

Investigation of the curing reaction of EVA by DSC and DMA

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ABSTRACT

In today's PV modules, the solar cells are commonly encapsulated in EVA. During lamination EVA undergoes a crosslinking reaction. From a practical point of view, two major interests arise. For quality control purposes, one needs to know the degree of curing of the EVA encapsulant after lamination. The focus in process optimization is on understanding the kinetics of the crosslinking as a chemical reaction. If this is known (and proven), one can predict appropriate crosslinking conditions (i.e. lamination temperature and time) that have to be matched to reach a certain degree of crosslinking. This contribution mostly deals with this latter aspect. DSC as well as DMA data and model-free kinetics were used in this study to establish the kinetics of the EVA crosslinking process. It was found that both techniques adequately predict the degree of crosslinking for any temperature as a function of the curing time.

Introduction

Solar cells are most commonly encapsulated in EVA (ethylvinylacetate), which serves as a sealant and adhesive to the front (most commonly glass) and the back layer (usually glass or tedlar – a polyvinylfluoride).

EVA is widely used because of its excellent long-term behaviour regarding strength, mechanical behaviour, encapsulation properties, high transmittance in the VIS, UV stability, electric insulation capabilities and its low cost. EVA is a block copolymer consisting of typically 65% polyethylene and 35% VA (see Fig. 1). Uncured EVA is a thermoplastic that exhibits a glass transition and melting. To become usable as an encapsulant for PV applications it has to be crosslinked, a task that is usually achieved by peroxides. Upon heating, peroxides decompose into two oxy radicals that may both withdraw a hydrogen atom from a single EVA molecule and thus initiate the crosslinking process. Only at this stage does EVA become a mechanically durable material as is needed in PV modules. For process and quality control purposes, it is important to have a tool providing information regarding the degree of curing reached after or during processing.

The usual way to determine the crosslink density of EVA is by solvent extraction [1]. DSC measurements can be used for this purpose, as recently demonstrated [2]. In this contribution, the aim is not only to determine the degree of curing but also to investigate the crosslinking process as a kinetic phenomenon and to describe the degree of curing as a function of temperature (dynamic experiments) or time (isothermal experiments). We show how this can be achieved by using DSC and DMA data and model-free kinetics.

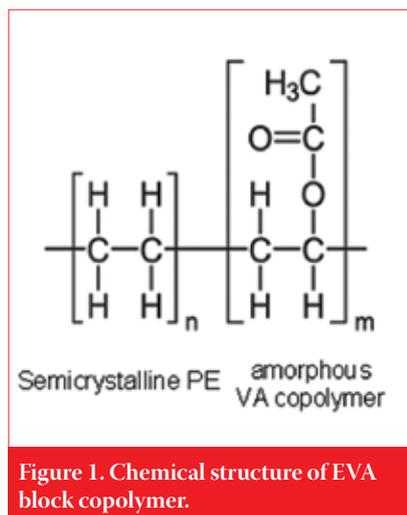


Figure 1. Chemical structure of EVA block copolymer.

Experimental

Samples

The EVA sample was available as a film with a thickness of 0.43mm. From this film, disk-like test specimens were cut out. To prepare the samples for the postcuring experiments (DMA and DSC), fresh EVA test specimens were kept isothermally in the DSC for the specified times.

DSC experiments

DSC experiments were performed using a Mettler Toledo DSC 1 equipped with an intracooler and FRS5 sensor. Samples were encapsulated in 40 μ l aluminium pans, the typical sample mass being between 5 and 6mg. The heating and cooling rates are indicated in the respective figures.

