Cross-linking characterization of polymers based on their optical dispersion utilizing a white-light interferometer

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ABSTRACT

Polymers are used in different applications with strict demands regarding their performance over long periods of time. Therefore, the mechanical, electrical and optical properties have to be controlled during the fabrication. As cross-linking is a crucial process step it is necessary to establish reliable technologies to monitor the degree of cross-linking at this point. This work analyses samples of the widely used encapsulant of photovoltaics modules, ethylene vinyl acetate (EVA). The samples were cross-linked using a lamination technique with different curing times (0 - 20 minutes). The cross-linking characterization is done by determinating the material dispersion with the aid of a combined temporal- and spectral-domain white-light interferometer. With the proposed technique it was possible to discriminate the differences in crosslinking for the given curing times. The measured data could be acquired and analysed automatically by an appropriate algorithm. The results showed that the used method was capable to obtain similar results with comparable errors like establlished reference techniques. One advantage was that the alternative method delivered more relevant information than other approaches. Furthermore it showed good potential for a future in-line application due to a fast and automated data processing procedure.

Keywords: white-light interferometry, polymer curing, ethylene-vinyl acetate (EVA), dispersion measurement, cross-linking characterization, photovoltaics, polymer characterization

1. INTRODUCTION

Polymers play a significant role in many applications. In many of these applications long-term mechanical resistance and temperature stability, as well as resistance towards hazards such as radiation and humidity are demanded; Especially in the field of photovoltaics (PV), polymers, used as encapsulants, have to maintain their properties over an operation time of 20 - 30 years. Mainly, these encapsulants serve as a protection to prevent damage from mechanical, electrical and humidity sources. It has to provide high strain and temperature stability to compensate for the different thermal expansion coefficients. Besides it has to compensate for stresses and prevent cracks of the substrate materials. Another important function is optical coupling of the light in the desired wavelength region. That demands a transmission of >90% with allowed loses of maximum 5% over 20 years, [1]. A material which suits these demands and is commonly used is ethylene-vinyl acetate (EVA), [2].

EVA is a random copolymer of ethylene and vinyl acetate with a percentage of vinyl acetate typically in the range from 28 to 33 weight-% for PV module applications. The native EVA would not fulfill the thermo-mechanical requirements due to its melting range between 60 and 70°C. By chemical crosslinking utilizing hydroperoxides during PV module lamination, the moldable EVA sheet is transformed into a highly transparent elastomer with the required thermo-mechanical stability up to 100°C, [1, 3]. It shows good adhesion, high transmission in the interesting wavelength region and it is sufficiently long-term stable regarding its properties.

In order to establish the desired properties of polymers like EVA, it is necessary to develop and control appropriate

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curing processes. Furthermore, it is vital to measure the degree of cross-linking of the material during all process steps. During the lifetime of a product, continuous monitoring of the properties can help to estimate the state of aging and its implications on the application. Considering modern manufacturing processes, several additional demands for cross-linking characterization techniques arise such as:

- High resolution of the degree of crosslinking for sensing of small process variations and slow aging effects
- Fast data acquisition and analysis for high production rate
- Possibility to perform in-line measurements for investigation of real materials
- Capability of in-situ measurements on products (i.e. PV modules) for continuous monitoring over lifetime
- Ability to measure spatially resolved for measurement of large samples or roll-to-roll processes

One of the most common methods to determine the cross-linking state of polymers is soxhlet-type extraction, [4]. Considered as the gold-standard within the PV industry it is well understood and standardized. For that purpose, a sample is exposed to a solvent, typically xylene isomer, in which non-cross-linked material will dissolve after a few hours. After 24 hours of drying, the degree of cross-linking can be calculated from the respective weights of cross-linked and non-cross-linked material. The result is very precise whereas the process is time consuming, destructive and not in-line ready. Another common method is differential scanning caliometry (DSC), [5–7]. This approach measures thermal features of a sample like heat flow, melting point and reaction enthalpy. By referencing the reaction enthalpy of differently cross-linked samples to a non-cross-linked sample, the degree of cross-linking can be calculated. Similar to chemical based methods, this approach is destructive to the sample and not in-line ready; Although measurements can be obtained within minutes instead of hours. Faster and non-destructive measurements can be obtained by using optical measurement technologies. One state-of-the-art technology is RAMAN spectroscopy, [8]. The analysis of spectral features of reactional groups and bonds before, as well as, after the curing process are utilized to calculate the degree of cross-linking. However this method is only applicable to samples with a relatively high amount of reactional groups. Materials which lack a dedicated cross-linking group, like EVA, are only to measurable under high instrumental and analytical effort.

