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Determining the degree of crosslinking of ethylene vinyl acetate photovoltaic module encapsulants—A comparative study ☆

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ABSTRACT

A total of 16 analytical methods, spanning from classical solvent extraction over different thermo-analytic and mechanical approaches to acoustic and optical spectroscopy, have been evaluated as to their ability to determine the crosslinking state of ethylene vinyl acetate (EVA), the prevailing encapsulant for photovoltaics applications. The key objective of this work was to create a systematic and comprehensive comparison, using a unified set of traceable test samples covering the full range of realistically occurring degrees of EVA crosslinking. A majority number of these tested methods proved fundamentally suitable for detecting changes in the polymer properties during crosslinking based on the effect e.g. its mechanical properties or its crystallinity. Interestingly, when investigated in detail, most of the methods showed mutually different dependencies on the lamination time, indicating a complex range of effects of the chemical crosslinking on the properties and behaviour of the material. Furthermore, Raman spectroscopy could be identified as a potential new method for measuring the degree of crosslinking in-line in the PV module manufacturing process, thus providing an interesting approach for improving process control in PV module processing.

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1. Introduction

With the rampant use of photovoltaic (PV) installations in both large-scale solar plants and house-top sites, increasing attention is given to their reliability and long-term performance over – expected – periods of use of up to 30 years. To be competitive in the market, PV module manufactures now (have to) warrant operational lifetimes of at least 20 years over which the total yield loss may not exceed 20% [1]. This resulted in a renewed interest in installing high-level quality assurance systems in PV module manufactories. Accordingly, a range of off-line and in-line control and analysis methods are being offered for examining both the single PV module components coming into and the assembled PV modules leaving the production line. While providing reliable information on the state of the modules directly after production, which is of both technical and commercial interest, very little information regarding the expectable long-term performance of the modules can be gained from this data [2].

When examining standard PV modules, one component known to be prone to aging, and hence likely to critically influence the long-term characteristics, is the solar cell encapsulant. Regardless of the chosen materials and the structural build-up of the PV module, the encapsulant has to fulfil several basic functions: firstly, it connects the components and provides structural support and mechanical protection to the solar cells, preventing over-stressing and cell cracking [3]. This includes dealing with the different thermal expansion of the various materials used in a PV module, i.e. glass, polymers, solar cells and interconnects [4]. Simultaneously, the encapsulant has to maintain electrical insula-tion and prevent the ingression of ambient media (humidity, etc.). Finally, it is essential to provide an optimal optical coupling (initial transmission≥90%) between the incident solar irradiation and the solar cells in the relevant spectral region. All these functions have

to be maintained over the entire operational lifetime of the module; for instance, the loss in light transmission deemed acceptable is less than 5% over 20 years [1]. Thus, the general characteristics of PV encapsulation materials are very similar: optically transparent, electrically insulating and soft but dimensionally stable, with good adhesion properties and lasting aging resistance—all at possibly low cost. While a range of materials have been described for this purpose, and new ideas and concepts are constantly being introduced, up to now the by far dominating encapsulation material for PV modules is crosslinked ethylene vinyl acetate (EVA).

EVA in general is a random copolymer of ethylene and vinyl acetate; for PV applications, the percentage of vinyl acetate is typically in the range 28–33% (w/w). Thermoplastic, with a melting range of 60–70 °C, mildly opaque, soft and easily plastically deformable, this native EVA material would fulfil neither the mechanical nor the optical requirements. However, by crosslinking the copolymer chains during module lamination, the mouldable EVA sheet is transformed into an elastomeric, highly transparent encapsulation. The underlying process is the formation of a loose 3-dimensional polymer network, thus increasing the mechanical and thermal stability of the then elastomeric material. Crosslinking EVA is only feasible via a radical reaction, using an organic peroxide or peroxycarboxylic acid as radical initiator ("crosslinker") [1]. Initially, this crosslinker is homolytically cleaved into two radical species, which then abstract hydrogen from the EVA chains, preferably from terminal methyl groups of the vinyl acetate sidechains. In this process, the active radical site is transferred to the methyl group, which then reacts with another active site in its vicinity, creating a chemical bond between the polymer chains and transforming the initially thermoplastic EVA into a "cured" three-dimensionally crosslinked elastomer [5]. In PV module manufacturing, this radical reaction is prevalently thermally activated, i.e. the homolytic cleavage is the result of a thermal decomposition ("thermolysis") of the radical crosslinker at typically ~150 °C during lamination. While the following crosslinking process comprises a myriad of possible radical reactions, many of which are unknown in detail, these are significantly faster than the initial homolytic thermolysis of the crosslinker. In combination with a vast excess of polymer over the amount of crosslinker present, this yields approximately (pseudo-)first order reaction kinetics of the crosslinking [6] with a rate constant controlled mainly by the cleavage reaction of the initiator. Assuming this reaction to follow the classical Arrhenius law equation, for a given radical initiator chemistry the lamination temperature is the only variable parameter affecting the rate of crosslinking. The degree of crosslinking is thus controlled by (i) the *lamination temperature* (affecting the amount of crosslinker activated per time unit), (ii) the *lamination time* and (iii) the initial *crosslinker concentration*.

