



Determining the Crosslinking and Degradation Reaction Kinetics in Photovoltaic Encapsulants Using Accelerated Aging

Preprint

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Determining the Crosslinking and Degradation Reaction Kinetics in Photovoltaic Encapsulants Using Accelerated Aging

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Abstract — Degradation of photovoltaic (PV) module encapsulant mechanical characteristics that lead to embrittlement and delamination remains a cause of failure in solar installations. A multiscale reliability model based on detailed molecular degradation reaction kinetics was previously published, connecting the encapsulant mechanical properties (elastic modulus, yield strength, and adhesion energy) to the degraded molecular structure and interfacial bond density to adjacent solar cell and glass substrates. The model, developed primarily for poly(ethylene-co-vinyl acetate) (EVA) encapsulants, remains to be experimentally validated. Determining the degradation and crosslinking kinetics of alternative encapsulants, such as polyolefin elastomer (POE) and EVA/POE/EVA composites (EPE), can further generalize the model. Importantly, the activation energy for crosslinking of fully cured PV encapsulant products from temperature or UV is presently unknown or unavailable. In this work, we subject EVA, POE, and EPE encapsulants to a set of accelerated aging conditions, varying the temperature, UV intensity, and relative humidity. We use DSC, FTIR, and Soxhlet extraction (gel content) to characterize the encapsulants' changing molecular structure. This allows for determination of the photochemical degradation and crosslinking kinetics of the encapsulants. Preliminary results show an increase in gel content (crosslinking) and a decrease in crystallinity of EVA, POE, and EPE encapsulants under hot-aerobic (90°C, 22% RH) and hot-anaerobic (90°C, sealed in N₂ air) accelerated aging, even in the absence of UV and crosslinking initiating agents. For a least squares regression with an assumed first-order crosslinking kinetics, the crosslinking rate parameters were computed for the three encapsulants under hot-aerobic and hot-anaerobic aging conditions. FTIR analysis showed insignificant encapsulant degradation for hot-aerobic and hot-anaerobic aging, demonstrating the critical role of UV and moisture in accelerating degradation. Aging conditions with UV exposure and elevated humidity are presently in progress.

I. INTRODUCTION

Solar photovoltaic (PV) modules undergo harsh conditions during field operation including UV exposure, extreme temperatures, and humidity stress. This leads to encapsulant degradation and loss of adhesion at its interfaces with the adjacent silicon cell or glass, allowing a host of other damage modes including corrosion and potential induced degradation [1] – [3]. To extend module lifetimes beyond 30 years, it is important to understand the fundamental molecular degradation and crosslinking mechanisms occurring within the encapsulants and their kinetics under different field aging conditions.

Poly(ethylene-co-vinyl acetate) (EVA) is the most widely used PV encapsulant, accounting for most of the present market

share due to its low cost and adequate adhesion with the adjacent silicon cell and glass [4]. However, it undergoes undesired degradation reactions that produce acetic acid, which catalyzes hydrolytic depolymerization degradation at the EVA/cell and EVA/glass interfaces (Figure 1) [4]. Recently developed polyolefin elastomers (POE) and EVA/POE/EVA (EPE) composite encapsulants are gaining market share due to the increasing demands on module performance and lifetimes [3]. The connection between the degradation mechanisms and the loss of mechanical performance of these encapsulants is important to establish to prevent premature debonding. It has also long been postulated that additional crosslinking of encapsulants occur under field aging because of unreacted crosslinking initiators from incomplete curing [1], [5]. However, there is little information about the crosslinking behavior of encapsulants once the crosslinking initiators have been fully depleted. The kinetics of crosslinking from UV and thermally generated radicals remains an area to be explored.