DMA experiments

DMA experiments were performed with Mettler Toledo's DMA/SDTA861^e. In a DMA the test specimen is subjected to a sinusoidally varying force. As a consequence the test specimen is deformed. However, it generally does not immediately react to the

periodically changing force, i.e. there is a phase shift between the applied force and the deformation. This phase shift characterizes the viscoelastic properties of the sample. Based on the force and deformation amplitudes, the phase shift and the geometry of the test specimen, the storage and loss components of the complex modulus can be calculated. Its real part (i.e. the storage modulus) is a measure of the mechanically stored energy in the test specimen. The imaginary part (i.e. the loss modulus) describes that part of the mechanical energy that is dissipated into heat and therefore irreversibly lost.

“Based on the force and deformation amplitudes, the phase shift and the geometry of the test specimen, the storage and loss components of the complex modulus can be calculated.”

The tangent of the phase shift, $\tan \delta$, is also known as the loss factor and is a measure of the damping behaviour of the material. The modulus and $\tan \delta$ depend on the temperature and the measuring frequency. At room temperature, rubbery materials (such as EVA) show typical storage modulus values between 0.1MPa and 10MPa. In dynamic mechanical analysis, the modulus is determined as a function of temperature, frequency and amplitude. Depending on how the force is applied to the test specimen, either the shear modulus (in shear mode), G , or the Young's modulus, E , (in tension or bending mode) is measured.

All measurements were carried out in shear mode for this particular study. Disks

with a diameter of 4mm and a thickness of 0.43mm were used as samples. The maximum applied force was 5N; the maximum displacement was 5µm; and all measurements were performed at 1Hz. The used heating rate is indicated in the respective figures.

Model-free kinetics

Chemical reactions are usually described by the general rate equation which relates the reaction rate, $\frac{d\alpha}{dt}$ to a function describing the temperature dependency of the reaction, $k(T)$, and a conversion-dependent model function that describes the course of the reaction, $f(\alpha)$, i.e.

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

The temperature dependence of the reaction rate is described by the well-known Arrhenius equation:

$$k(T) = k_0 e^{-E_a/RT}$$

Here k_0 is the pre-exponential factor, E_a is the activation energy of the reaction, R the gas constant, and T the temperature. The model function is generally unknown and needs to be specified for each reaction separately. For complex reactions this is generally not possible, especially because it is not only chemistry that determines the course of a reaction but also

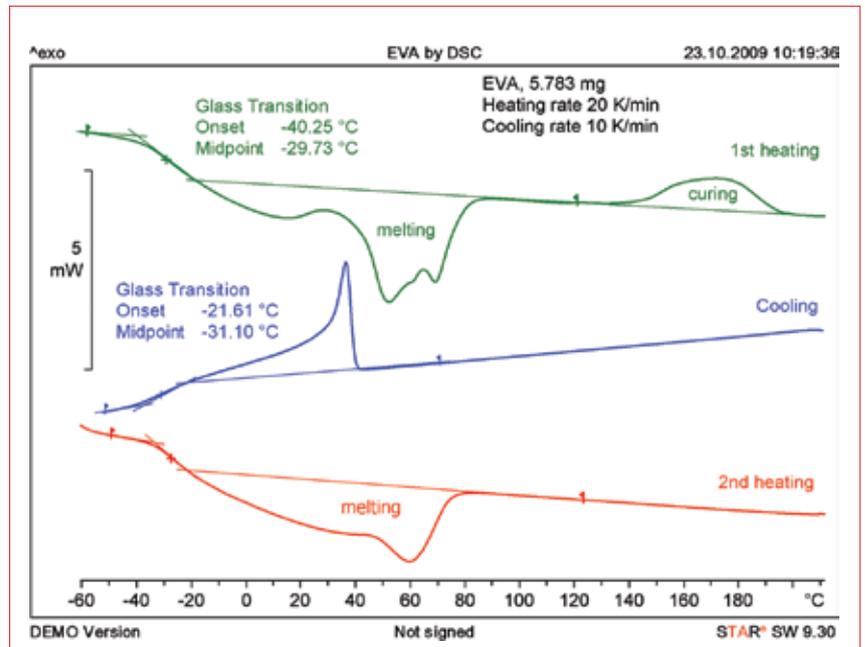


Figure 2. Graph showing 1st and 2nd heating and the intermediate cooling experiment on a fresh EVA sample. Basic effects are the glass transition (around -30°C), melting (between -30 and 80°C) and the curing reaction (around 170°C), the latter showing up only during the first heating. The exothermal peak during cooling is due to crystallization.

