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Contact-free determination of ethylene vinyl acetate crosslinking in PV modules with fluorescence emission

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Abstract

The degree of crosslinking of ethylene vinyl acetate (EVA) is a decisive factor for the photovoltaic (PV) modules reliability. Numerous chemical or physical methods may be applied to determine the extent of crosslinking reaction in the EVA material. The usual and most accurate ones are destructive as they require a sample of material from the module. In this work we present a contactless and non-destructive method for monitoring the crosslinking process of EVA based on fluorescence spectroscopy. We show the correlation of fluorescence emission intensity of EVA when submitted to UV light with its curing grade determined by a rheological method. This approach is of interest for in-line monitoring of the crosslinking during the lamination step and for quality control after production.

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1. Introduction

Ethylene vinyl acetate is still the most employed encapsulation material in crystalline silicon PV modules. During the module lamination, EVA melts and eventually crosslinks by forming covalent bonds between the polymer chains, leading to an infusible and insoluble material. The extent of this crosslinking reaction is a key factor for the durability of the photovoltaic modules. The most commonly used method for qualifying the extent of crosslinking is the Soxhlet extraction which consists in measuring the insoluble part of a material sample extracted from the PV

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module after the lamination process. Alternative methods rely on measurement of the material stiffness over time with rheological measurements, the determination of the unconsumed crosslinking initiator by differential scanning calorimetry [1] or the determination of swelling of the material when immersed in a solvent. These methods are also all destructive, as they require a sample of material from the module. Some non-destructive alternative techniques have been developed, relying on the sound velocity in the material [2], the change of dielectric properties of EVA during crosslinking [3], the diffusion of visible light in transmission [4] through glass-glass modules, or the measurement of stiffness through the backsheet with an indenter [5]. These methods can either not be used in-line, require the insertion of a supplementary device in the module or are constraining the module design. Nevertheless, measurements of punctual material modifications at a molecular level have been recently done after the lamination process with Raman spectrometry [6] and show a good correlation to degree of crosslinking.

Photovoltaic modules constituted of EVA emit fluorescence under excitation with black light. The intensity of this fluorescence emission is increasing over time under exposure to natural ultraviolet radiation or humidity both in conditions of duty [7-9] or in accelerated tests in a climate chamber [10]. The molecular degradation mechanism provoking this fluorescence is not clearly determined and is suspected to be due to the formation of polyenes on the polymer chain [7] or to degradation of additives present in the polymer matrix [11]. It has been observed that oxygen diffusion in the modules through the backsheet and the cell cracks causes a local extinction of the fluorophores, thus allowing a fast acquisition of crack patterns in a module [8]. We show here that a fluorescence emission of the material can be detected at the early stages of module production and that it can be used to monitor the crosslinking reaction in modules. method to evaluate the extent of curing of EVA in a whole module instantaneously, basing on simple and fast fluorescence intensity measurements. This method may also be extended for punctual or lateral in-line monitoring during lamination [12].

2. Experimental method

2.1. Determination of EVA crosslinking

The crosslinking of EVA samples is monitored by measuring the storage shear modulus G' of material over time for a typical lamination process temperature profile [13] by dynamic mechanical analysis (DMA) with an Anton Paar Physica MCR 301 rheometer. This shear modulus is correlated to the EVA crosslink density by Eq.1.

$$G = \nu_e \cdot R \cdot T + G_0 \quad (1)$$

where G is the shear modulus, ν_e the crosslink density, R the universal gas constant, T the temperature and G_0 the shear modulus of molten uncured material. The curing state or degree of crosslinking χ is the ratio of crosslink density in the material over the maximal reachable crosslink density and can be practically calculated according to Eq. 2.

$$\chi = \frac{100 \cdot G'}{G'_{MAX} - G'_0} \quad (2)$$

where G'_{MAX} is the maximal storage modulus reached for the totally cross-linked material. With help of this method, we can determine the crosslinking grade of the EVA in a laminate over time according to any temperature curve [13]. The lamination duration required for each targeted partial crosslinking is calculated out of at least 3 repetitions of the dynamical mechanical measurements on fresh EVA samples.

