the formulation. Because the thin-film mock modules were constructed such that light passed through the polymer, it is

not known if these effects are driven by heat, UV light, or the combination of the two. However, it does indicate that typical EVA formulations would be expected to crosslink with time and mitigating the potential for thermally induced creep.

B. Creep and its Consequences

Because the three TPOs and PVB, did not have exponential-like increases in creep with temperature, it is shown that exposure to high temperatures caused crosslinking reactions to dominate over chain scission. So similarly to EVA, it is probable that they too would crosslink with time in field exposure. In contrast, the TPU thin-film mock module began to creep at 100°C and also formed a large number of bubbles in the interior of the module. At higher temperatures the effective viscosity dropped dramatically and the front plate contacted the bottom of our chamber causing creep that was too high to be measured in our chambers (see the dashed arrow in Fig. 3 for TPU). The TPU seemed to degrade dramatically at elevated temperatures. In contrast, all the polymers with only carbon-carbon bonds in the backbone (EVA, TPOs, and PVB), appear to crosslink when exposed to high temperature. This will help to mitigate the potential for creep in these thermoplastic encapsulant materials.

The onset of creep correlates reasonably to the melting points determined by DMA using the phase angle of 45°, Table 1. The three thermoplastic polyolefins showed much greater creep than PVB, despite its glass transition at 16°C, because of the greater viscosity of PVB [8]. However, DMA measurements indicate the phase angle of PVB reaches 45°, when measured at 0.01 rad/s, at temperatures of 115°C, which correlates better with its onset of its creep.

None of the crystalline Si modules demonstrated measureable creep when deployed outdoors. Only the TPO-3 module demonstrated a statistically significant performance loss that was due to a cracked cell presumably weakened or cracked during lamination because of TPO-3's higher viscosity relative to EVA [8]. Despite reaching what could be considered nearly the highest temperatures possible for a fielded module, none of the crystalline Si modules experienced a detectable safety or performance failure due to the use of a thermoplastic encapsulant. However, the modules were mounted with the cell strings arranged vertically. If the NC-EVA module had been mounted with the cells strings horizontal, it is more likely that some creep would have occurred in the cells in the center of the module. Subsequent accelerated stress tests (humidity freeze) will be performed on these modules to see if longer-term deployment may result in deformation and/or performance degradation.

In indoor studies, the onset of creep for the NC-EVA silicon module occurred at 75°C. Here, despite the fact that the sides of adjacent rows of cells were touching, there was no discernible performance loss with step stress tests up to 100°C, (Fig. 5 (A-B)). Even though this significant cell movement did not directly create a performance issue, it is

likely that longer term exposure to thermal cycling, after this creep, would increase the mechanical stress on the tabbing and solder bonds increasing the long term failure rates.

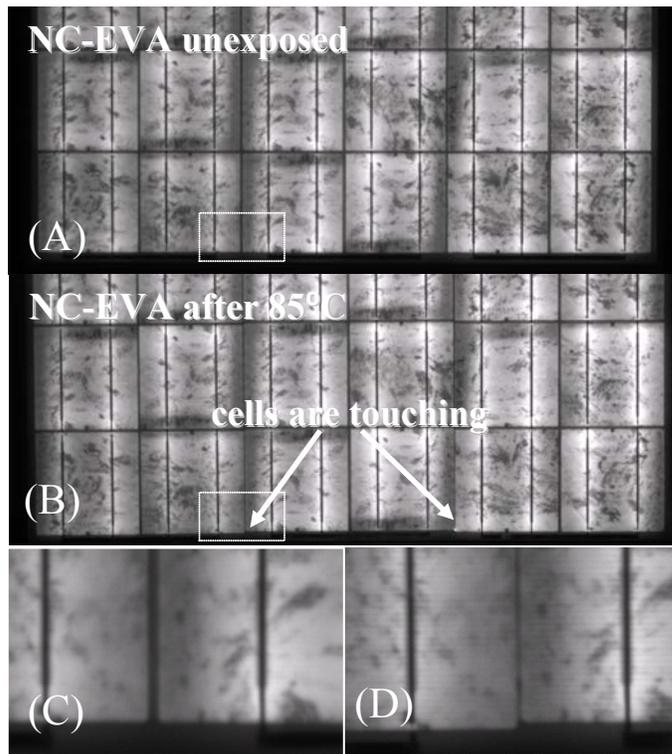


Fig. 5. Electro-luminescent images of the NC-EVA crystalline Si (A) before thermal exposure and (B) after the 85°C exposure step of the indoor step-stress test. (C,D) Close-up of bottom cells as indicated by the boxes in A and B.

V. CONCLUSIONS

These results here indicate that the potential for creep of the examined thermoplastic materials is negligible for the majority of PV installations. Even when a typical polymer-backed crystalline Si module was exposed outdoors in Arizona during the summer with insulation on the back to simulate a roof-top mounting configuration, the module did not creep, even when made with EVA containing no cure chemistry. Thus, we were not able to detect a short term durability or safety issue likely to result from completely uncured EVA.

Only modules with an unrestrained glass frontglass were shown to have any propensity to creep outdoors. This is due in part to the nonuniformity of temperature resulting in small areas that significantly resist creep. Evidence was also presented for the NC-EVA, TPO-1, and TPO-3 indicating that they are thermally crosslinking despite the absence of peroxide. This unintended crosslinking actually serves to mitigate the potential for creep in some materials.

The use of 85°C in IEC standards necessitates crosslinking of EVA to achieve gel contents in excess of around 60%; however, even if the EVA of a framed, polymer-backed Si PV module had a very low gel content, it would have to be deployed in an extreme environment in close contact to an mounting structure restricting heat transfer, in the hottest time of the year for there to be a significant chance of creeping before it eventually thermally crosslinked on its own [9]. Therefore, to assess the potential for creep, manufacturers should consider not only the location of phase transitions and the viscosity at temperatures between 85 and 100°C, but also the effects of degradation (chain scission or crosslinking) on those material properties.

ACKNOWLEDGEMENT

This work was part of a large collaborative effort of a number of people working on standards development at many institutions. The authors gratefully acknowledge the support of the following individuals: Adam Stokes, Alain Blosse, Ann Norris, Bernd Koll, Bret Adams, Casimir Kotarba (Chad), David Trudell, Dylan Nobles, Ed Gelak, Greg Perrin, Hirofumi Zenkoh, James Galica, Jayesh Bokria, John Pern, Jose Cano, Kartheek Koka, Kate Stika, Keith Emery, Kent Terwilliger, Kolakonu, Masaaki Yamamichi, Mowafak Al-Jassim, Nick Powell, Niki Nickel, Pedro Gonzales, Peter Hacke, Ryan Smith, Ryan Tucker, Steve Glick, Steve Rummel, Tsuyoshi Shioda, and Yefim Brun.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08-GO28308 with the National Renewable Energy Laboratory.

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