An initial analytical model addressed EVA degradation reaction kinetics, such as deacetylation, β -scission, and hydrolysis (Figure 1), and connected it to the fracture resistance, G_c , of the EVA/cell and EVA/glass interface using simplified fracture mechanics [1]. We then subsequently improved the model by addressing important additional considerations including the continued molecular crosslinking that occurs under field conditions, the fundamental connection between encapsulant molecular structure and its mechanical- and fracture-properties, and a formal treatment of the plasticity contribution to G_c using finite element models [6]. However, this model is still limited because it utilizes approximate degradation and crosslinking kinetic rate parameters, k (Figure 1). Although the model is validated relative to Golden (Colorado), Phoenix (Arizona), and Miami (Florida), it is not generally applicable to other regions with drastically different environmental conditions. Therefore, understanding how environmental stressors (UV dose, temperature, relative humidity) influence the encapsulants' molecular degradation and crosslinking reaction kinetics is crucial in generalizing the model to any field aging condition for accurate prediction of debonding failures. There is little available information about the reactions and their kinetics occurring in field-aged encapsulants, especially rate dependence on UV weathering and encapsulant chemistry. Therefore, we use multiple

accelerated aging conditions, with varied environmental stressors, to determine the reaction rate parameters.

In this work, we utilized three different accelerated aging conditions to investigate the effects of temperature, UV, and moisture/oxygen on the competing bond scission and crosslinking processes occurring in the bulk encapsulant. Hydrolytic depolymerization, an interfacial reaction, was the key subject of a recent study [4]. We used three different encapsulants (EVA, POE, EPE) here to investigate the role of encapsulant chemistry and structure on the reaction kinetics. We quantify how the encapsulant chemistry and the exposure environment (open-air vs. N₂ sealed in a test tube) affect the rate parameters of thermal-induced crosslinking.

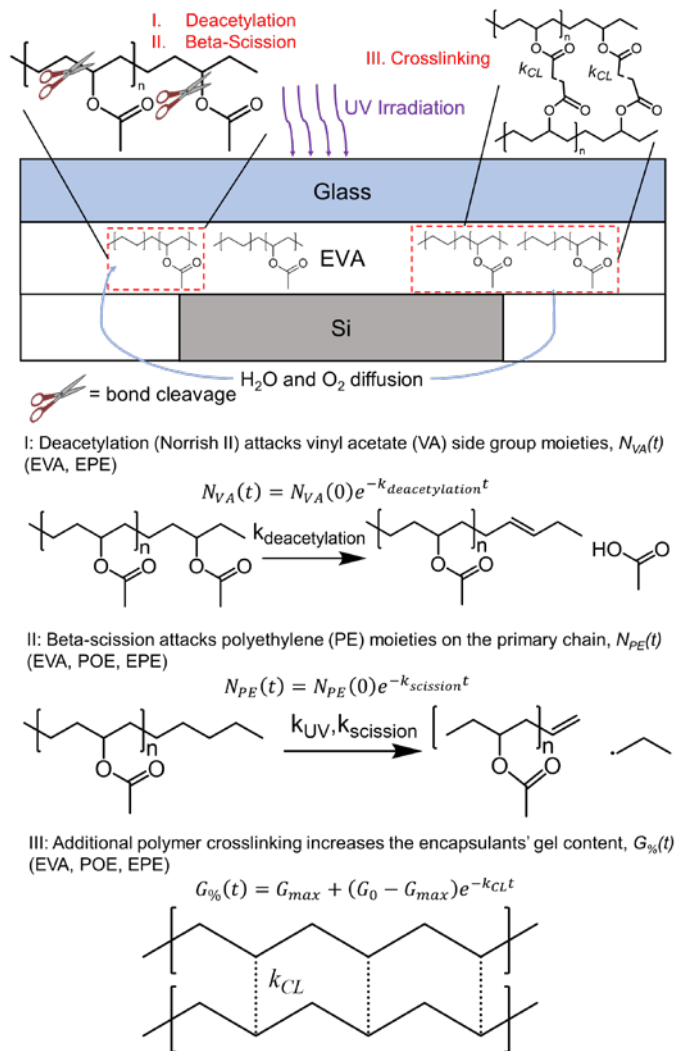


Figure 1. Degradation and crosslinking reactions that occur in the encapsulant and its interfaces, adopted from Liu et al. [6]. First-order reaction kinetics are assumed for rate parameter (k) determination.