The aspiration for an alternative approach to the cross-linking characterization of polymers originates from the named drawbacks of most state-of-the-art technologies. This work aims to present an approach based on interferometric dispersion measurement. The aspired properties are in-line capability, high resolution and fast data acquisition as well as analysis.

2. EXPERIMENTAL APPROACH, SETUP AND SAMPLES

Polymerization and cross-linking determine the resulting mechanical, optical and electrical properties of a polymer, [9] . Due to the formation of characteristic molecular bonds, properties such as absorption and the refractive index are determined. Some studies have found that the measurement of the refractive index over the cross-linking process can be used as an indicator for the degree of cross-linking of a sample, [10]. However, a more detailed evaluation can be possible when considering the dispersion of the refractive index over a wavelength range as opposed to one single value, [11].

Under the simplified assumption of a classical oscillator model instead of a quantum mechanical model, the absorption of a material is related to the eigenfrequency of the bond charges between its molecules. An incident electromagnetic wave will cause a vibration of the bond charges. Depending on the wavelength of the incident light a certain amount of energy is dissipated by the vibration of the bond charges. This mechanism leads to a wavelength dependent slope of the absorption coefficient k and the refractive index n which can be described as, [12]

$$(n - ik)^2 = \frac{e^2}{2\pi c \varepsilon_0 m} \sum_j \frac{N_j f_j \lambda_j^2 \lambda^2}{2\pi c(\lambda^2 - \lambda_j^2) + i\gamma_j \lambda_j^2 \lambda} \tag{1}$$

Where N_j is the number of molecules per unit volume for a given oscillation, c is the velocity of light in vacuum, m is the mass and e is the charge of the electron, ε_0 is the permittivity of free space and γ_j describes the damping.

The eigenfrequency λ_j and the oscillator strength f_j are unique to every material. These parameters also change within the cross-linking process as new molecular structures are formed. Therefore, the measurement of the wavelength dependent refractive index $n(\lambda)$ can deliver an indicator for the cross-linking state of the material. Furthermore, the first derivative of $n(\lambda)$, known as the dispersion parameter $D(\lambda)$, can provide additional information on the trend of the cross-linking.

The chosen experimental setup to determine the material dispersion of solid samples is based on a combination of time- and spectral-domain white-light interferometry, Fig. 1 a). A broadband light source, here a supercontinuum source (ilum 1, Fiberware GmbH, Germany), is fed into a Michelson interferometer core. While a transmissive sample is placed in the object arm, the reference arm holds a moveable mirror (aluminum on piezo stage SLC-24120, SmarAct GmbH, Germany). As a detector for the recombined signal a grating spectrometer (AvaSpec 3648XL, Avantes, France) is incorporated.

