



Examination of a Standardized Test for Evaluating the Degree of Cure of EVA Encapsulation

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ABSTRACT

The curing of cross-linkable encapsulation is a critical consideration for photovoltaic modules manufactured using a lamination process. Concerns related to ethylene-co-vinyl acetate (EVA) include the quality (*e.g.*, expiration and uniformity) of the films or completion (duration) of the cross-linking of the EVA within a laminator. Because these issues are important to both EVA and module manufacturers, an international standard has recently been proposed by the Encapsulation Task-Group within the Working Group 2 of the International Electrotechnical Commission Technical Committee 82 for the quantification of the degree of cure for EVA encapsulation. The present draft of the standard calls for the use of differential scanning calorimetry (DSC) as the rapid, enabling secondary (test) method. Both the residual enthalpy- and melt/freeze-DSC methods are identified. The DSC methods are calibrated

against the gel content test, which is the primary (reference) method. Aspects of other established methods, including indentation and rotor cure metering, were considered by the group. Key details of the test procedure will be described.

1. INTRODUCTION

The majority of today's photovoltaic (PV) modules use cross-linkable ethylene-co-vinyl acetate (EVA) to encapsulate the cells. Formulated EVA is chemically cross-linked to fix its location so that it may protect PV cells from the mechanical and physico-chemical stresses encountered in the field. Even early in the development of PV technology, the peroxide-facilitated curing of EVA was identified as application critical.^[1] The motivations to control the curing of EVA also include proper activation of the primer(s) to establish good adhesion as well as the establishment of the molecular structure for good optical transmittance (reduced haze). The curing of EVA

is often considered by manufacturers concerned with the module qualification protocol, including the “damp heat” test. However, the final extent of the cross-linking that occurs with aging in the field may not be as important as originally believed.^[2] The material manufacturing issues of adequate content of additives, including the crosslinking initiators (peroxides), and shelf life apply to EVA, because these additives will tend to volatilize or decompose over time. The time and temperature conditions applied during lamination greatly affect EVA, including module performance with time in the field. On the other hand, the cost of lamination during module manufacturing motivates using minimal time and temperature for the lamination process. Based on the needs of EVA and module manufacturers, many methods to evaluate the curing of EVA have emerged in the literature.

2. METHODS OF EXAMINATION

The use of differential scanning calorimetry (DSC) to evaluate curing of EVA based on the enthalpy of the peroxide-triggered reaction has been proposed.^[3] Figure 1 shows the heat-flow profile for a partially cured test specimen, relative to an uncured specimen composed of the same formulation. An offset has been provided for the reference specimen so that it may be compared to the test specimen. The exothermic cross-linking reaction is evident at 155°C in the profile of the reference specimen. As in ASTM E2160^[4], the “degree of cure,” G_e {unitless}, can be defined as the relative ratio of enthalpies, h {J·g⁻¹}, for the given temperature interval, T {°C} (shown in Figure 1 for 100°C ≤ T ≤ 200°C), in Equation 1:

$$G_e = 100 \frac{(h_u - h_t)}{h_u} \quad (1)$$

The results of the DSC residual enthalpy method do depend on the EVA formulation, *e.g.*, the type and concentration of peroxide used.

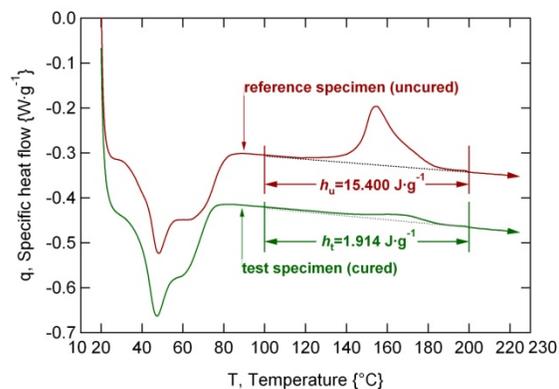


Figure 1: Heat-flow profile (obtained by DSC at 10°C·min⁻¹) for a partially cured test specimen, shown relative to an uncured specimen composed of the same EVA.

As shown in Figure 2, the temperature and shape of the freezing transition (crystallization) intrinsically vary with the molecular structure (cross-linking) of the EVA. Therefore, the degree of cure can be determined based on the average of the (maximum) crystallization temperature, T_c {°C}, the onset crystallization temperature, T_o {°C}, and the concavity (shape factor, SF , examined to 20°C below T_c).^[5] This is accomplished by first heating the specimen (*e.g.*, to 100°C, so that it is melted) and then cooling the specimen (*e.g.*, to -20°C, so that it is frozen in its rubbery state).^[5] As with the DSC residual enthalpy method, a minimal specimen size (5–9 mg) is required for the DSC melt/freeze method. Also like the DSC residual enthalpy method, the results will vary with the EVA formulation, including its concentration of vinyl acetate.