II. EXPERIMENTAL DETAILS

A. Accelerated Aging of Encapsulants

In this work, we utilized four different accelerated aging conditions for a period of 30 weeks: 1) 90°C, 22% RH, with no UV, a hot-aerobic aging condition similar to MST 37 in IEC 61730-2; 2) 90°C, inert air sealed, no UV; and 3) 90°C, 20% RH, 0.8 W/(m²-nm) at 340 nm Xenon lamp (Ci5000 Weather-Ometer, Atlas Material Testing Technology LLC), the IEC TS 62788-7-2 method A5; and 4) 65°C, inert air sealed, no UV to allow for the activation energy of thermal degradation to be determined. The aging conditions will be referred to as hot-aerobic, hot-anaerobic, A5, and temperate-anaerobic, respectively. The conditions were chosen to investigate the effects of temperature, UV, moisture, and oxygen on the crosslinking and degradation reaction rate parameters, k , of three encapsulants formulated with polymer resins: EVA, POE, and EPE obtained from a commercial source. The encapsulants were cured at 145°C for 45 minutes 5x the nominal cure duration) to ensure that the crosslinking initiators (peroxides, silanes, or others) are fully reacted prior to accelerated aging. These samples are described as “5x cured” in subsequent discussion. The absence of residual crosslinking initiators in the encapsulants was confirmed with differential scanning calorimetry with a heating ramp, which showed no curing exothermic peak between 100°C to 220°C. Hot-aerobic and hot-anaerobic aging have been completed at this time.

B. Soxhlet Extraction (Gel Content)

Soxhlet extraction were performed to determine the encapsulants' gel content, $G_{\%}$, with aging time. Highly crosslinked polymers tend to incorporate chains in a gel network, that is insoluble [7]. Lightly crosslinked or uncrosslinked chains are soluble and can be dissolved into solution [7]. Gel content is the percent mass fraction that is insoluble and is linearly correlated with the degree of cure [7]. We follow the established IEC 62788-1-6 standard for determining the $G_{\%}$ [8]. A cellulose thimble was first dried at 110°C for 2 hours and then weighed (m_i). Approximately 1 gram of encapsulant material (m_i) was put into the cellulose thimble and then refluxed in mixed xylenes solvent for approximately 200 cycles (8 to 10 hours of extraction time) to ensure complete extraction of the soluble portions of the encapsulant. The encapsulant and thimble were vacuum dried at 115°C for 4 hours and weighed (m_f). $G_{\%}$ is computed as:

$$G_{\%} = \frac{m_f - m_t}{m_i} \quad (1)$$

C. Differential Scanning Calorimetry (DSC)

DSC (TA Instrument Q2000) was used to investigate crosslinking initiator concentrations for uncured and “5x cured” encapsulants. A heating ramp from 40°C to 295°C at a rate of 10°C per minute was used. Curing exothermic peaks (if present) were integrated in the TRIOS software using a linear baseline.

For investigating changes in the degree of crystallinity (χ_c) of the encapsulants over time, the following conditions were used: 2 heating cycles and 1 cooling cycle from 0°C to 120°C at a rate

of 10°C per minute, then cool at 20°C per minute from 120°C down to -85°C. The enthalpy of fusion, ΔH_f , is computed by integrating the area under the endothermic peak of the first heating cycle between 35°C to 75°C for EVA, 35°C to 80°C for POE, and 35°C to 80°C for EPE with a sigmoidal baseline in TRIOS. The first heating cycle was chosen to compute crystallinity to not erase the materials' unique exposure history. χ_c is then computed by normalizing ΔH_f against ΔH_f^{PE} , the enthalpy of fusion of fully crystalline polyethylene (290 J/g), following previous work [1], [4]:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^{PE}} \quad (2)$$

D. FTIR-ATR

Fourier transform infrared spectroscopy (FTIR, Nicolet iS50 Spectrometer) in attenuated total reflectance (ATR) mode was used to investigate the absorbance of characteristic bonds that could change with bond scission or the production of degradation species. Sample IR spectra were averaged over 64 scans at a resolution of 0.241 cm^{-1} data spacing. Scans were taken on both sides of encapsulants aged through different durations. Spectrum baselining was done manually with 12 linearly-interpolated points. Increases in absorption of certain peaks indicative of polymer thermo-oxidative and photo-oxidative degradation has been identified in previous studies of EVA and polyethylene (polyolefin elastomers are polyethylene-based encapsulants), which are useful for subsequent analysis [9], [10].

