Curing kinetics of EVA using DSC, DMA and model free kinetics

The use of solar panels is well-known for converting sunlight to electricity. This so-called photovoltaic electrical power is expected to make an important contribution to providing a sustainable supply of energy in the future.

Introduction

A photovoltaic module consists of arrays of jointly connected solar cells. An important step in the manufacture of a photovoltaic module is encapsulation. In this production step, solar cells are encapsulated between a glass sheet and a Tedlar film as backing sheet.

Encapsulation is commonly performed using a 0.4-mm thick ethylene-vinyl acetate (EVA) film. It seals the module and protects it against environmental influences such as moisture, oxygen, and weathering. This is very important because a guaranteed lifetime of 25 years is nowadays usual. In this article, we show how DSC and DMA experiments followed by evaluation with model free kinetics were used to investigate the curing behavior of EVA during the lamination process. Studies like this allow the optimum lamination conditions to be determined; the results can also be used for quality control.

In modern photovoltaic modules, the solar cells are encapsulated between a glass sheet and a backing sheet, usually a Tedlar® film [1, 2, 3], as illustrated in Figure 1. Sheets of ethylene-vinyl acetate (EVA) are placed between the solar cells and the backing sheet and the glass. In
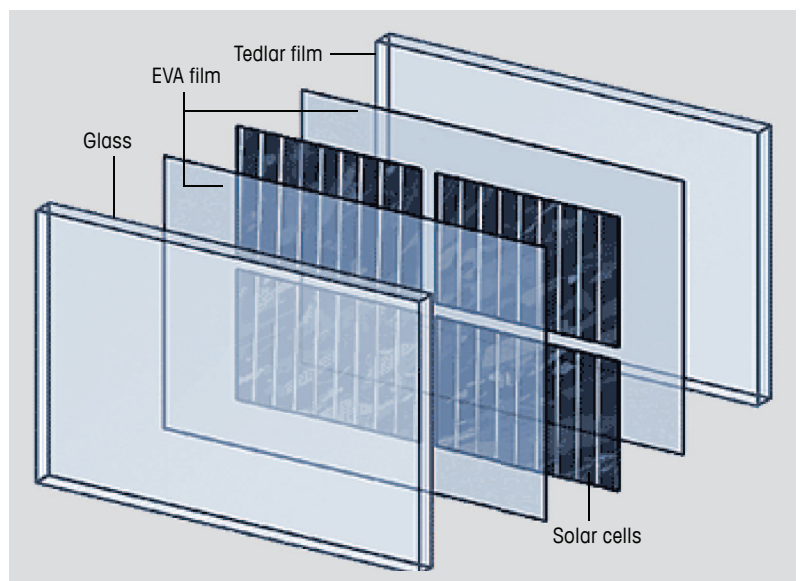

Figure 1: Construction of a photovoltaic module.

the production process, the sandwich is pressed into place and heated. The EVA cures and provides a permanent and tight seal.

EVA has many excellent long-term properties such as its optical transmittance in the visible region, chemical resistance toward UV light, and electrical insulation. EVA is a block copolymer and in this application typically consists of 67% polyethylene and 33% vinyl acetate (see Figure 2). Uncured EVA is a thermoplastic material that on heating first

exhibits a glass transition and then a melting process. In the curing process, the EVA chains underg§o crosslinking.
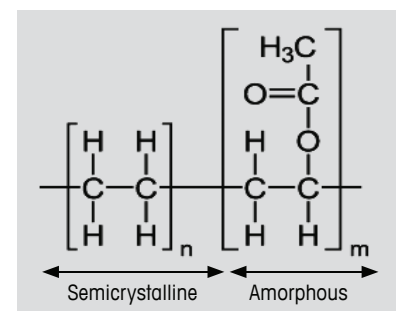

Figure 2: Chemical structure of EVA.

The curing reaction is initiated by a peroxide compound. This decomposes on heating and splits into two oxyradicals that promote the crosslinking of the EVA polymer. EVA only becomes mechanically and chemically resistant at the high temperatures that occur in photovoltaic modules (up to 80 °C) after this curing process.

It is important to determine the degree of cure of the EVA in order to optimize the lamination conditions and control the quality control of the finished photovoltaic modules. In the past, this was done using a method based on solvent extraction. Recently it was shown that DSC measurements can also be used [4].

In this article, we show how the curing reaction can be described by model free kinetics using data from DSC and DMA measurements. This allows the lamination process to be optimized with regard to temperature and lamination time.

Experimental details

Samples

The sample consisted of a piece of uncured EVA film, 0.4-mm thick, such as is used in the solar industry. Disks with a diameter of 3 mm were then punched out from this sample and used for the different experiments. The mass of a disk was typically about 5.8 mg.

DSC measurements

The DSC measurements were performed using a DSC 1 equipped with an Intra Cooler and an FRS5 sensor. The disks were measured in 40-µL aluminum crucibles with a hole in the lid. The purge gas was nitrogen at 50 mL/min.

DMA measurements

The DMA measurements were performed in the shear mode using the DMA/SDTA861ᵉ. The maximum force and displacement amplitudes were 5 N and 5 µm.