EVA used in this work are the following commercial compositions: A: STR E Photocap 15455P/UF, B: Hangzhou FirstEVA Su-806, C: STR E Photocap 15420P, D: Solutia Vistasolar 486.10, E: Bridgestone EVASKY S87. According to their datasheets, the EVAs A to D show a transmission cutoff at 360 nm and the EVA E shows a transmission lower than 5% at 324 nm and lower than 0.5% at 315 nm

2.2. Preparation of laminates with a controlled degree of crosslinking

Sample laminates containing each 2 solar cells are prepared on 20 cm x 30 cm glass plates out of EVA materials A, B, C and D with a degree of crosslinking of 0%, 50% and 90% and an Isovoltaic Icosolar APA 2552 backsheets. To achieve this, the test modules are laminated at a programmed set temperature of 150°C for 15 to 26 minutes, varying on the targeted curing state and the employed material. The temperature in the modules is not constant during lamination, starting at 40°C and increasing slowly to stabilize at a temperature lower than 150°C. The uncured EVA laminates with a degree of crosslinking of 0% were prepared by stopping the temperature ramp at 90°C and maintaining the sample at this temperature for 8 minutes. The laminates with the longer lamination time are maintained between 5 and 10 minutes at lamination temperature after the estimated complete crosslinking is achieved.

Another group of sample modules is prepared according to the same method with another EVA material and 4 different backsheets on each sample. 3 different commercial backsheets foils and a household aluminum foil are used as backsheets. The employed backsheets are A: Isovoltaic Icosolar APA 2442, B: 13 µm household aluminium foil, C: Akasol PTL 3 HR, D: Isovoltaic Icosolar APA 2116. The household aluminium foil is used as reference as its surfaces does not comprise any organic surface treatment susceptible to influence the fluorescence.

A full size module (1465 mm x 975 mm) containing 40 unconnected 156 mm x 156 mm solar cells is prepared in a Meier photovoltaic modules laminator. In order to generate a temperature gradient and a subsequent degree of crosslinking inhomogeneity over the module, a third of the laminator heating plate is held at 80°C meanwhile the other end of the plate is heated according to a 150°C lamination program.

2.3. Fluorescence emission measurements

Fluorescence emission is observed under the excitation of samples with an UV-lamp array with a main emission band at 375 nm, illuminating the modules with a light intensity of approx. 100 W/m² at the PV module surface. Images are taken with a Sencicam QE camera from PCO equipped with a long pass filter, blocking the wavelength under 440 nm and a band pass filter centered on 534 nm with a bandwidth of 43 nm. The fluorescence intensity is then evaluated by calculating the mean grayscale value. For the sake of clarity the photos presented in this work are reformatted and annotated. The numerical analysis is performed on the original photos.

A prelaminated sample module is prepared by melting and pressing the EVA between the glass and the backsheets foil at 80°C during 5 minutes. The obtained laminate is then cured sunny side up at 150°C on a heating plate under UV irradiation and an image is taken every minute with the abovementioned camera. A type K temperature sensor inserted in the sample before lamination records the temperature during the crosslinking. A rheological measurement of a fresh EVA sample according to the measured temperature profile allows estimating the evolution of the degree of crosslinking over time in the laminate.

Fluorescence spectra are recorded with BWTEK UV-Vis spectrometer equipped with an optical fiber allowing the measurement perpendicular to the glass plate at the surface of the module.

3. Results and discussion

3.1. Fluorescence emission of modules with known degree of crosslinking

The Fig. 1 shows the fluorescence emission at 534 nm under black light excitation of 16 laminates prepared with the same backsheets, EVA A to D laminated over durations corresponding to a degree of crosslinking of 0%, 50%, 90% and complete crosslinking. This latter case is designated by $t > t_{99\%}$. The fluorescence intensity increases with the degree of crosslinking and is depending on the EVA used. Contrary to the fluorescence appearing by UV-aging, this fluorescence emission is not accompanied by an observable yellowing.