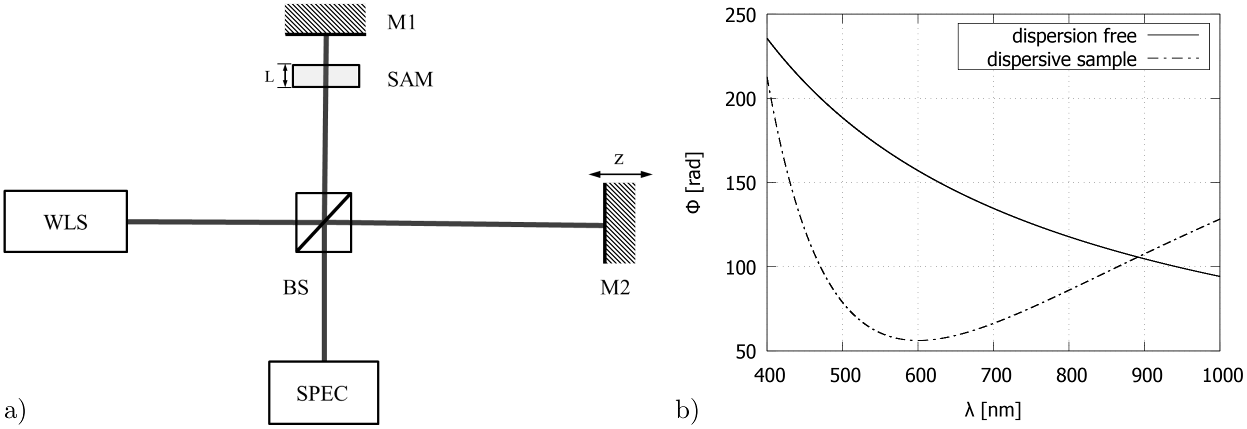

Figure 1. a) experimental setup with WLS - white-light source, BS - beam splitter, SAM - dispersive sample with thickness L, M1 - fixed object arm mirror, M2 - moveable reference mirror, SPEC - spectrometer and b) example plot of the phase in a dispersion-free interferometer in comparison to a interferometer with a dispersive sample

Initially, without a sample, the interferometer can be considered as dispersion free. When both arm lengths show no difference to each other the so called white light point (WLP) is adjusted. Under the assumption of a small optical path difference between the two arms (OPD) the detector shows interference over the spectral range of the light source with a continuous phase, Fig. 1 b). The signal can be described using general two beam interferometer formulas.

$$I(\lambda) = I_0 \cdot (1 + \cos\phi) \tag{2}$$

$$\phi = \frac{2\pi\delta}{\lambda} \tag{3}$$

The introduction of a sample into the object arm changes the OPD as well as the interference signal at the detector. The phase of the interference signal becomes dependent on the thickness of the sample L and the wavelength dependent refractive index $n(\lambda)$, Fig. 1 b)

$$\phi_{sam} = 2\pi\frac{(n(\lambda)-1)L-\delta}{\lambda} \tag{4}$$

This leads to a modification of the interference signal, where the phase reaches a global minimum for defined OPDs, noted with δ. Using an a spectrometer as detector, the minimum of the phase can be measure as the corresponding position in the spectral range, named as equalization wavelength λ_{eq}. After recording λ_{eq} for a given range of δ over the spectral range of the light source, here 400 - 1000 nm, the calculation of the difference in position of λ_{eq} to the WLP is a measure of the dispersion introduced to the setup by the sample. This can be denoted as a spatial difference $z(\lambda)$ or a temporal difference $\tau(\lambda)$ which both can also easily be expressed as $n(\lambda)$.

In order to evaluate the new approach to cross-linking characterization, samples of EVA have been used which were well investigated with a number of reference technologies, [3]. These EVA test samples, varying only in the degree of crosslinking, were produced in a standardized process. One commercially available EVA type (Vistasolar 486) was chosen and the degree of crosslinking was varied solely by changing the duration of the lamination process. For the purpose of this study, the lamination time was systematically varied from 0 to 20 min (0, 1, 2, 3, 4, 5, 6, 8, 10, 20 min) with the lamination temperature kept constant at 150°C. The lamination process itself was carried out in a manual laminator following standard lamination procedures, [3].

3. RESULTS AND DISCUSSION

The prepared EVA samples of different cross-linking states were cut from sheets in appropriate pieces with a thickness of around $400 \mu m$. The temporal delay τ of each sample in relation to the white-light point was recorded repetitve (10 times each). The data was then normalized to the corresponding sample thickness L and plotted as an averaged curve in relation to the wavelength, Fig. 2 a). The data points were also fitted using the Sellmeier equation