transport processes among the reactants. Furthermore, the concept of a constant activation energy throughout the reaction is doubtful if several reactions are running in parallel. Therefore, a holistic model-

free approach to describe the kinetics of complex reactions has been proposed. In model-free kinetics (MFK), the activation energy depends on the degree of conversion. Apart from the ongoing

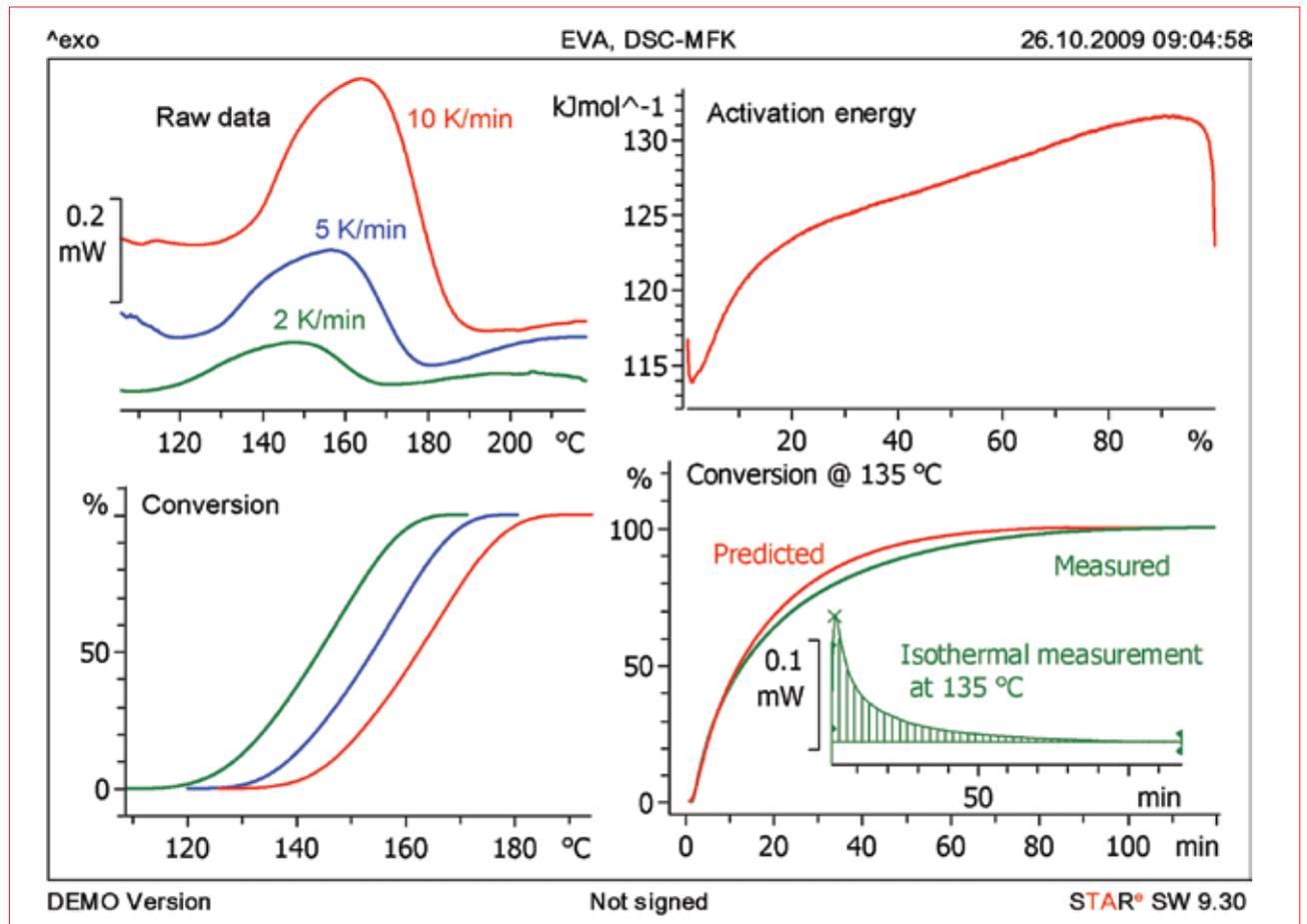


Figure 3. Model-free kinetics of the curing reaction of EVA based on three DSC experiments with different heating rates.

chemical reactions, it also describes other processes such as diffusion among the reactants. Therefore, it is understood as an apparent activation energy, thus lacking the strict interpretation of the activation energy.

“In model-free kinetics (MFK), the activation energy depends on the degree of conversion.”

