Advanced methods for determining PV module process optimization potential

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ABSTRACT

Ethylene vinyl acetate (EVA) is still the dominant material used for encapsulation of solar cells. During PV module lamination, a three-dimensional network is formed by a chemical cross-linking of the polymer chains in order to increase the thermal stability of the material and to prevent the material from melting when exposed to application-relevant temperatures of up to 100°C. The cross-linking reaction, which is discontinuous and can take up to 30 min (depending on the EVA type), is the time-determining step in PV module lamination. The main objective of this paper is to gain a comprehensive understanding of the thermomechanical material behaviour during the PV module lamination process, and to develop a basis for the optimization of the PV module manufacturing process. The results presented will demonstrate that dynamic mechanical analysis (DMA) is a valuable and reliable characterization method for the investigation of the curing behaviour of EVA for solar cell encapsulation. DMA in shear mode allows a continuous measurement of the thermomechanical properties, even in the molten state, and therefore an in situ monitoring of the cross-linking reaction. Whereas it is possible to use temperature scans on partially cured EVA films to determine the state of cross-linking, isothermal scans on uncured samples allow the curing kinetics of EVA to be investigated. On the basis of an enhanced knowledge of the cross-linking reaction, the material-related process-parameter optimization potential of the PV module lamination process can be identified, and optimum processing temperature ranges and minimum cross-linking times can be derived.

Introduction

During the last few years the PV industry has seen remarkable growth. For these high growth rates to continue, and for additional market volumes and new fields of applications to be developed, investment in comprehensive R&D programmes is necessary. To achieve grid parity, and therefore to contribute to the overall power requirement, there needs to be in particular a significant reduction in costs. Achieving this cost reduction will depend not only on scale-up benefits, but also on the costs of the encapsulation materials and the PV module lamination process [1].

The main solar cell encapsulation material for PV modules is currently ethylene vinyl acetate (EVA) copolymer. The solar cell encapsulant has to fulfil several basic functions, which include providing structural support and physical isolation of the solar cells, maintaining electrical isolation, and being highly transparent in a selected spectral region, according to the cell technology used [2]. To deal with different thermal expansions of the materials (glass, solar cell, interconnects, polymers) used in a module, and to avoid over-stressing and cracking, the encapsulant material must have a low-modulus, elastomeric property. Furthermore, a maximum optical coupling between the solar cell and the incident solar irradiation in a prescribed spectral region, with an initial transmission of at least 90% and a loss of less than 5% after 20 years of module lifetime, has to be achieved.

EVA is a semi-crystalline copolymer of ethylene and vinyl acetate (VA); for PV applications, the VA content usually ranges from 28 to 33%. The thermal, mechanical and optical properties can vary over a broad range, depending on the VA content. Polyethylene copolymers are random copolymers that consist of linear ethylene sequences and regions with short-chain branches introduced by the co-monomers (e.g. VA, octane) [3,4]. The VA side groups of the EVA do not enter the crystalline regions, which can be attributed exclusively to the ethylene sequences. Both melting temperature and degree of crystallinity depend on the co-monomer content: the higher the VA content, the lower the melting temperature and degree of crystallinity [5]. Consequently, a higher VA content also leads to a higher mechanical flexibility of the polymers. Finally, the VA content also influences the optical properties, as the introduction of side groups to the ethylene chain reduces the degree of crystallinity and thus the light-scattering at the crystalline regions [6]. The melting temperature of PV-grade types of EVA is between 60 and 70°C, whereas the lamination temperature is around 150°C, depending on the peroxide curing agent that initiates the cross-linking reaction. During lamination, a three-dimensional network is formed by a chemical cross-linking of the polymer chains in order to increase the stability of the material and to prevent the material from melting when exposed to application-relevant temperatures of up to 100°C [2].

> “The degree of cross-linking is mainly controlled by the lamination temperature and the lamination time.”

Apart from the concentration of the curing agent, the degree of cross-linking is mainly controlled by the lamination temperature and the lamination time. Previous studies have shown that dynamic mechanical analysis (DMA) in shear mode allows a continuous measurement of the thermomechanical properties, even in the molten state, and therefore an in situ monitoring of the cross-linking reaction [7–10]. A good correlation between DMA results and the Soxleth extraction test was also found. Furthermore, it was shown that DMA measurements yield the highest sensitivity and reproducibility as regards the first few minutes of the reaction [7]. Hence, the main aim of this paper is to gain a comprehensive understanding, by using DMA in shear mode, of the thermomechanical material behaviour during the PV module lamination process, and to establish a basis for the optimization of the PV module manufacturing process.