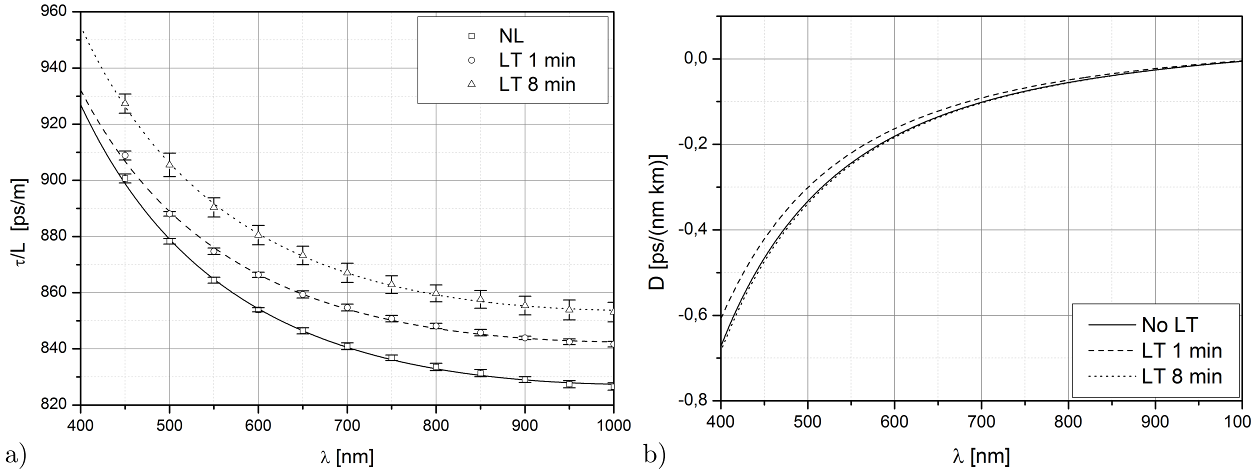

Figure 2. a) Results for the measured temporal delays τ due to the different lamination times normalized to the material thickness L for three representive lamination times with NL - no lamination, LT 1 min - 1 minute and LT 8 min - 8 minutes lamination and b) Derivation of the temporal delay according to eq. (6)

$$\tau(\lambda) = \frac{A_1}{\lambda^2} + A_2 + A_3\lambda^2 \tag{5}$$

From the plot it becomes visible that the differences in the delay due to dispersion are $\leq 10 ps/m$. It is even more visible that the difference between an un-laminated sample (NL) and a laminated sample (LT 1 min) is rather high. That is to consider especially in relation to a longer lamination period from LT 1 min to LT 8 min. This fact leads to the assumption that the curing reaction starts fast at the begining of the lamination process. More information can be gathered from the examination of the slope of the temporal delay, Fig. 2 b). For that purpose the first derivative of the fitted data was calculated

$$D(\lambda) = \frac{\partial\tau(\lambda)}{\partial\lambda \cdot L} = \frac{2}{L}(A_3\lambda - \frac{A_1}{\lambda^3}) \tag{6}$$

where D is known as the dispersion parameter. The results reveal that no particular trend is obvious. Although there are some differences in the wavelength range of 400 to 600 nm. Further investigations are planned to examine this range with higher resolution. At this point only the magnitude, not the slope, gives a significant measure on the cross-linking state of one polymer. Other investigations have shown that the dispersion parameter can be used to distinguish between different polymers, [11].

The most important information, the degree of cross-linking, can be extracted by plotting the differences in