MFK is based on the isoconversion principle, which states that at any particular conversion, the reaction rate depends only on the temperature, and is independent of the heating rate. A practical implication of the isoconversion principle is that in order to calculate the apparent activation energy, at least three experiments have to be performed under different thermal conditions, each also requiring calculation of each experiment's respective conversion curves. Based on the conversion curves the apparent activation energy is determined as a function of the conversion. Several different procedures have been proposed to calculate the apparent activation energy. This study uses the procedure developed by Vyazovkin (see [3] and references

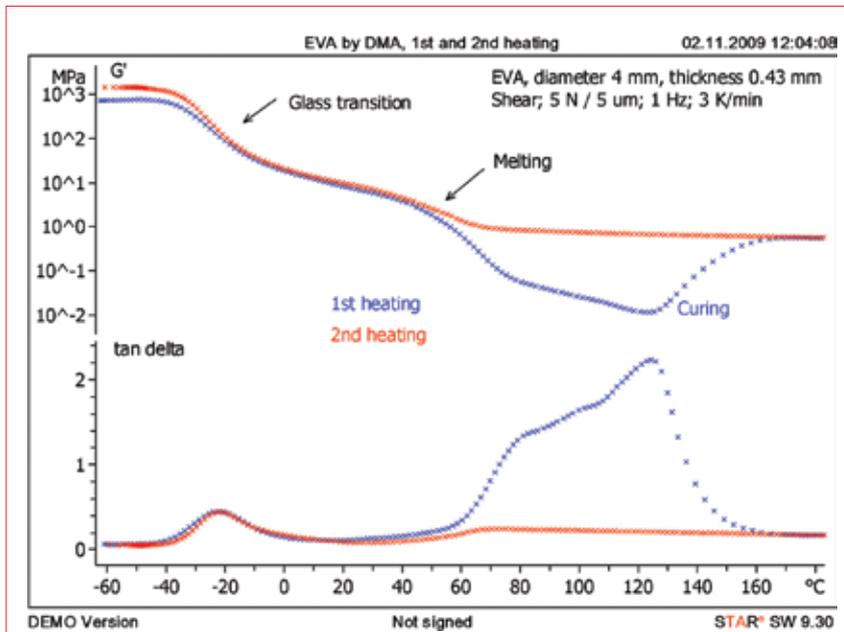


Figure 4. DMA experiments of uncured and cured EVA.

therein). In principle, the MFK approach can be used for any kind of experimental data that describe the reaction and that can be converted into a conversion curve.