To meet the objectives, a systematic investigation of the influence of the cross-linking process on the thermomechanical properties of EVA films was undertaken. Two different DMA measurement and evaluation concepts were chosen and are presented in this paper. On the one hand, temperature scans were carried out on partially cross-linked EVA in order to examine the changes in the thermomechanical properties due to the cross-linking process. On the other hand, isothermal scans on uncured samples were performed in order to study the curing kinetics. Finally, the potential for lamination process optimization is then determined from the results obtained.

Experimental and materials

Two commercially available EVA encapsulation films from two different manufacturers were selected for the studies (Table 1).

To ensure realistic processing conditions, two uncured EVA films were laminated together between two release films and a glass plate and cured at 146°C in a PV module laminator (Incapcell 43–24, Spaleck-Stevens, Bocholt, D). The lamination processing cycle consisted of four phases: evacuation (500 sec), compression (310 sec), cross-linking (varied between 300 and 1200 sec) and ventilation (50 sec). To obtain different degrees of cross-linking, the cross-linking time was varied systematically between 300 and 1200 sec. Table 2 summarizes the variation of the cross-linking and total lamination times.

The thermomechanical analysis was performed by DMA using a Perkin Elmer DMA 8000. Measurements were taken on a circular specimen (9mm diameter) in shear mode. Temperature scans of uncured and partially cured samples were carried out between room temperature and 200°C at a heating rate of 3K/min. The isothermal characterization of uncured samples was done at temperatures of 130, 140, 150, 160 and 170°C. Sample displacement was set to 20µm and the test frequency to 1Hz.

The thermal analysis was carried out using a Mettler Toledo DSC 821e instrument. Two heating runs needed to be performed in order to compare the uncured with the cured material and to ensure that the whole cross-linking process had occurred. A circular sample disc was cut with a punch, placed in a 40µl pan and closed with a perforated lid. In the first step, the material was heated up from 25°C to 200°C at a defined heating rate of 10K/min. The temperature was held at 200°C for 10 min and then the sample was cooled down to 25°C at a cooling rate of 10K/min. A second heating run up to 200°C was then started at the same heating rate of 10K/min in order to ensure that a complete cross-linking reaction had been achieved in the first run and that no exothermic peak was visible. The melting point and melting enthalpy were evaluated in accordance with ISO 11257-2 and ISO 11257-3.

Designation	Type	Film thickness [mm]	
		Uncured	Cured
EVA A	Ultra-fast cure	0.46	0.9–1
EVA B	Fast cure	0.45	0.9–1

Table 1. Materials selected for the studies.

Stage of curing	Duration [sec]	Total lamination time [min]
I	300	19.33
II	360	20.33
III	480	22.33
IV	600	24.33
V	720	26.33
VI	1200	34.33

Table 2. Variation of the cross-linking times.

Results and discussion

DMA in shear mode has proved to be a suitable tool for measuring the degree of cross-linking [7–10], as the cross-linking reaction directly affects the thermomechanical properties of the EVA films. In the following discussion the results of the temperature scans and the isothermal characterization will be presented. Furthermore, it will be shown how optimum processing parameters – such as cross-linking time and lamination temperature – can be derived from the results obtained.

> "DMA in shear mode has proved to be a suitable tool for measuring the degree of cross-linking."

Thermal behaviour

Fig. 1 shows the differential scanning calorimeter (DSC) thermograms of the

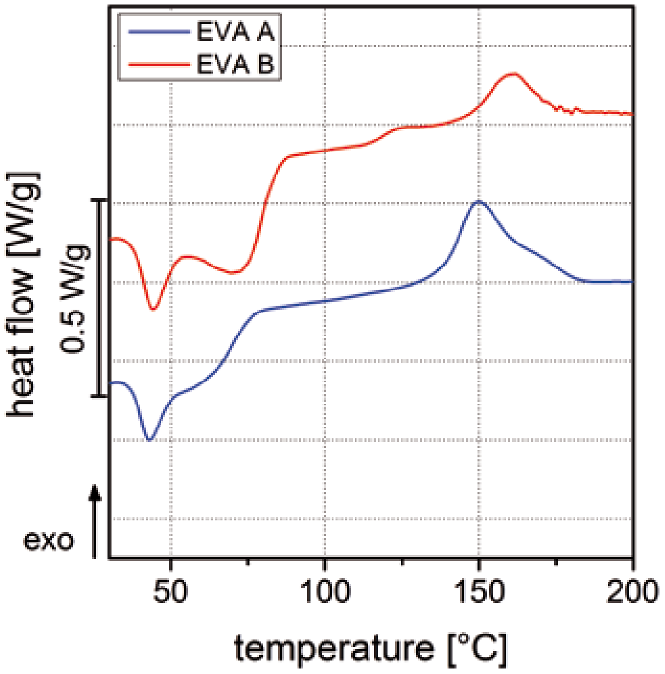


Figure 1. DSC curves of the uncured EVA films.

uncured EVA films. A melting stage can be seen between 30 and 80°C, with a single peak around 45°C and a shoulder between 60°C and 75°C, which is the thermodynamic melting point of EVA.