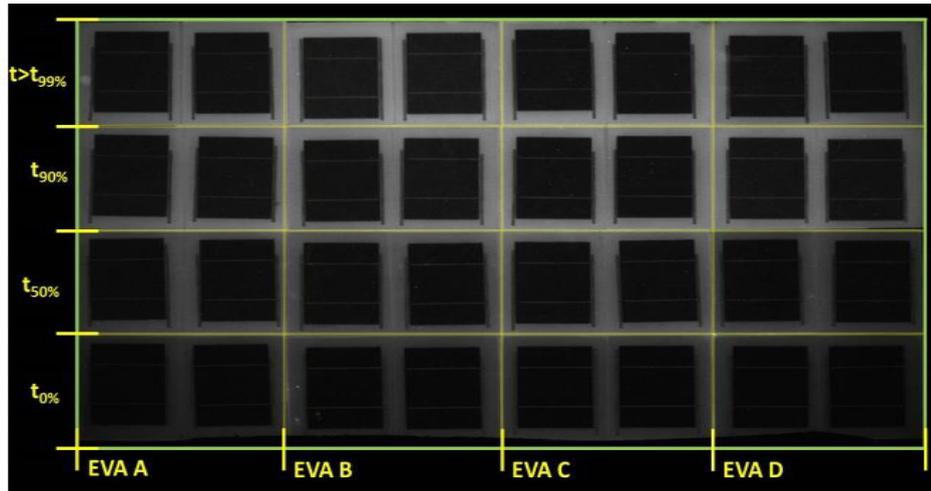


Fig. 1. Fluorescence image at 535 nm under black light excitation of laminates prepared with two photovoltaic cells, EVAs A to D and Isovoltaic Icosolar APA 2552 backsheet. The degree of crosslinking of the samples are 0%, 50%, 90% and the last serial is laminated longer than necessary to attain the maximal degree of crosslinking.

Fig. 2 (a) shows the fluorescence emission under blacklight excitation of 4 laminates consisting on the EVA E laminated over durations corresponding to a degree of crosslinking of 0%, 50%, 90% and longer than the complete crosslinking. In the fourth laminate the temperature sensors used for the determination of the temperature profile of the lamination program in the encapsulant are still present. The Fig. 2 (b) shows the dependence on the degree of crosslinking of the fluorescence intensity measured from the gray value on the picture. The fluorescence intensity observed is depending on the backsheet used but increases with the degree of crosslinking.

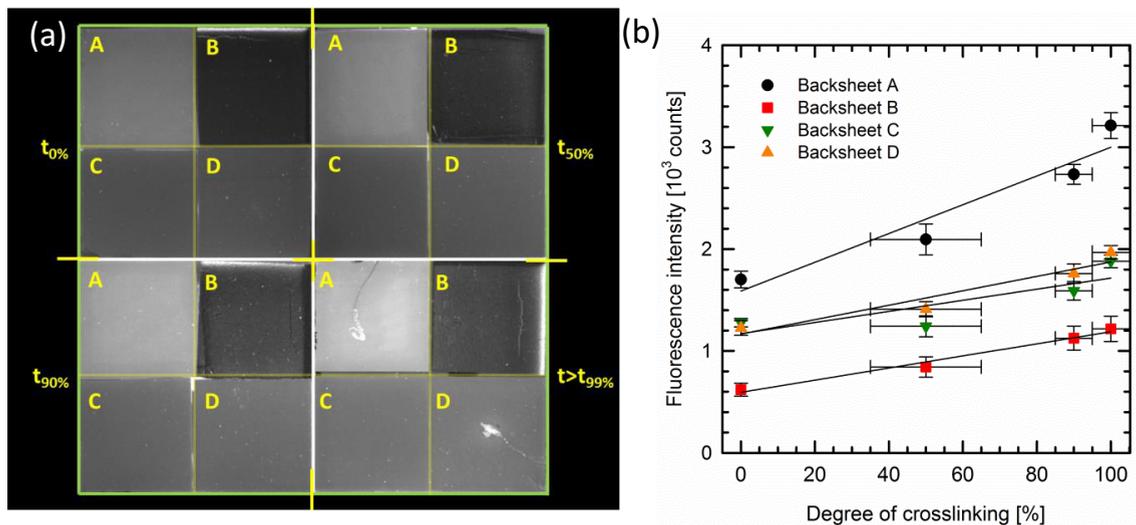


Fig. 2. (a) Fluorescence emission image and (b) measured fluorescence intensity of laminates of Bridgestone EVASKY S87 with lamination durations corresponding to degrees of crosslinking of about 0%, 50%, 90% and 10 minutes after complete crosslinking.

Fig. 3 shows a standard size laminate prepared on an inhomogeneously heated laminator. The side laminated at a higher temperature is showing a more intense fluorescence emission. Nevertheless the contrast cannot be maximal as the cold side of the heating plate is finally heated by conduction which leads to a partial crosslinking of the material on the cold side.