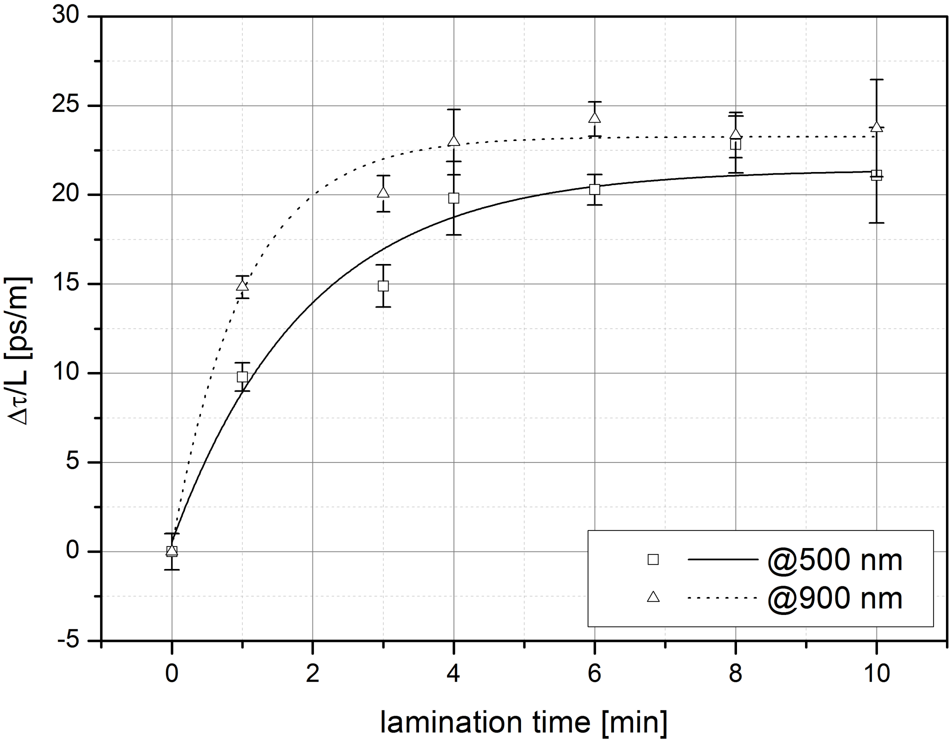

Figure 3. Plot of the differences in $\Delta\tau/L$ over the curing time at different wavelengths

temporal delay $\Delta\tau/L$ versus the lamination time, Fig. 3. The data acquisition over a broad spectral range enables the analysis at different wavelengths. For comparision purposes two representive wavelengths, 500 and 900 nm, have been choosen. The data fits a pseudo-first order reaction kinetics model. This model is commonly used for different cross-linking characterization approaches, [3]. The fitted results indicate that information on the degree of cross-linking can be obtained over large spectral range. For a practical usage of this technology it can be favorable to average the cross-linking information at multiple spectral points. The additional statistical security gained from is an advantage of this approach over established methods.

In comparison to other technologies, the presented work shows reasonable errors. Also the trend of the data is in good analogy to the reference approaches. Optical methods like RAMAN spectrocopy as well as thermal (e.g. DSC) or thermo-mechanical methods (e.g. DMA) show comparable results. EVA samples show a fast cross-linking at the begining of the lamination process which slows down significantly after 3-4 minutes, [3]. The calibration of the $\Delta\tau/L$ data to a degree of cross-linking on a percentage scale can be done by choosing an appropriate reference technology.

4. CONCLUSION AND OUTLOOK

This work demonstrated an alternative approach to the cross-linking characterization of polymers. By utilizing a combined time- and spectral domain white-light interferometer, samples of ethylene-vinyl acetate were investigated. The samples were manufactured with defined and well characterized degrees of cross-linking. As a measure for cross-linking the temporal delay τ in one interferometer arm due to material dispersion was recorded in relation to the wavelength. Additionally, the dispersion parameter, as first derivative of τ was calculated. The results showed that the temporal delay is a clear indicator for a change in the degree of cross-linking while the derivative not lead to distinct additional information.

Furthermore, the resolution of the interferometer was sufficient to measure the cross-linking dependent differences in τ in the range of 10 ps/m. The plot of the temporal delay of different samples over their respective lamination times could be interpreted with a pseudo-first order reaction kinetics model. That is in good correspondence to established measurement techniques. The results still showed some significant error bars. The sources where rooted in the sample material itself. The investigated reference technologies to determine the degree of cross-linking showed comparable results, [3].

The experiments proved that the approach enables a fast and reliable cross-linking characterization of polymers. A clear advantage of the proposed method is the ability to gather information on the degree of cross-linking over a large spectral range. This enables a higher statistical security of the method.

Due to the relatively simple data acquisition and analysis, good process integration can be proposed. The resolution for cross-linking related features is sufficient while a measurement on dedicated samples as well as on PV-modules is possible.

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