E. Reaction Kinetics Fitting

Following previous work, we adopt simplified first-order reaction kinetics to determine k with the following equation: $G_{\%}(t) = G_{max} + (G_{initial} - G_{max})e^{-k_{CL}t}$ [6]. $G_{initial}$ was determined experimentally using Soxhlet extraction on unaged encapsulants, and G_{max} was set to the maximum value measured over the course of the aging experiment. The rate parameter k_{CL} was then determined for the encapsulants at different aging conditions from a least-squares fit to the gel content data using the *fit* function in MATLAB. The degradation kinetics, if observable in FTIR-ATR, would be fitted to absorbance values at characteristic peaks with the same approach.

III. RESULTS AND DISCUSSION

A. Crosslinking Behavior Under Thermal Aging

DSC heating profiles were used to determine whether crosslinking initiators were present in encapsulants after lamination at 145°C for 45 minutes (5x cured), with representative curves shown in Figure 2 for uncured and 5x cured encapsulants. With the uncured encapsulants, an exothermic peak was observed between 100°C and 175°C. The enthalpy (for the integrated exothermic peak areas) for uncured

EVA, POE, and EPE were 12.6 ± 1.3 J/g, 6.7 ± 1.6 J/g, and 11.3 ± 1.7 J/g, respectively. This revealed the presence of crosslinking initiators in the uncured encapsulants which react between 100°C and 175°C. For the 5x cured encapsulants, there were no exothermic curing peaks, indicating that the crosslinking initiators were fully reacted during the lamination process. The uncured EVA and EPE exothermic peak areas were larger than that of the uncured POE. This may be due to higher densities of crosslinking initiators in the encapsulants or that the crosslinking process was more efficient in the EVA and EPE. This could also explain why the EVA and EPE had higher initial gel contents when compared with POE in Figure 3.

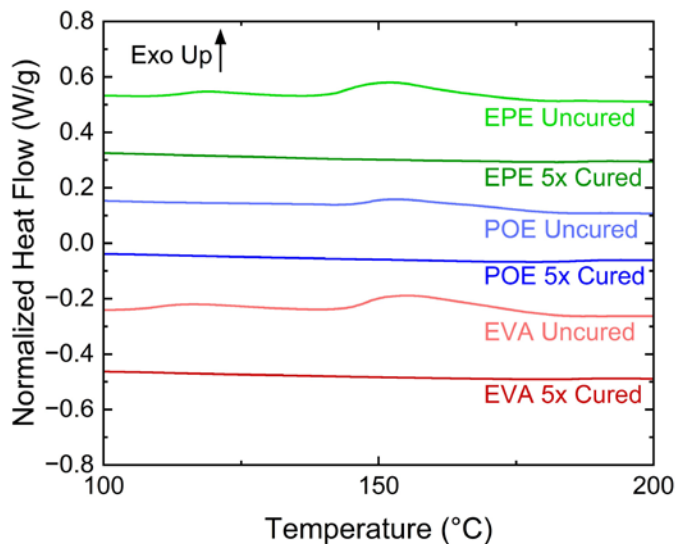


Figure 2: DSC profiles of unaged, 5x cured encapsulants showed no exothermic curing peak between 100°C and 200°C, while the profiles of unaged, uncured encapsulants showed crosslinking exotherms.

Decreases in the degree of crystallinity, χ_c , and increases in the gel content, $G_{\%}$, of all three encapsulants (5x cured) were observed over 30 weeks of hot-aerobic and hot-anaerobic aging, despite the prior depletion of the crosslinking initiators (Figure 3). χ_c decreased by ~15% to ~25% of its initial value for all three encapsulants between 0 to 700 hours, with little change after 700 hours. There were small increases in the degree of crystallinity for EVA and POE after 2350 hours (14 weeks) of thermal aging. However, these increases were sporadic and may be due to systematic error in the DSC measurement technique. Furthermore, the degree of crystallinity for the aged encapsulants never exceeded that of the unaged encapsulants. The gel content of the encapsulants all increased over time to a plateau value: EVA from 82.5% to ~90%, POE from 78.9% to ~83%, and EPE from 86.9% to ~91% for both hot-aerobic and hot-anaerobic conditions. The final gel content values did not depend on the aging condition. However, there was an observable difference in the rate of increase between the two aging conditions, most notably for EVA.