Results and discussion

DSC experiments

In Fig. 2 the DSC curves of the 1st heating, the subsequent cooling and the 2nd

heating experiment on a fresh EVA sample are shown. During the 1st heating one can first see the glass transition followed by melting. The exothermic peak at around 170°C is due to the curing reaction of EVA. The cooling and 2nd heating curve of the sample support this interpretation: the glass transition shows up on both experiments; during cooling we

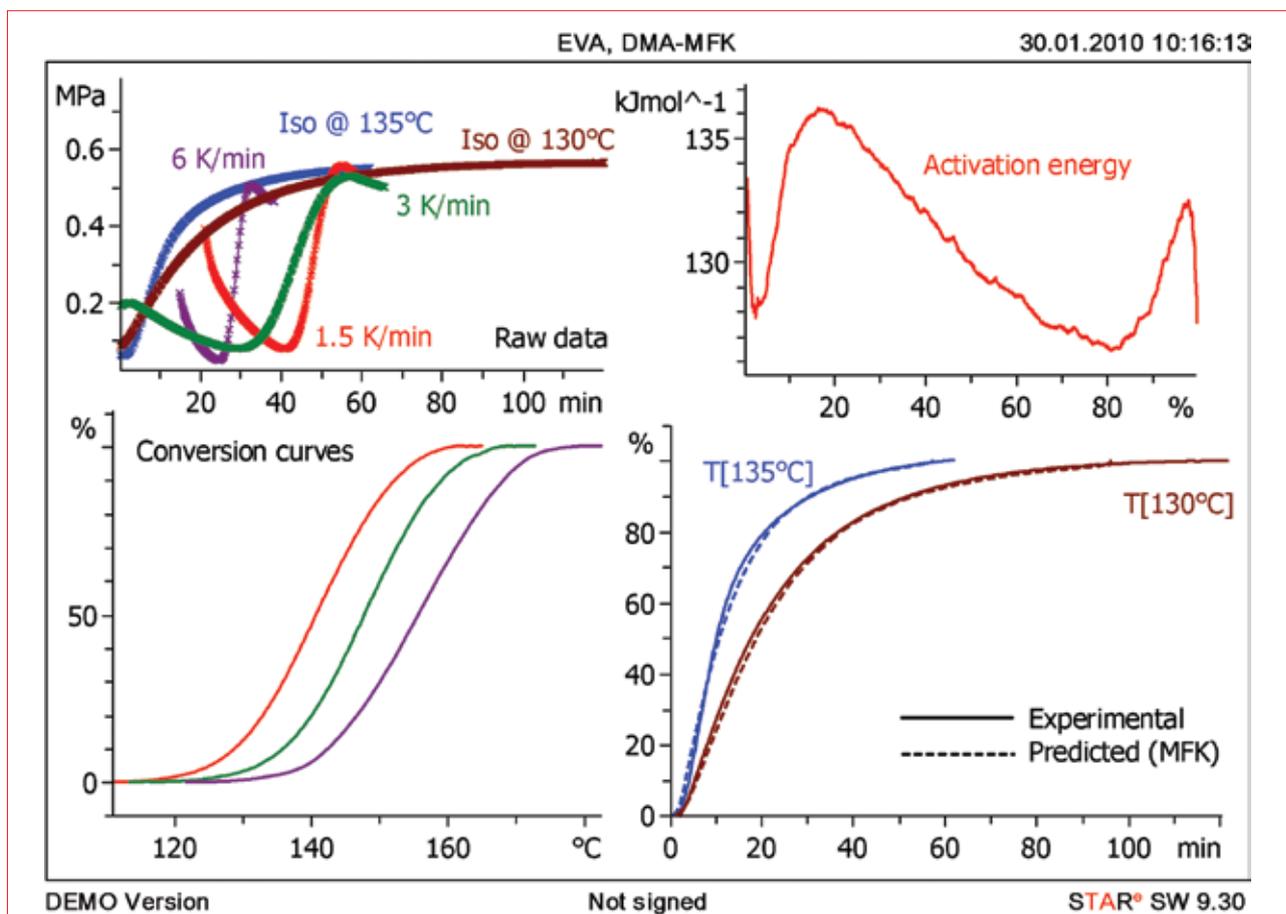


Figure 5. Model-free kinetic analysis of DMA data.

additionally find crystallization and upon the 2nd heating, another melting takes place. The different shape of the melting peaks of the 1st and the 2nd heating is due to the changing thermal history of the sample.