The peak at 45°C can be attributed to secondary crystallization, which occurs in the area between the primary crystals during slow cooling, storage at ambient temperature or exposure to elevated temperatures [3–5]. An exothermic reaction of the chemical cross-linking reaction due to peroxide decomposition can be observed between 115 and 190°C. Of course, different curing agents were used, which can be deduced from the differences in temperature limits, reaction enthalpy, or shapes of the peaks. A peak temperature of 150°C was measured for EVA A, whereas for EVA B a value of around 159°C was obtained. Furthermore, the two peaks of EVA B indicate a dual curing agent system, with the secondary peak around 125°C and the main reaction peak around 159°C [11].

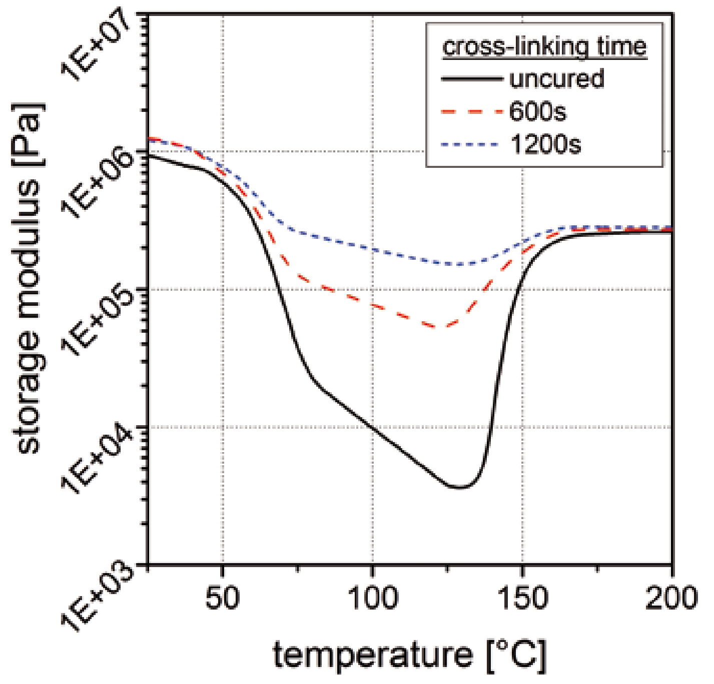
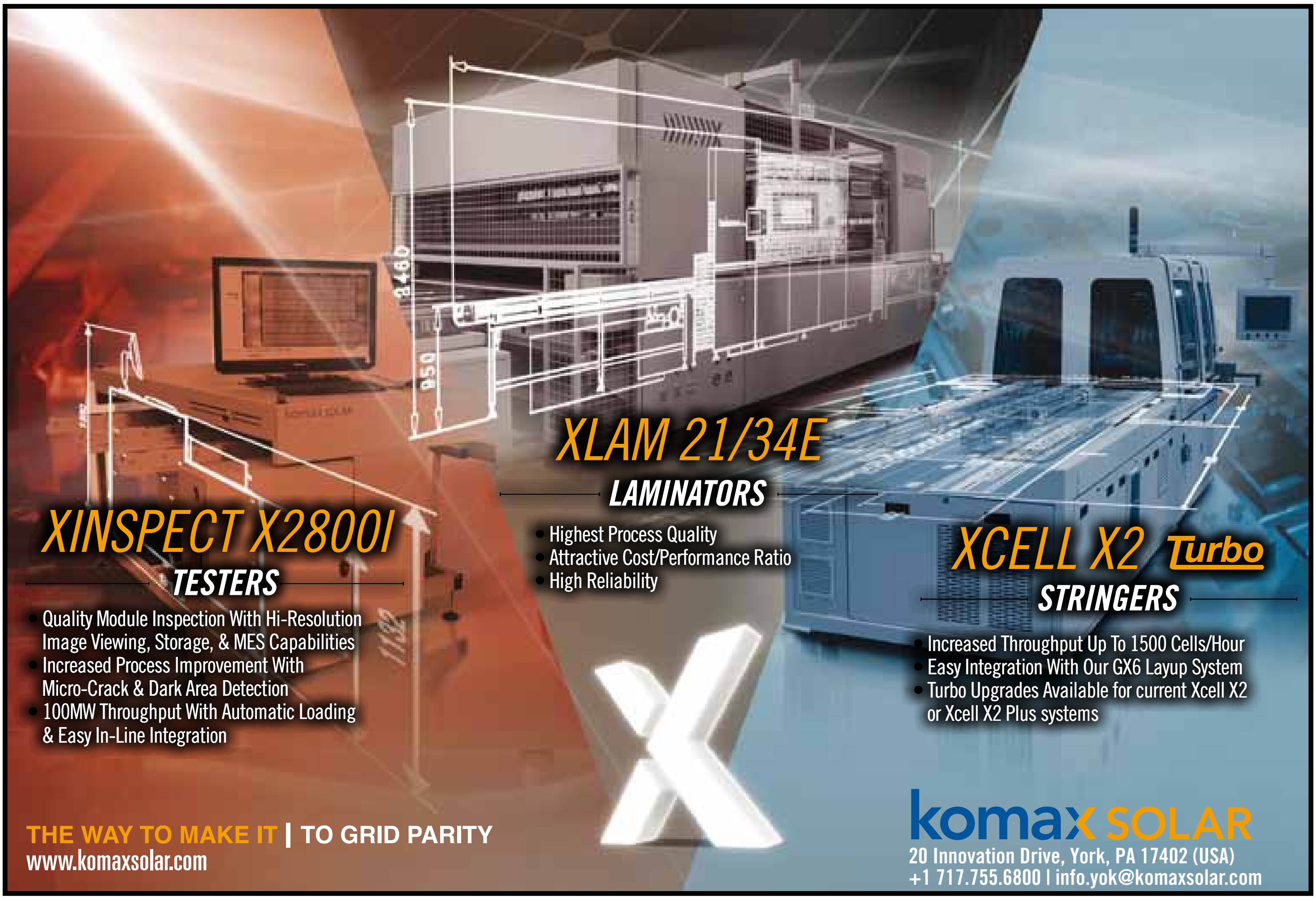