This chemical assessment of the crosslinking reaction kinetics has been validated in practice. Lange et al. have shown that the degree of crosslinking is indeed strongly affected by both lamination time and lamination temperature [7]. However, while controlling these two parameters is a requisite for high-quality module production, it is still insufficient to warrant sustainably high product quality, in particular over several decades of operational lifetime. At the same time, studies of the long-term characteristics of elastomers and their change over time have shown that these are strongly influenced by the initial degree of crosslinking [1]. This renders the degree of crosslinking of the EVA encapsulant – or other elastomeric encapsulation materials for PV applications – a key control parameter for PV module production. Given the increasing degree of automation, PV manufacturers would hence be very much interested in a reliable method for measuring the degree of encapsulant crosslinking, preferably in-line and in-situ, for use in process development and optimisation as well as in quality control.

In strong contrast to these demands, the standard method to measure the degree of EVA crosslinking is a Soxhlet–type extraction process [8], which determines the amount of non-linked and hence soluble/leachable polymer. While comparatively simple in design and procedure, this method has some fundamental disadvantages: first, with typical test durations > 24 h, the method is clearly off-line and hence limited to method development and post-production quality control, but hardly applicable for real-time process control. Secondly, the method requires sampling of the crosslinked EVA, which is hard to come by from an assembled PV module. Thirdly, the method cannot differentiate between singly and multiply crosslinked polymer chains; this number of bonds formed, however, is likely to strongly influence the thermo-mechanical properties of the encapsulant, and hence its long-term performance in use.

To overcome these issues, a number of alternative analysis methods based on thermal or mechanical principles have been investigated [9–15,17], but none of them could be established in the PV industry up to now. One reason for this is that all these methods require sampling and are hence destructive, making it impossible to use them for quality control of assembled PV modules. A second reason is a lack of a systematic evaluation and comprehensive comparison of the different approaches for measuring the degree of crosslinking of EVA encapsulation materials. Hence, the key objective of this paper was to evaluate and compare the various possible methods using a unified set of traceable EVA test samples covering the full range of realistically occurring degrees of crosslinking in a PV-module. The results were evaluated against the established standard and also against each other. Additionally, the findings were interpreted with respect to applicable chemical and physical fundamentals. In a final step, the methods were assessed as to their ability to provide reliable indicators describing the degree of EVA crosslinking and their potentials for future industrial (in-line) application.

2. Materials and methods

2.1. Unified test substrates

To provide a reliable basis for the subsequent evaluation and comparison, EVA test samples varying only in the degree of crosslinking was produced in a standardised process. The experimental design followed the industrial practice of controlling the degree of crosslinking mainly via the lamination time while keeping the lamination temperature and the composition of the EVA foil constant. Hence, the degree of crosslinking was varied solely by changing the duration of the lamination process.

The EVA used for the tests was a standard PV encapsulation material (Vistasolar® 486, SolutiaSolar GmbH). The lamination process itself was carried out in a manual laminator following standard lamination procedures. First, the panel components, i.e. two 150×100 cm² solar glasses, each covered with a fluorinated separating foil (FEP500C, DuPont), and a single 450 μm EVA sheet in between, were stacked manually. The fluorinated sheets were added to prevent adhesion of the cured EVA to the glass and allow recovering the test samples. These stacks were then placed in the pre-heated laminator, the lamination chamber evacuated for 4 min to raw vacuum levels and the module stack shifted to the heating plate. Upon contact, the chamber was evacuated to the final fine vacuum (60 Pa), followed by applying a pressure of ~85 kPa to the stack via a pressure plate. At that step, the stack made full contact with the heating plate, thus initiating the EVA crosslinking and starting the clock on the *lamination time*. For the purpose of this study, the lamination time was systematically varied from 0 to 10 min (with 7–8 min being the industrial