To study the kinetics of the reaction, model-free kinetics were applied using three different heating rates (2, 5 and 10K/min; see top left diagram in Fig. 3). In order to get the degree of conversion at a certain temperature, the partial area of the reaction peak up to this temperature, $\Delta H_p(T)$, is normalized to the overall reaction enthalpy, ΔH_{tot} as follows:

$$\alpha(T) = \frac{\Delta H_p(T)}{\Delta H_{tot}}$$

Based on the conversion curves of the reaction peaks (bottom left diagram in Fig. 3), the activation energy is calculated as a function of the conversion (top right diagram in Fig. 3). The conversion-dependent activation energy can now be used to make isothermal predictions, as illustrated in the bottom right diagram in Fig. 3 for 135°C. The diagram also shows the result of the corresponding isothermal experiment. In conclusion, a reasonable agreement is found between what is predicted by model-free kinetics and actual experimental data.

Using DSC data for this particular reaction is questionable in that as apart

of the curing reaction the peroxide decomposes during the reaction. This of course also affects the measured DSC signal; i.e. the measured signal in the curing temperature range arises as the sum of the curing reaction and the degradation of the peroxide. Therefore, to exclusively follow the curing reaction and thus to validate the DSC results, an alternative experimental technique is needed.

“Based on the activation energy, the isothermal course of the curing reaction can be predicted at any temperature.”

DMA experiments

Network density increases during a curing reaction. For low network densities, as is the case for the EVA sample investigated here, the modulus is proportional to the network density. Thus, the curing process can also be monitored by measuring the modulus, and can be carried out experimentally using DMA. Fig. 4 shows the shear storage modulus, G' , and $\tan \delta$ during the 1st and 2nd heating as measured by DMA. One can clearly distinguish the glass transition at around

-20°C followed by the melting and the curing reaction, which begins at around 125°C. The variation of the modulus during the curing reaction depends on the applied frequency, which decreases as the frequency is increased. The selected frequency of 1Hz compromises a short measurement time (resolution) and high sensitivity towards the cross linking.

In order to apply model-free kinetics, the curing effect on the modulus has to be transformed into a conversion curve describing the progress of the curing reaction. This can be done by normalizing the difference of the modulus during curing, $G'(T)$, and the modulus before curing, G'_{bc} , to the difference of the plateau modulus, G'_p , and the modulus before curing, as illustrated in the following equation:

$$\alpha(T) = \frac{G'(T) - G'_{bc}}{G'_p - G'_{bc}} \quad (1)$$

Using this equation, the three curves for G' shown in the top left diagram of Fig. 5 result in the respective DMA conversion curves (bottom left diagram, Fig. 5). The conversion-dependent apparent activation energy can be calculated from these curves (top right diagram, Fig. 5). Based on the activation energy, the isothermal course of the curing reaction can be predicted at any temperature (bottom right diagram,

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Fig. 5; predictions are shown for 130°C and 135°C). Again the predicted and actually measured isothermal conversions agree reasonably well with each other.

In Fig. 6 the conversion-dependent activation energy as well as the predictions on the curing reaction and its corresponding experimental isothermals at 135°C are compared for the DSC- and DMA-based data. It can be seen that the gross value of the activation energy is the same for both techniques, and while the predicted conversion curves agree reasonably well, DMA predicts slightly higher degrees of conversion. The reason for this is due to the fact that the DMA degree of conversion depends on the plateau modulus (see Equation 1). The plateau modulus, however, changes during the experiment (see Fig. 4, 2nd heating). This analysis assumed the modulus value at the end of the curing reaction as the plateau modulus, leading to an overestimation of the DMA conversion of – in a worst-case scenario – about 8%.

“For large degrees of curing, the postcuring effect may become difficult to quantify.”