Figure 2. Temperature-dependent storage modulus for uncured and partially cured EVA B film.

Temperature scan

Fig. 2 shows the temperature-dependent shear storage modulus *G′* of the uncured and partially cured EVA B; Fig. 3 shows the temperature-dependent damping factor tan δ. The DMA measurements revealed a clear influence of the lamination time on the modulus and damping factor of the differently cured EVA films. From 60°C up to approximately 75°C, the storage modulus in shear mode (*G′*) drops, where the entire material is in the molten state. At the minimum of the modulus curve, around 125°C, the post-cross-linking reaction is thermally initiated, which is associated with a significant increase in the modulus. This correlates well with



the DSC measurements, where the onset of the exothermic cross-linking reaction was found to be around 115°C (see Fig. 1). The increase in storage modulus that follows can be attributed to the formation of a three-dimensional network. After 170°C the modulus levels off, becoming almost independent of temperature, which indicates the end of the cross-linking reaction.

For the differently cross-linked specimens, with increasing cross-linking time there is a smaller reduction in the shear modulus at temperatures above 60°C. The decrease in the modulus G' in the melting region is reciprocally proportional to the lamination time. At temperatures above 60°C, the longer the cross-linking time, the higher the molecular mass and the cross-linking density, and therefore the higher the modulus value.

Regarding the damping factor, however, the opposite behaviour was observed: after the melting region around 60°C, a strong increase in damping factor, which peaked around 125°C, was seen. This can be explained by the higher mobility of the polymer chains in the molten state. At 125°C the cross-linking reaction started and the mobility of the polymer chains was reduced by the increasing cross-linking density. With increased curing time, the damping factor of the partially and fully cross-linked specimen decreased significantly.

> "With increased curing time, the damping factor of the partially and fully cross-linked specimen decreased significantly."