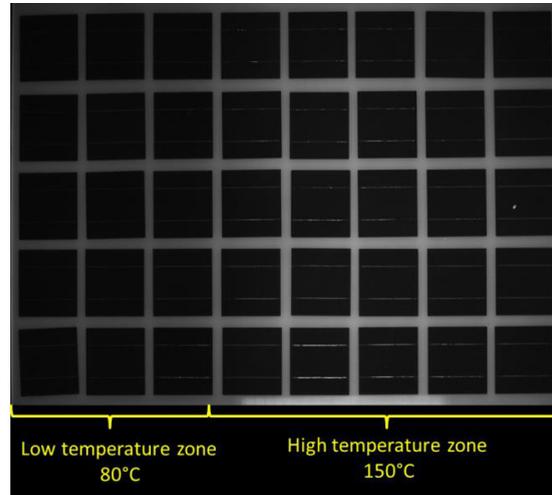


Fig. 3. Fluorescence emission of an inhomogeneously crosslinked module. The heating plate of the laminator in contact with the left side was deactivated and the right side was heated according a 150°C lamination program. The direction of the temperature gradient is indicated by the yellow arrow.

3.2. Fluorescence spectra

UV-Visible light spectra recorded under UV exposure on the surface of samples laminated with different degrees of cross linking are shown in the Fig. 4. On the spectra are the excitation light bands at 375 nm, 430 nm and 695 nm observable and intense compared to the variation of the signal intensity attributed to the emission in the range 450-550 nm. The intensity of the emission is increasing with the degree of crosslinking.

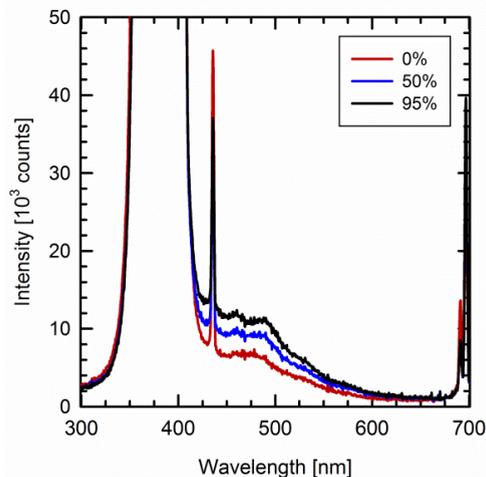


Fig. 4. UV-visible light spectra collected under UV excitation on the surface of sample laminates with different degrees of crosslinking.

3.3. Real-time measurement of fluorescence during crosslinking

To avoid the problem of uncertainty on the degree of crosslinking induced by the preparation of partially crosslinked laminates we measure the fluorescence emission during the crosslinking of the EVA. Fig. 5 shows the fluorescence emission intensity of a laminate prepared with EVA C over time and the curing grade of the material as measured with the DMA following the same temperature curve.

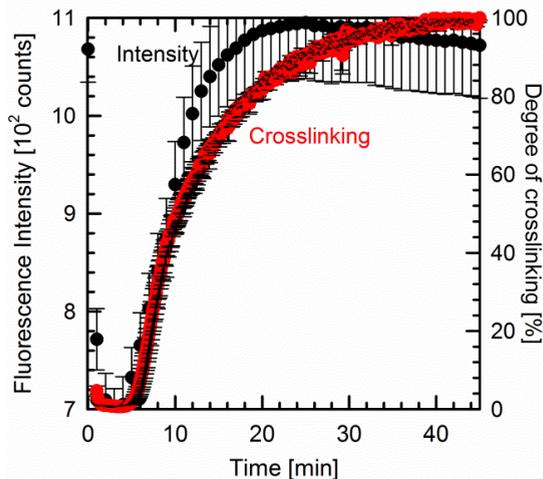


Fig. 5. Fluorescence emission intensity under blacklight excitation during crosslinking of a glass/EVA/aluminium foil laminate at 150°C and estimated degree of crosslinking.

4. Discussion

The figure Fig. 1 shows that EVA is showing a more intense fluorescence emission with increasing degree of crosslinking. The intensity as seen with bare eye increases between degrees of crosslinking of 0% and 50% and between 50% and 90%. Nevertheless, the evolution after the fast complete curing over 90% does not result in an increase of the same extent. This suggests that the root cause of the development of fluorescent products in the material is not the heating of the laminate and that the fluorescence intensity is linked to the crosslinking itself. This behavior is observable with all the EVA of this study and may therefore not be limited to a particular chemical formulation.