Postcuring experiments

For quality control purposes, one has to rely on postcuring experiments, i.e. comparing the postcuring effect of a processed sample to a previously measured overall curing effect. In a similar way, isothermal process conditions can be experimentally verified and optimized. Postcuring studies can be performed both with DMA and DSC. Several samples have been precured for different times at 135°C and then dynamically postcured. Respective results are shown in Fig. 7.

The bottom diagram in Fig. 7 displays DSC postcuring. It illustrates that the postcuring peak is relatively broad and the related enthalpies are rather small. Consecutive experiments on samples that have been precured the same way indicate that the reproducibility regarding the degree of curing is around 5%. The top diagram in Fig. 7 shows the data for DMA postcuring experiments. For large degrees of curing, the postcuring effect may become difficult to quantify. Based on the data shown in Fig. 7 one can plot the degree of curing as a function of the curing time, as shown in Fig. 8. It is clear from Fig. 8 that the DMA experiments deliver slightly lower degrees of curing. This can be explained by the fact that due to degradation of the peroxide in the EVA,

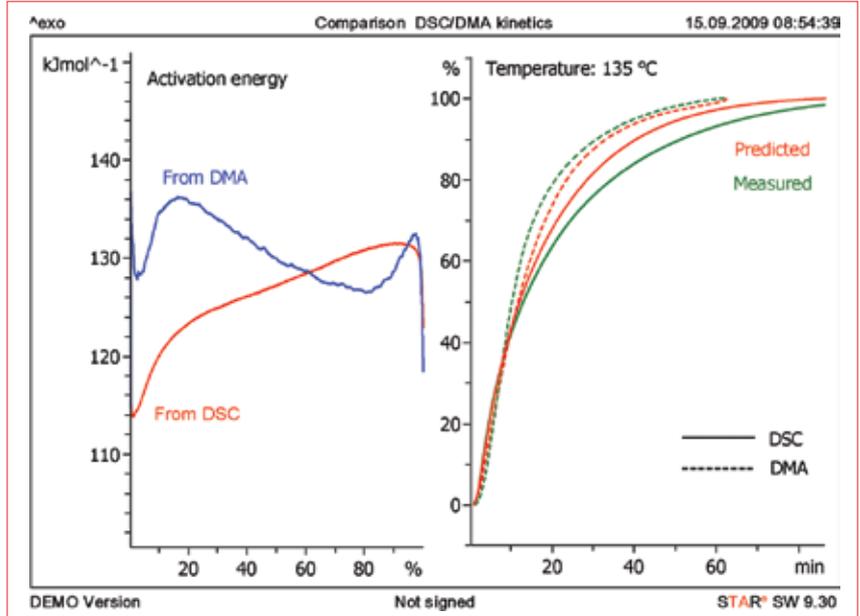


Figure 6. Comparison of DSC and DMA results on the curing of EVA.