Additional methods that may be used to assess curing include gel content, rheometry, indentation, and rotor cure metering. The gel-content test is a solubility test, where the insoluble cross-linked gel remains in a solvent, *e.g.*, tetrahydrofuran (THF), toluene, or xylene (mixed isomers, CAS 1330-20-7). Rheometry (including dynamic mechanical analysis, DMA)

may also be used as a primary method, because the specimen modulus depends on the cross-link density.^[6] Micro-indentation may be applied for non-destructive in-line assessment of the curing of modules with a backsheets.^[7] A rotor cure meter requires a larger sample size but might also be used to assess a laminator or its settings.^[8] A recent comparative study examined tensile testing, ultraviolet-visible (UV-Vis) spectroscopy (including optical haze), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, laser Doppler vibrometry, laser scanning vibrometry, and scanning acoustic microscopy.^[9] All these methods may be used to assess EVA used in the PV industry, which typically has 28%–33% vinyl acetate content (VAc). However, many of the aforementioned methods do not quantify the network formed during cross-linking, *e.g.*, the bond density and intermolecular connectivity.

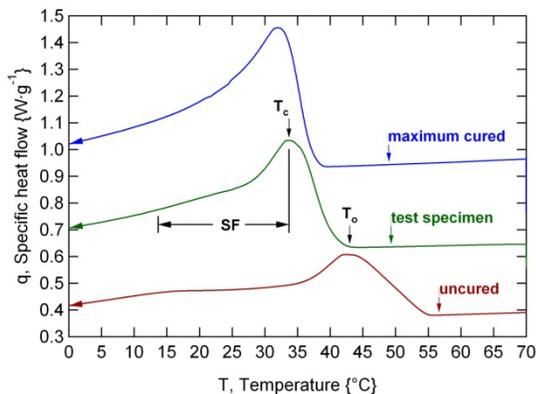


Figure 2: Cooling profiles for an EVA specimen obtained by DSC at $10^{\circ}\text{C}\cdot\text{min}^{-1}$, relative to samples of the same formulation with no thermal history (“uncured”) or that are extensively (“maximum”) cured. An offset has been provided so that the specimens may be compared.

3. DISCUSSION

3.1 APPROACH FOR THE STANDARD

The Encapsulation Task-Group within the Working Group 2 of the International

Electrotechnical Commission Technical Committee 82 proposed that the degree of cure standard include a more thorough primary method that may be used to refer between EVAs (including different formulations, grades, suppliers, and fabrication lots), and a secondary method that may be rapidly implemented in a manufacturing environment. Although a rheometry method directly examining the mechanical characteristics of interest would be preferred, it requires expensive or patented test equipment. Therefore, the gel-content test was chosen based on its widespread, historic application in PV. Although other techniques could also be used as valid secondary methods, the Task Group chose to focus on the DSC-enabled methods. Because the secondary methods do not provide universal results, they must be calibrated by comparing the results of the primary and secondary methods. For example, adequate degree of cure for a particular lamination machine might be assessed directly from DSC measurements after a correlation between the gel-content test and DSC method(s) have been performed over a range of processing times.

3.2 DETAILS OF THE STANDARD

Certain details of the primary and secondary methods are critical to the standardization of a test for the degree of cure. For example, toluene solvent and glass jar containers are used at Springborn Laboratories (now STR Inc.). However, the use of xylene solvent and a flask/reflux condenser (or Soxhlet extractor) was common in a survey of EVA and PV module manufacturers. A key requirement for the gel-content test is that the temperatures and time durations used must not inadvertently cure the test specimen. An antioxidant should be added to the solvent and thimble to help prevent

decomposition of the specimen and prevent curing during solvent immersion.

Regarding the DSC methods, using a specific specimen mass improves test standardization. The specimen mass must be adequately small to limit the maximum heat flow, *e.g.*, <8 mW, thereby preventing adiabatic heating of the sample, resulting in “leaning” data profiles.^[4] The small sample volume inherent to DSC instruments allows the heterogeneity of the peroxide concentration to be assessed within a roll of EVA.^[10] It remains to be established whether the typical variation in peroxide concentration exceeds the repeatability and reproducibility of the DSC methods.

The maximum temperature used for the secondary DSC methods must not exceed the limitations of the test material. For EVA, loss of the formulation additives may begin to occur above ~200°C, with thermal decomposition by deacetylation above ~250°C, followed by thermal decomposition of the polymer backbone above ~400°C.^[11] The behavior of EVA at high temperature is also relevant to the bounds of integration used for the DSC residual enthalpy method.

Another concern for the test is the loss of additives, *i.e.*, peroxide and primer, that occurs when EVA is stored. Although the primer is often the most volatile component, substantial (*i.e.*, ≥50%) loss of the peroxide can occur within days. To prevent evaporative loss and undue reaction, EVA should be stored in a dark, cool environment within proper packaging, *e.g.*, an aluminized bag.

4. CONCLUSIONS

Many valid techniques have been used to examine the degree of cure for EVA encapsulation, including indentation, rheometry, FTIR spectroscopy, Raman spectroscopy, and vibrometry. The Encapsulation Task-Group is

developing a standardized procedure using the gel-content test as the primary (reference) method and DSC as the secondary (test) method. A round-robin experiment will follow to elucidate the details of the procedure, including its repeatability and reproducibility. The round-robin will examine the gel-content and DSC methods, and will benefit from the results of additional methods, *e.g.*, rotor cure metering, applied to the same test materials.

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