For the correlation of thermomechanical properties with gel content, an appropriate indicator from the DMA curve has to be defined. Two possible candidates are the minimum of the shear modulus and the maximum of the damping factor as a function of lamination time. Both indicators show a clear correlation with lamination time and therefore with the actual state of cross-linking. Nevertheless, both indicators exhibit strong scattering between and during the different stages of curing, as these values can be influenced by various external factors, such as the positioning and clamping of the samples, the contact between the shear plates and the specimen, and the uniformity of the specimen preparation. To eliminate these variables, a recently developed self-referencing alternative method for determining the degree of cross-linking from DMA data [7] was applied here. This method involves determining the gradients of the linear sections on either side of the shear modulus minimum, and on the steady-state post-cross-linking section, as shown in Fig. 4. The intersection of these linear extrapolations on either side of the minimum yields the measurement point G'_1, while the intersection of the rising slope and the steady-state section gives the reference modulus G'_2. Taking the modulus ratio G'_2/G'_1 yields highly reliable and reproducible values. A further advantage of this method is that the modulus ratio always converges asymptotically to a value of one for fully cured materials.

Fig. 5 shows the modulus ratio for the EVA films investigated. Different curing behaviour was found for all materials. As expected, the fastest conversion was

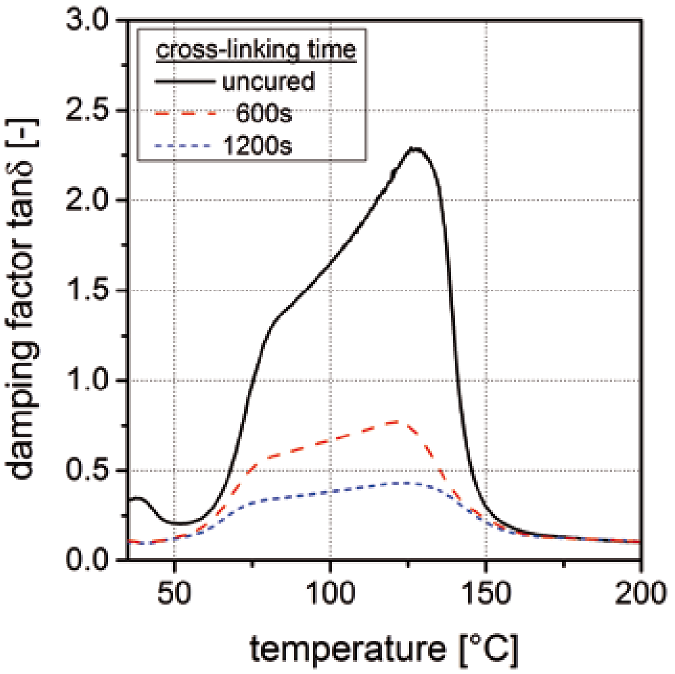


Figure 3. Temperature-dependent damping factor for uncured and partially cured EVA B film.

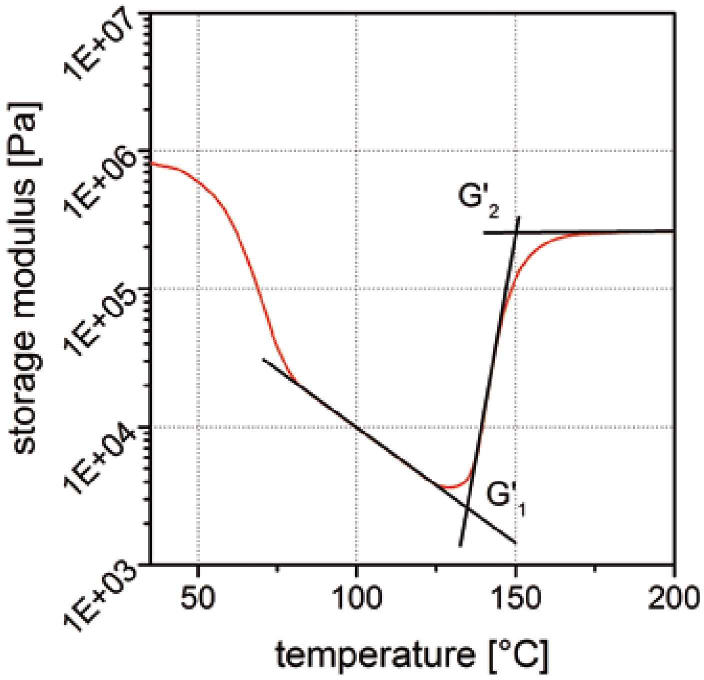


Figure 4. Formation of modulus ratio G'_2/G'_1.

observed for the ultra-fast-type EVA A, already reaching a sufficient state of curing after 360 sec of cross-linking time. The modulus ratio also reveals that a given lamination temperature of 146°C is far too low for a sufficient cross-linking of EVA B: a comparable state of curing was reached only after 1200 sec of cross-linking time. Temperature measurements during PV module laminations have shown that during the first few minutes the temperature of the EVA layer is usually up to 10°C lower than the given lamination temperature. Only by using longer processing times is a complete heating through of the EVA layer achieved. This assumption is supported by the comparison of the modulus ration curves over lamination time. For the ultra-fast-cure EVA A, significant cross-linking was already observed during the evacuation and compression cycle of the lamination process. For EVA B, however, no significant cross-linking could be detected up to 20 min of lamination time. The slight decrease after 20 min of lamination indicates the heating through of the EVA layer by achieving a sufficient temperature for the start of the cross-linking reaction. The temperature was nevertheless insufficient for a fast cross-linking reaction.