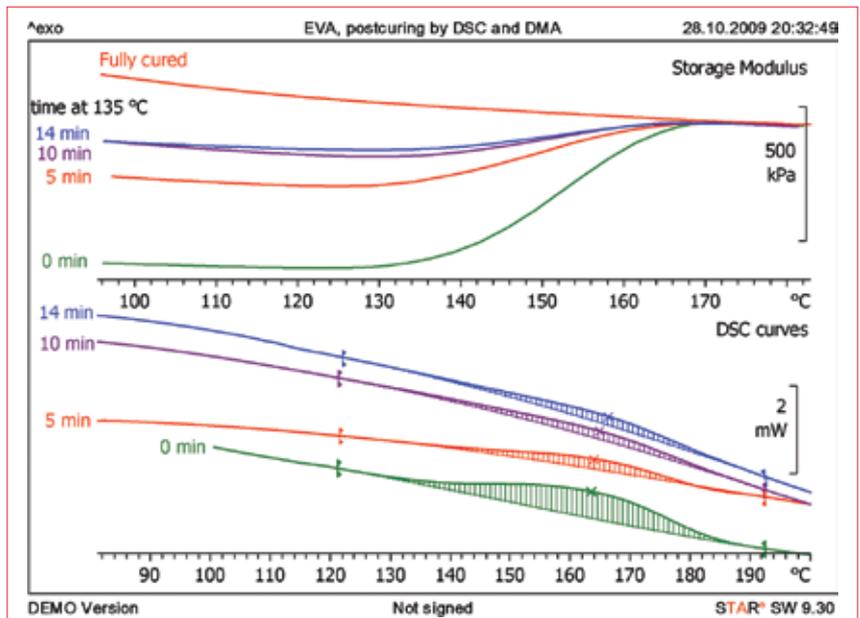


Figure 7. Postcuring by DSC (bottom) and DMA (top).

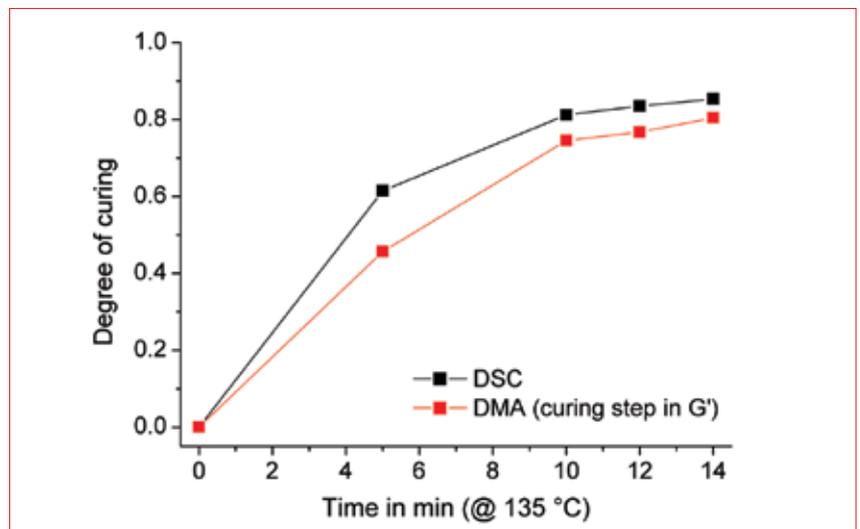


Figure 8. Degree of curing at 135°C as a function of curing time.

the 100% curing enthalpy as measured by DSC is too low. Consequently, the measured postcuring enthalpies are slightly too high.

“The comparison of DSC and DMA results shows that both techniques deliver consistent results.”

The degree of curing of processed samples was also analyzed. From DSC a degree of curing of about 68% was seen, the uncertainty being in the region of 5%. This value again agrees well with respective DMA measurements, which delivered a degree of curing of 71%, the uncertainty being also around 5%. It can therefore be concluded that within an uncertainty range of about 5%, DSC and DMA results deliver equivalent results regarding the degree of curing.

Conclusions

Both DSC and DMA experiments can be used to investigate the kinetics as well as the postcuring, and thus the degree of curing of EVA. DMA delivers the more

reliable results because it is sensitive only to the curing process. DSC on the other hand is affected by the degradation of peroxide acting as a curing agent for EVA. However, the comparison of DSC and DMA results shows that both techniques deliver consistent results. Thus, optimization of lamination process conditions can be achieved by applying model-free kinetics to either DSC or DMA data. The benefit of using DMA lies in the fact that this approach also delivers information about the temperature and frequency-dependent viscoelastic properties of EVA.

Acknowledgment

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About the Author



Dr. Markus Schubnell graduated from Bern University, Switzerland with a Ph.D. in physics. He has been working at Paul Scherrer Institute in Switzerland in the field of solar energy (high temperature solar chemistry, thermophotovoltaics) for about 10 years. He is now working at the University of Applied Sciences Northwestern Switzerland as well as with Mettler Toledo GmbH. His interests are focused on the use of thermal analysis (DSC, DMA) of polymers, among other materials.

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