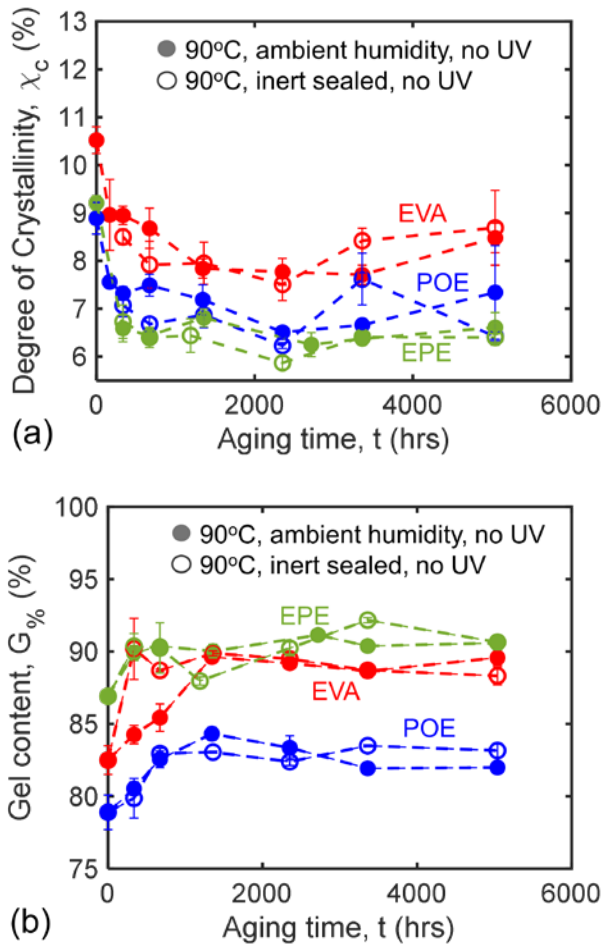


Figure 3. (a) Degree of crystallinity and (b) gel content data over cumulative time for EVA, POE, and EPE encapsulants through thermal accelerated aging.

The results in Figure 3 revealed a thermally-activated crosslinking reaction mechanism that may also occur in fielded PV modules, even in the absence of UV, high humidity, and crosslinking initiators. The initial decrease in the degree of crystallinity could be explained by an increase in the degree of crosslinking during thermal aging, forming branches that covalently link polymer chains. These branches prevent polymer chains from packing into a regular, crystalline array when the encapsulants are taken out of the aging chambers and cooled from 90°C to room temperature [7]. This was corroborated by the $G_{\%}$ data, which showed an increase in the first 700 hours of aging and a subsequent plateau after 700 hours. An increase in the encapsulant's degree of crosslinking affects its mechanical and thermal properties such as the storage modulus, degree of crystallinity, glass transition temperature, and fracture toughness [11], [12]. For example, the encapsulants' lower degree of crystallinity could decrease its storage modulus from loss of closely packed crystalline content. These changes may lead to a loss in interfacial delamination resistance, shown in previous studies [1].

Figure 4 shows an example of fits to the EVA gel content data. Table 1 shows the fitted crosslinking rate parameters. The temperate-anaerobic (65°C, inert air, no UV) test condition will be used to verify the activation energy for crosslinking and the lack of observed thermal degradation (see subsection B).

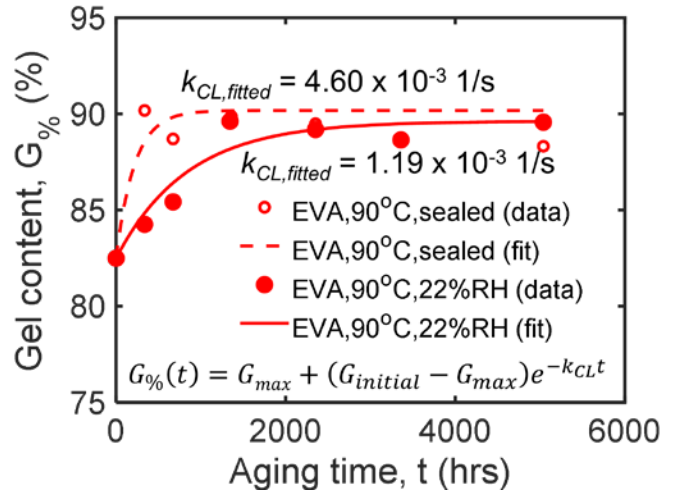


Figure 4. Crosslinking kinetics fitting for EVA encapsulant aged under hot-aerobic and hot-anaerobic conditions. For EVA, thermally activated crosslinking occurs faster under hot-anaerobic than hot-aerobic conditions. The same fitting procedure was performed for the POE and EPE encapsulants.