Furthermore, Fig. 2 shows that the more recent UV-transparent EVAs are also showing this behavior. This allows excluding a potential thermal degradation of the UV absorber as the source of fluorescence emission.

According to Fig. 2, the backsheets have very little influence on the phenomenon. The increase in fluorescence intensity is observed with every foil although the intensity itself differs. This is attributed to the different reflectivities of the foils. It is worth to note that the fluorescence is also observed when a simple aluminum foil or a solar cell is used as background, excluding thus the possibility that this fluorescence is emitted by a layer or a surface treatment of the commercial multilayer backsheets foils. The fluorescence emission measured from pictures of partially and totally crosslinked modules shows a near linear correlation with the degree of crosslinking in the material.

The Fig. 3 reveals that the emission phenomenon is intense enough to highlight cold zones in a lamination process.

The emission spectra of EVA under blacklight on the Fig. 4 show an increase of the fluorescence intensity in the domain 450 nm to 550 nm during the crosslinking of the material. Nevertheless the configuration of the measurement device does not allow obtaining a spectrum without the more intense excitation light masking a part of

the emission spectrum. Furthermore it reveals that the wavelength targeted by the filters of the camera used for the image capture is not the maximum of the emission and the measurement still can be optimized by choosing a wavelength allowing wider scale of fluorescence intensity, increasing thus the precision of the measurement.

The storage modulus curve of the EVA on the Fig. 5 decreases over the first two minutes as the material is melting. Remarkably the fluorescence emission intensity is also decreasing during the melting of the material. The crosslinking reaction is then observed after approximately 5 minutes and the storage modulus increases and reaches a saturation value. The increase of fluorescence intensity during the heating of a laminate at 150°C follows a logarithmic curve and reaches a plateau. By correlating the maxima of both the fluorescence intensity over time curve and the storage modulus curve of the material, the fluorescence intensity and the degree of crosslinking curves show a remarkable correlation, especially for degrees of crosslinking ranging from 0% to 60%. For higher degrees of crosslinking, the correlation is less precise but the fluorescence intensity remains in the domain of uncertainty of the normalized storage modulus curve. Furthermore, the fluorescence intensity seems to decrease over time after the completion of the crosslinking reaction. As in this case the sample is not cured under vacuum, this decrease may be attributed to the oxygen diffusion occurring over time at high temperature from the side of the laminate, which leads to partial extinction of the formed fluorophores. It has been shown in a previous study [10] that a degree of crosslinking of 50% corresponds to a gel content in EVA of about 70%, which is considered by modules manufacturers as the standard required curing. The good correlation between both curves until a degree of crosslinking of 60% is suggesting that this method might be reliable enough to monitor the lamination process to reach the industrial standards.

The development of fluorescent products in the material may be due to a thermal degradation of the polymer itself or to the byproducts of additives degradation during crosslinking. The exact composition of the studied EVAs cannot be well known as it is kept as a fabrication secret. Nevertheless some species mentioned on the provided safety datasheets as well as some studies from the literature may orientate our conclusions. Organic peroxides typically used in EVA compounds are not likely to issue fluorescent aromatic or conjugated byproducts by themselves [7, 10]. Nevertheless common antioxidizing additives added in EVAs such as butylhydroxytoluene [10], aromatic ketones [14] or tris(alkylphenyl)phosphites [7,14] are conjugated products and undergo degradation during the crosslinking reaction [10]. Some compounds of the latter class are known to issue fluorescing species by reacting with the peroxides [7], and one of them is present in at least EVA C according to its safety datasheet. This is compatible with the stabilization of the fluorescence intensity increase observed in Fig. 5: the maximal degree of crosslinking is reached after complete consumption of the peroxide and the fluorescence caused by the degradation of additives by the peroxide cannot increase. This supports the possibility to use the evolution of fluorescence emission as a visual monitoring to detect the end of the crosslinking reaction.

Furthermore, the thermal degradation of UV filters such as hydroxybenzophenones present in some of the studied materials according to their safety datasheet may also lead to this fluorescence emission. Nevertheless, the observed fluorescence of the UV-transparent material suggests that conjugated UV absorbers are not the only species generating this fluorescence emission. This shows that the monitoring of the crosslinking reaction by means of fluorescence emission may also be applicable to the most recent generation of encapsulation EVAs.