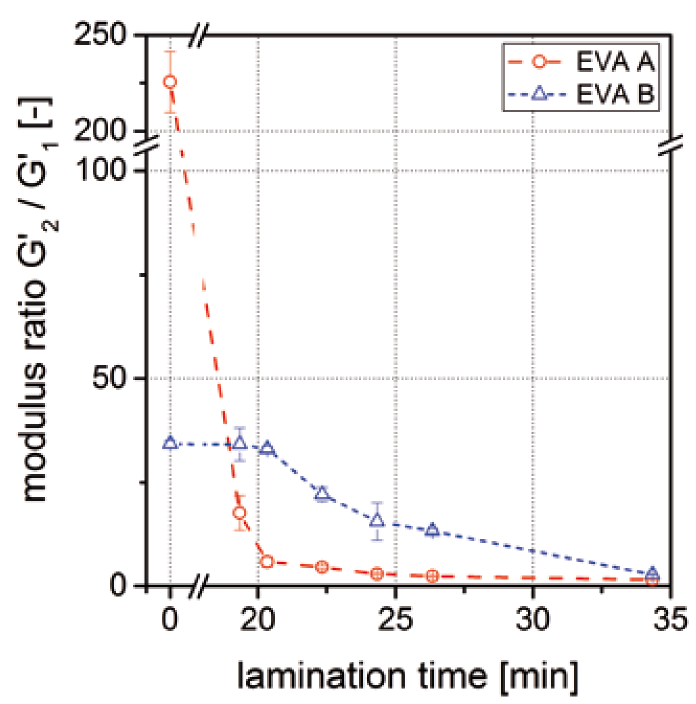


Figure 5. Modulus ratio G'_2/G'_1 as a function of lamination time.

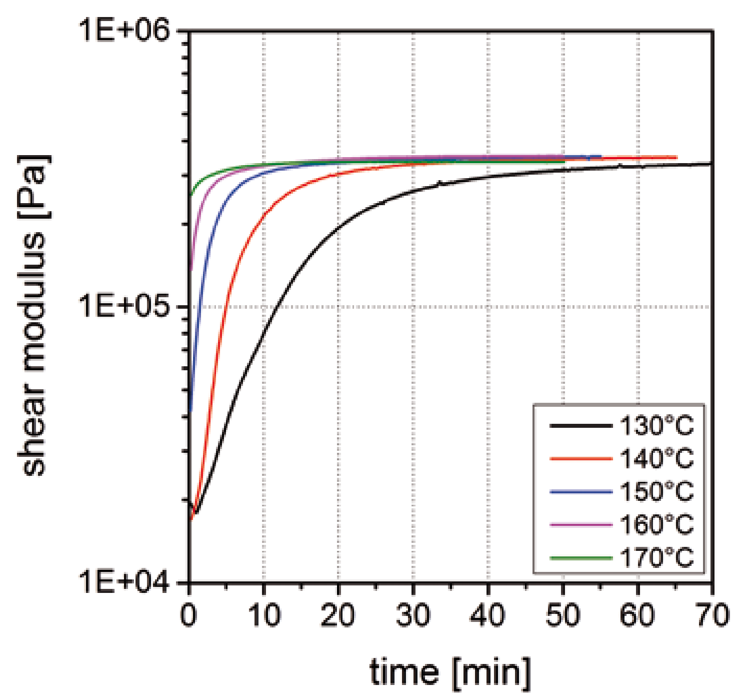


Figure 6. Storage modulus of EVA B as a function of time at constant temperatures between 130 and 170°C.

In a recent study a total of 16 different methods, ranging from classical solvent extraction through different thermoanalytic and mechanical approaches to acoustic and optical spectroscopy, were evaluated in order to investigate the state of cross-linking of EVA [7]. A good correlation between gel content and DMA measurements was found. Moreover, the analytical reliability of the DMA measurements was found to be superior to those of the reference methods, especially for short cross-linking times. From a thermodynamic point of view, a modulus ratio value of less than five indicates a sufficient state of cross-linking, which corresponds to gel-content values between 70 and 80% [7]. Further cross-linking above this state no longer has a significant effect on the thermomechanical properties.

