

Towards in-line determination of EVA Gel Content during PV modules Lamination Processes

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ABSTRACT: Poly (ethylene-co-vinyl acetate) (EVA) is the major polymer used for photovoltaic (PV) modules encapsulation. Its degree of cross-linking (related to its gel content) is taken as a major quality reference. Differential Scanning Calorimetry (DSC) has been proven to be fast and effective but is to determine the gel content, however, destructive for the PV module. With the aim to develop a non-destructive quality assessment tool, a detailed discussion on the DSC thermogram of EVA PV encapsulant is presented here. A possible path towards a fast and non-destructive method for determining EVA gel content is proposed based on the DSC analysis.

Keywords: PV Module, Encapsulation, Qualification and Testing, EVA, Gel Content

1 INTRODUCTION

In outdoor application, the solar cell faces various natural stresses [1, 2, 3]. Thus, to realize the guaranteed 25-years module life time, fast, reliable and preferably non-destructive quality control method are in high demand. Nowadays the main parameters for the quality control of the PV modules after production are sun simulation tests (electrical output) and EVA gel content determination. Poly (ethylene-co-vinyl acetate) (EVA) is the most widely used PV encapsulant, taking nearly 80% part of the market [4]. In practice, the commercial EVA encapsulants are typically formulated with additives such as curing agent (CA), UV stabilizer, antioxidant and adhesion promoter [5, 6]. During the encapsulation process, the EVA is cured to the desired gel content (typically 80%) [7]. EVA gel content determination is considered important for the PV modules quality control. The determination of the EVA cross-link density using a solvent-extraction method (Soxhlet) usually exceeds 24 hours [8]. Differential scanning calorimetry (DSC) has been introduced to reduce this time to 30-60 minutes [9]. The conventional DSC method measures the remaining amount of curing agent present in the EVA after encapsulation and a calibration curve is used to provide the relation between the DSC and the Soxhlet measurements. Recently, Dynamical-Mechanical Analysis (DMA) was proposed as a fast tool for EVA gel content determination [10]. Even though the DSC and DMA methods allow a significant faster determination time as compared to the Soxhlet method, they are still both destructive meaning that some EVA has to be taken out of a broken module in order to perform the gel content test.

The destructive nature makes it impossible to check the EVA gel content inside every module produced, although it is desired. Therefore, for that purpose, a both fast and non-destructive method has to be developed. Here, we report our progress towards such a method by understanding the DSC thermograms of EVA. Our aim is to identify any curing-time dependent quantities that could possibly be detected by a fast and non-destructive way. Once this is accomplished, it will significantly contribute to the process quality control that is needed in the future PV modules production lines.

2 EXPERIMENTAL SET-UP

2.1 Lamination process

A commercially available EVA grade was tested [11]. The lamination and thus the curing of EVA were performed in a controlled manner in a flat-bed laminator (3S S1815). The plate temperature was set at 140°C. After a preheating step on pins, the pins were removed and a 1-bar pressure was immediately applied on the laminates. The counting of the curing time started from this moment. The curing process undergoes in the vacuum of about 1mbar. After a set curing time (from 0s to 1300s), the pressure was removed and the cooling process started [7].

2.2 Gel content determination

For the EVA cured for different times, the gel contents were measured by a solvent extraction method (soxhlet). The process was performed according to ASTM D 2765 [8]. The cured EVA about 1g is weighted (m_0) and cut into pieces. The 6 h soxhlet extraction was done at 110 °C using toluene as solvent. After the extraction, the EVA was dried till the weight reached constant (m_1) at 80 °C. The gel content was calculated as the ratio of the final weight to the initial weight ($100\% \cdot m_1/m_0$).

2.3 Differential Scanning Calorimetry (DSC)

EVA samples were analyzed using two DSC setups: Mettler Toledo DSC1 and TA instruments Q100. Thermograms were recorded under a Nitrogen flow from -100 to 200 °C at a heating rate of 15 K min⁻¹, unless otherwise mentioned. The DSC sample was prepared as a circular disc weighted about 5mg in a crucible. The temperature-modulated (TM) DSC was performed on a TA Q100 at a lower heating rate of 5 K min⁻¹.

3 DSC ANALYSIS

A characteristic DSC thermogram of the EVA PV encapsulant under study is shown in Fig.1. Within the

temperature range from -50 to 200 °C, several phase transitions are evidenced. First, a broad transition is observed above approximately -30 °C, which is known to be the glass transition of EVA [12]. As the PV modules are rated for use at the temperature as low as -40 °C in qualification tests like UL 1703, the relatively high T_g is listed as one major drawback of EVA as PV encapsulants [13]. The other three transitions are analyzed in details in the following paragraphs.

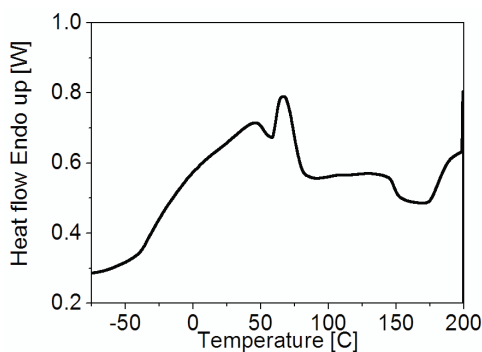


Figure 1: Typical DSC thermogram of EVA [14]. The glass transition appears at ~ -30 °C; The overlapped endothermic peaks centered at about 45 and 60 °C respectively correspond to different melting transitions; The broad exothermic peak from 110 to 190 °C corresponds to the thermal decomposition of the peroxide and subsequent curing of EVA.