TABLE I.
SUMMARY OF COMPUTED CROSSLINKING RATE PARAMETERS

Encapsulant	Hot-aerobic k_{CL} , (hr^{-1})	Hot-anaerobic k_{CL} , (hr^{-1})
EVA	1.19×10^{-3}	4.60×10^{-3}
POE	1.02×10^{-3}	1.52×10^{-3}
EPE	1.86×10^{-3}	4.87×10^{-4}

For EVA and POE, the computed crosslinking rate parameters were higher in hot-anaerobic compared with hot-aerobic conditions. For EPE, the rate parameter was higher in hot-aerobic conditions. This suggests that the aging environment dictates the encapsulants' crosslinking behavior. Moisture and oxygen (as in the aerobic periphery of a cell in a PV module) may play a role in slowing down crosslinking in EVA and POE. This phenomenon has been observed in previous studies where the encapsulant's measured gel content is higher at locations closer to the center of an uncut cell (anaerobic environment) compared to the gel content measured from the aerobic periphery [13]-[15]. EVA's crosslinking rate parameters were higher than those of POE in both hot-aerobic and hot-anaerobic conditions. This may be because the hydrogen on the tertiary carbon (attached to vinyl acetate side groups) are more easily abstracted by thermally-generated free radicals, enabling the crosslinking step between two polymer chains [16], [17]. The hydrogens on the polyethylene backbones of the polyolefin are not as easy to abstract and would slow the crosslinking reaction relative to EVA.

B. Degradation Behavior Under Thermal Aging

In previous studies of encapsulants aged with UV, increases in peak intensities at 1600 cm^{-1} , 1718 cm^{-1} , and 3500 cm^{-1} were observed, indicating formation of degradation products such as polyenes and acetic acid [18], [19]. FTIR-ATR scans were taken on encapsulants on both sides at 0, 2, 4, 8, 14, 20, and 30 weeks of aging to characterize the encapsulants' chemistry and check for degradation products (Figure 5a to 5f). Through 30 weeks of 90°C aging, the encapsulants' chemical structure remained the same as the unaged encapsulants. Additionally, when analyzing the 3500 cm^{-1} region more closely (Figure 5g), no quantifiable hydroxyl byproducts moieties were detected. Figure 5f shows that there were some absorbance peaks detected between 1500 cm^{-1} and 1600 cm^{-1} . However, these peaks were relatively small, and do not vary with thermal aging time. Therefore, they are not indicative of encapsulant molecular changes nor degradation product formation.