5. Conclusion

In this paper we show that during the lamination of EVA in PV modules, the crosslinking reaction of the material is accompanied by the formation of fluorophores. We propose the degradation of stabilizers by peroxides during the lamination process as an explanation for the origin of this fluorescence. As this degradation stops after complete consumption of the peroxides the fluorescence intensity increase stops when the crosslinking is achieved. Further investigations with a wider range of EVA may nevertheless allow assessing the universality of this process. We suggest that the method may be applicable to the punctual monitoring of the crosslinking of EVA during the production of modules or used for quality control to evaluate the degree of crosslinking over a whole module and reveal the cold spots in a laminate for quality control purposes.

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References

- [1] Stark W., Jaunich M., Investigation of Ethylene/Vinyl Acetate Copolymer (EVA) by thermal analysis DSC and DMA, *Polym. Test.* 2012; 30 (2):236-242.
- [2] Mühleisen W., Biebl-Rydlo M., Spielberger M., Acoustic in situ Determination of EVA features, *Proc. of 26th EU PVSEC, Munich, Germany*; 2011:3480-3483.
- [3] Schulze S., Verfahren und Vorrichtung zur Steuerung der Temperaturführung bei einem thermischen Laminationsprozess, *Patent DE 10 2010 025 204.2*.
- [4] Li H., Perret-Aebi L.E., Théron R., Ballif C., Luo Y., Lange R., "Optical transmission as a fast and non-destructive tool for determination of ethylene-co-vinyl acetate curing state in photovoltaic modules", *Prog. Photovolt. Res. App.* 2013; 21 (2):187-194.
- [5] Doble D., Mickiewicz R., Lloyd J., Jaeger M., Hartman W., Methods and apparatus for detecting cross-linking in a polymer, *US Patent 2012/0118071 A1*.
- [6] Hirschl C., Biebl-Rydlo M., DeBiasio M., Mühleisen W., Neumaier L., Scherf W., Oreski G., Eder G., Chernev G., Schwab W., Krafta M., Determining the degree of crosslinking of ethylene vinyl acetate photovoltaic module encapsulants-A comparative study, *Sol. Energy Mater. Sol. Cells* 2013; 116:203-218.
- [7] Pern F.J., Ethylene-vinyl acetate (EVA) encapsulants for photovoltaic modules: degradation and discoloration mechanisms and formulation modifications for improved photostability, *Angew. Makromol. Chem.* 1997;252:195-216.
- [8] Köntges M., Kajari-Schröder S., Kunze I., Cell cracks measured by UV fluorescence in the field, *Proceedings of the 27th EU PVSEC, Frankfurt, Germany* 2012:3033–3040
- [9] Schlothauer J., Jungwirth S., Köhl M., Röder B., Degradation of the encapsulant polymer in outdoor weathered photovoltaic modules: Spatially resolved inspection of EVA ageing by fluorescence and correlation to electroluminescence, *Sol. Energy Mater. Sol. Cells.* 2012;102:75–85.
- [10] Morlier A., Klotz S., Sczuka S., Kunze I., Schaumann I., Blankemeyer S., Siebert M., Döring T., Alshuth T., Giese U., Denz M., Köntges M., Influence of the curing state of ethylene-vinyl acetate on photovoltaic modules aging, *Proc. 28th EU PVSEC, Paris, France*; 2013:2832-2837.
- [11] P. Klemchuk, M. Ezrin, G. Lavigne, W. Holley, J. Galica, S. Agro, Investigation of the degradation and stabilization of EVA-based encapsulant in field-aged solar energy modules, *Polym. Degrad. Stab.* 55 (1997) 347–365.
- [12] Morlier A., Köntges M., Blankemeyer S., Kunze I., Verfahren und Vorrichtung zum Einlaminiere von Gegenständen, insbesondere von Solarzellen, *German Patent Application DE 10 2012 015 439.9*.
- [13] Kajari-Schröder S., Eitner U., Oprisoni C., Alshuth T., Köntges M., Brendel R., Modelling the curing dynamics of ethylene-vinyl acetate, *Proc. of the 25th EU PVSEC, Valencia, Spain* 2010: 4039-4043.
- [14] Hintersteiner I., Sternbauer L., Beissmann S., Buchberger W., Wallner G., Determination of stabilisers in materials used as encapsulants in photovoltaic modules, *Polym. Test.* 2014;33:172-178.