Isothermal scan

In order to optimize the PV module lamination process, not only the final degree of cross-linking but also the kinetics of the curing reaction is of importance. The progress of the curing reaction can be monitored by measuring the thermomechanical properties at various constant temperature levels. The method will be presented next by showing the results of EVA B, which is representative of all the films investigated. Fig. 6 shows the storage modulus of the EVA film under investigation as a function of time at constant temperatures from 130 to 170°C. A significant increase in shear modulus with time was observed. The increase in shear modulus can be attributed to the formation of a three-dimensional network by radical chain reaction. The moment when the shear modulus levels off and becomes almost independent of temperature indicates the end of the cross-linking reaction. Moreover, a significant influence of temperature on the curing reaction can be observed. Whereas at 170°C the shear modulus values reach an almost constant level between 5 and 10 min, at 130°C the shear modulus values are still increasing after 60 min and have not yet reached a plateau. The significant temperature dependence of the curing reaction can be explained by the temperature profile of the exothermic reaction observed with DSC measurements (see Fig. 1)

To further evaluate the reaction kinetics, the shear modulus data have to be scaled and normalized. The scaling of measurement data is also necessary in order to compensate or reduce scattering due to measurement inaccuracies caused by sample preparation and handling. The conversion rate X can be calculated from the shear modulus $G'(t)$ as follows [10]:

$$X = \frac{G'(t) - G'(\mathrm{t}_0)}{G'(\mathrm{t}_\infty) - G'(\mathrm{t}_0)} \qquad (1)$$

where $G'(\mathrm{t}_0)$ is the initial shear modulus and $G'(\mathrm{t}_\infty)$ is the shear modulus of the fully cross-linked material.

> “There is no further acceleration of the cross-linking reaction with temperatures higher than 150°C.”

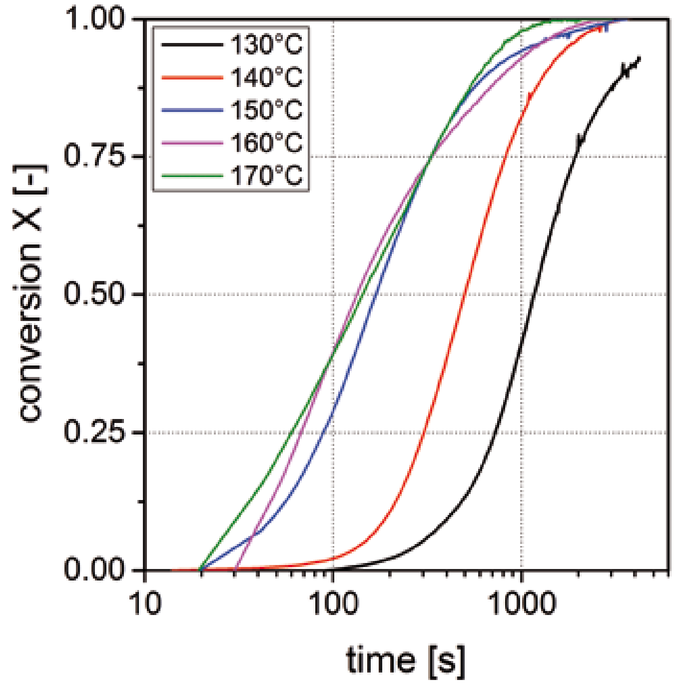


Figure 7. Conversion rate of EVA B as a function of temperature.