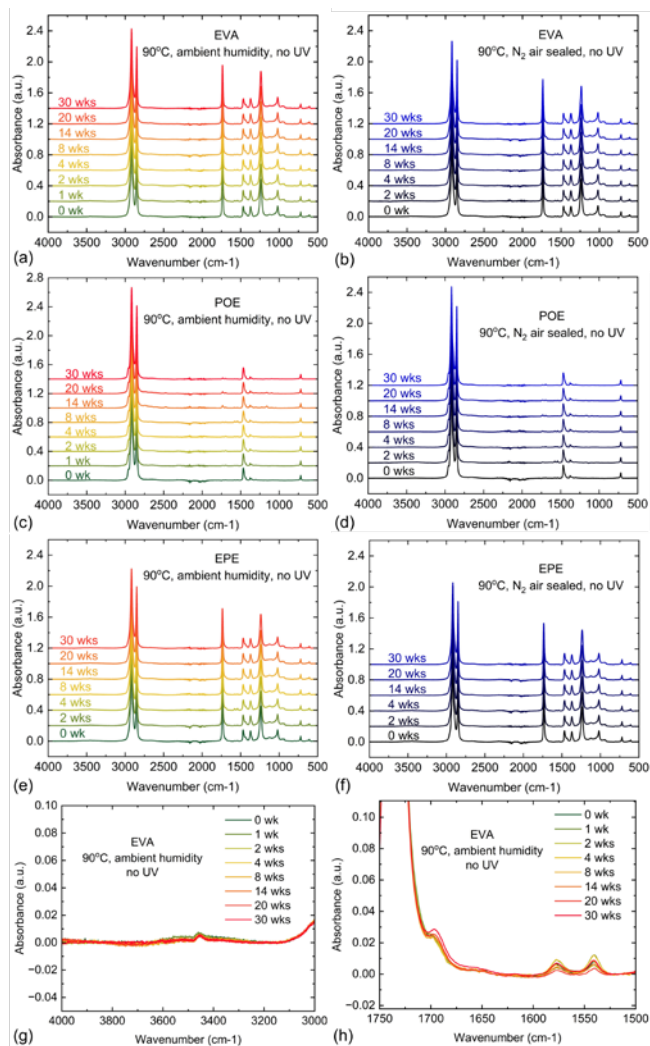


Figure 5. (a)-(f) FTIR of EVA, POE, EPE encapsulants under hot-aerobic (left) and hot-anaerobic (right) conditions. No new peaks nor differences in intensity are observed that would indicate changes in the polymer structure. Analysis of the (g) 3500 cm^{-1} region and (h) 1500 cm^{-1} to 1750 cm^{-1} region for EVA under hot-aerobic aging.

Under hot-aerobic and hot-anaerobic aging conditions, which only have thermal stresses, the encapsulants crosslinked further but did not degrade via deacetylation or scission. The lack of observed degradation without UV matches well with a previous study which measured the G_c of laminated coupons (glass/encapsulant/Si-cell) under “light” (65°C , 30% RH, 340-nm UV light) vs. “dark” (85°C , 13.5% RH, no UV) conditions for 10,000 hours [20]. Degradation was significant under the “light” condition, characterized by a drop in G_c , but remained stable under “dark” condition. Since 1000 hours of aging at 90°C corresponds to about 25 years of indoor (no UV) thermal aging in Miami, Florida, the 5000 hours of hot-aerobic and hot-anaerobic aging corresponds to ~ 125 years of indoor aging, much longer than the normal 25 years operating lifetime of a module [21]. It is postulated that the activation energy barriers of deacetylation and main-chain scission are lowered significantly in the presence of UV and moisture.

IV. OUTLOOK AND CONCLUSION

Understanding the location-specific crosslinking, chain scission, and other reactions within the encapsulants and how environmental stressors influence their reaction rates is increasingly important as the industry seeks to improve module lifetimes to 50 years. Much work has been done in connecting the polymer molecular structure with the encapsulants' mechanical properties. However, the reaction kinetics remains to be understood, especially the activation energy of crosslinking of the polymer from UV weathering in addition to the degradation of the siloxane adhesion promoter at the PV encapsulant interface during hygrometric aging. In this work, we have provided fitted crosslinking rate parameters, k_{CL} , for EVA, POE, and EPE encapsulants aged under hot-aerobic and hot-anaerobic conditions, which impart elevated thermal stresses. The encapsulants' gel content, measured by Soxhlet extraction, increased during the first 700 hours of thermal aging at 90°C , followed by a plateau. The increase in molecular crosslinking led to decreases in the degree of crystallinity. FTIR-ATR analysis confirmed that degradation reactions are not significant at 90°C aging even after durations greater than 5000 hours in the absence of UV and elevated humidity.

Upcoming work will use modulated thermogravimetric analysis (TGA) to investigate the temperatures and activation energies of thermal decomposition. TGA will also be used to estimate the weight fraction of vinyl acetate in the commercial EVA and EPE. Dynamic mechanical analysis (DMA) will be used to measure the storage and loss moduli of unaged and 30 weeks aged encapsulants. Aging of laminated cell/encapsulant/glass adhesion coupons will also be conducted to investigate the moisture-driven degradation of the siloxane bonds at the encapsulant/cell and encapsulant/glass interfaces.

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