3.1 The exothermic curing peak

In Fig.1, the broad exothermal peak starting from app. 110 °C is directly related to the curing process of the EVA [15]. Currently, its enthalpy has been widely used to fast determine the EVA gel content in the industry. With this method, this enthalpy is assumed to be proportional to the amount of residual peroxide in the EVA [9]. It then can be indirectly related to the peroxide consumed in the EVA crosslinking reaction. Thus it is related to the EVA gel content as well.

To confirm the DSC method, a number of EVA samples were prepared with various curing time and both their gel content and their dissociation heat were measured. As shown in fig. 2, the results confirmed that there is a quantitative correlation between the EVA gel content and the dissociation heat measured by DSC. All the EVA samples with a dissociation heat below 10 J/g have a gel contents above 80%. Scattered data may be due to a loss of peroxides (in the form of volatiles) during the preparation of the EVA film.

3.2 The two overlapped endothermic peaks

As shown in fig 1, from 40 °C to 70 °C, two overlapped endothermic peaks are frequently observed in the DSC thermograms of EVA. Peak 2 at app. 55 to 65 °C is widely agreed to be the melting peak of the ethylene segment, while the origin of peak 1 centered at about 45 °C remains to be clarified [16].

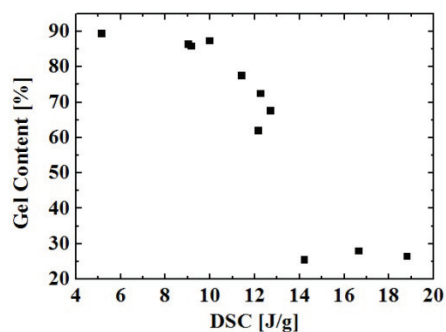


Figure 2: Correlation between the EVA gel content and the corresponding heat of dissociation (HD) measured by DSC.

To study these two overlapped peaks, identical DSC measurements were run on the same EVA sample twice consecutively. After the first cycle, the EVA sample was cooled at a controlled rate of 20 °C min^{-1} . The result is shown in Fig. 3a. One spectacular change is the diminution of the 1st peak. It clearly suggests that the presence of this peak is related to the thermal history of the sample. Similar observation was reported previously for ethylene acrylic acid copolymer [17]. In the mentioned work, the origin of this peak was attributed to the melting of less ordered crystalline phase formed in between the primary crystals during ambient storage or slows cooling. For the 2nd peak, it is well present and centered at almost identical temperature in both measurements. The results presented here fit the idea that the 2nd peak corresponds to the melting transition of the primary crystals in EVA.

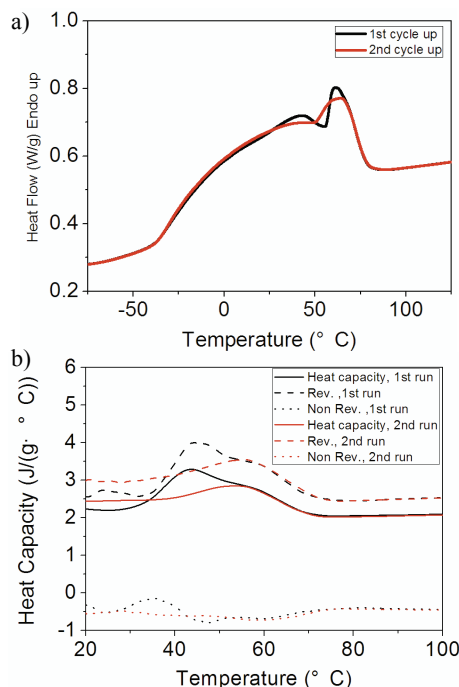


Figure 3. a: DSC thermograms on one EVA sample in two consecutive runs. (With endo up) **b:** Temperature-Modulated DSC(TM-DSC) on the EVA encapsulant. The dash and dotted lines represent the reversible and non-reversible processes respectively.

To gain more understandings on the 1st peak, TM-DSC was performed on a cured EVA sample for the

temperature range of -100 to 180°C at heating rate of 5 °C min⁻¹. The TM-DSC can separate the reversible and non-reversible transition processes in one single scan [18]. As seen in fig.3b, the double peaks between 40 and 60°C are actually composed of three processes, two reversible and one non-reversible. The two reversible processes probably correspond to the melting transition of the primary crystals and secondary crystals in the EVA respectively. The nature of the non-reversible endothermic process still remains unclear. However, in the 2nd measurement performed immediately after the 1st one, it disappeared together with the reversible process at about 45°C. This strongly suggests that both the processes are related to the storage.

The analysis above suggests that the origin of the endothermic peak at 40-50°C corresponds mainly to the melting transition of the secondary crystals formed in between the crystals in the EVA encapsulants during storage or slow cooling process.

4 CONCLUSION AND OUTLOOK

The conventional DSC method for determining EVA gel content using the broad exothermic curing peak is examined to be effective but with drawbacks of being destructive and inconvenient.

The origin of the 1st endothermic peak in the DSC of EVA is discussed and believed to be related to the thermal history of the EVA. Our results reconfirm that the 2nd endothermic peak corresponds to the melting transition of EVA.

It is known that the level of crosslinking will influence both the amount and the size of the crystals in the binary mixtures of PE and EVA [19]. Thus the same effect could be expected on EVA as well. In a next step, we will study the influence of the EVA curing time on the 2nd melting peak. If the change of EVA crystallinity due to the curing time is confirmed, the detection of such a change by a fast and non-destructive method will be investigated.

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