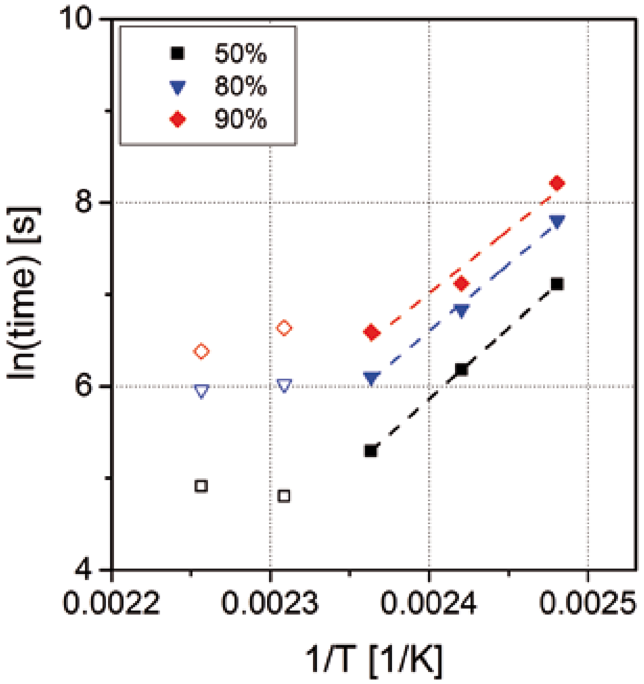


Figure 8. Arrhenius plot of EVA B for conversion rates of 50, 80 and 90%.

Fig. 7 shows the conversion rates at different temperatures. In general, higher lamination temperatures lead to faster initiation of the cross-linking reaction. Two main conclusions can be drawn from the calculated conversion rates: first, lamination temperatures of at least 140°C are necessary for full conversion to take place in realistic processing times (<900 sec); second, and more importantly, there is no further acceleration of the cross-linking reaction with temperatures higher than 150°C.

This can be seen even more clearly by using an Arrhenius law equation for the description of the cross-linking reaction. The Arrhenius law describes the rate constant k of chemical reactions for a certain temperature T and activation energy E_a:

$$k = \mathrm{A}e^{-E_a/\mathrm{R}T} \qquad (2)$$

where A is a pre-exponential factor and R is the universal gas constant. The only variable parameter and driving factor affecting the reaction rate (i.e. decomposition rate of the radical initiator) is the temperature. Fig. 8 shows the Arrhenius plot for the EVA film under investigation for conversion rates of 50, 80 and 90%. Between 130 and 150°C the Arrhenius plot reveals a linear correlation between the logarithmic time and the inverse temperature, with the activation energy as the gradient. A value of 125±7kJ/mol was calculated for the activation energy, which is in agreement with values found in the literature [10]. A further increase in temperature does not lead to an ongoing acceleration of the reaction rate, which can be seen in the more or less constant times for reaching the desired conversion rates at temperatures above 150°C.

This shows that optimum processing times and parameters can be derived using Arrhenius plots. At 150°C, conversion rates of 50, 80 and 90% can be achieved after 200, 330 and 730 sec, respectively, for the investigated material. Note that the lamination temperature on the laminator does not equal the temperature of the EVA layer presented here. Depending on the heating properties of the laminator and the module geometry, a delayed heating of the EVA layer takes place, usually resulting in lower temperatures in the EVA layer than the given lamination temperature.

The main advantage of isotherm scans is that no specific sample preparation is required – the investigations can be done on uncured EVA films. On the basis of the linear relationship between cross-linking time and temperature, and knowledge of the activation energy, a prediction of the progress of the curing reaction at any given temperature is possible. However, phase transitions and decomposition temperatures of polymers or curing agents must not be exceeded, and this must be taken into account. Generally, a prediction of the cross-linking time should only be done within the measured temperature range.

Summary and conclusion

The results presented in this paper demonstrate that DMA is a valuable and reliable characterization method for investigating the curing behaviour of EVA for solar cell encapsulation. DMA in shear mode allows the thermomechanical properties to be continuously measured (even for EVA in the molten state), and therefore the cross-linking reaction to be monitored in situ. The degree of cross-linking can be determined by performing temperature scans on partially cured EVA films. Isothermal scans on uncured samples enable the investigation of curing kinetics of EVA. On the basis of an enhanced knowledge of the cross-linking reaction material, the related process parameter optimization potential of the PV module lamination process can be identified, and optimum processing temperature ranges and minimum cross-linking times can be derived.

> “DMA is a valuable and reliable characterization method for investigating the curing behaviour of EVA for solar cell encapsulation.”

Regarding EVA B, temperature scans revealed that the chosen lamination temperature of 146°C was too low for a sufficient state of cross-linking within a reasonable processing time. The assumption was confirmed by DSC measurements, where the main cross-linking reaction peak was found at 159°C, whereas the temperature in the EVA layer during the first few minutes of cross-linking time is usually up to 10°C lower than the given lamination temperature. Only by using longer processing times can a complete heating through of the EVA layer and thus a full conversion be achieved.

Moreover, isothermal scans showed that temperatures greater than 140°C in the EVA layer are necessary for full conversion of the cross-linking reaction. Even more interestingly, further evaluation of the data using the Arrhenius law showed that temperatures above 150°C do not lead to a further acceleration of the cross-linking reaction.

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