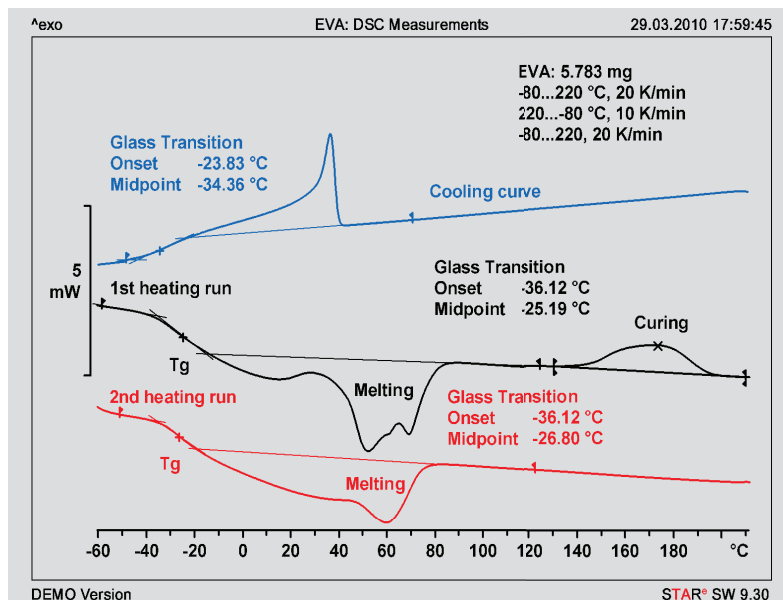### TGA measurements

The TGA measurements were performed

Figure 3: EVA measured at 20 K/min: first heating run, the cooling curve, and the second heating run.

using a TGA/DSC 1 equipped with a DTA sensor. The purge gas was nitrogen at 50 mL/min.

Results

DSC-and TGA experiments

Figure 3 shows the first and second DSC heating runs of EVA measured in the range −60 °C to 220 °C at a heating rate of 20 K/min. In the first heating run, the glass transition is clearly visible at about −30 °C. The sample then melts and the exothermic curing reaction occurs at about 170 °C. The glass transition is also observed in the second DSC heating run. The melting peak appears different because the thermal history of the sample was eliminated in the first heating run. An exothermic peak no longer occurs at 170 °C, which indicates that the sample reached its maximum degree of cure during the first heating run. The cool-
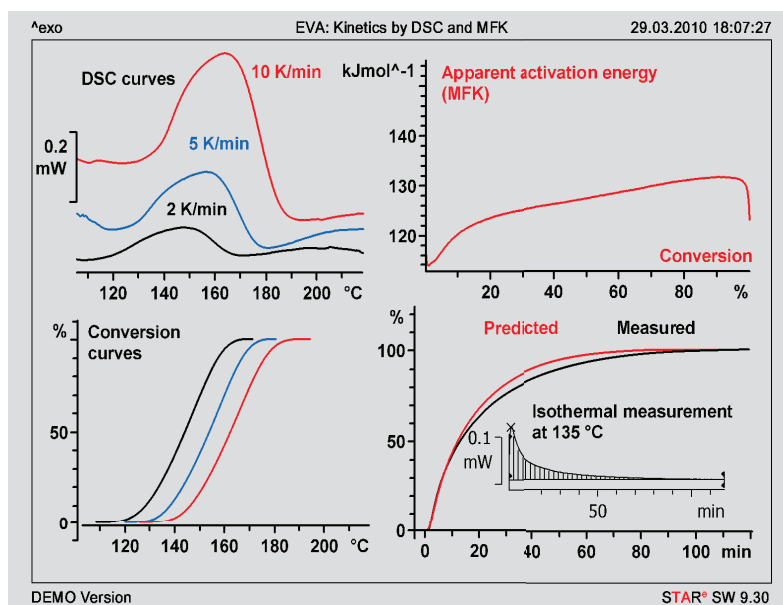

Figure 4: DSC/MFK evaluation. Above left: DSC heating curves. Below left: the calculated conversion curves. Above right: the apparent activation energy curves. Below right: predicted curve for isothermal curing at 135 °C and the isothermal measured curve.

ing curve shows a very broad exothermic crystallization peak followed by the glass transition. The latter does not appear to be significantly influenced by the curing reaction.

The kinetics of the curing reaction was investigated using model free kinetics (MFK) [5, 6].

This method requires data from at least three experiments performed at different dynamic heating rates, in this case at 2, 5, and 10 K/min (Figure 4, above left). The corresponding conversion curves were then calculated from the DSC curves (Figure 4, below left) and the data used to calculate the activation energy as a function of the degree of conversion or curing (Figure 4, above right). The activation energy is used to make predictions about the degree of cure as a function of the curing time under isothermal conditions. This is illustrated in Figure 4 (below right) for a temperature of 135 °C. The curve measured in an isothermal DSC measurement performed at the same temperature is also shown. A comparison of the two curves shows that the MFK prediction agrees well with the experimental data.

A TGA measurement of an uncured EVA sample (Figure 5) showed that a small loss in weight of 0.66% occured between 100 and 220 °C. This indicates that the decomposition reaction of the peroxide and the curing reaction of the EVA occur simultaneously. The DSC signal of the uncured EVA in this temperature range is therefore the sum of the decomposition reaction of the peroxide and the curing reaction of the EVA. The question therefore arose as to how accurately the kinetics of the curing reaction of EVA can be described by DSC. This led us to look for a method that is sensitive only to the curing reaction.

DMA experiments

During a curing reaction, molecules undergo crosslinking and form a network. The network density increases with in-
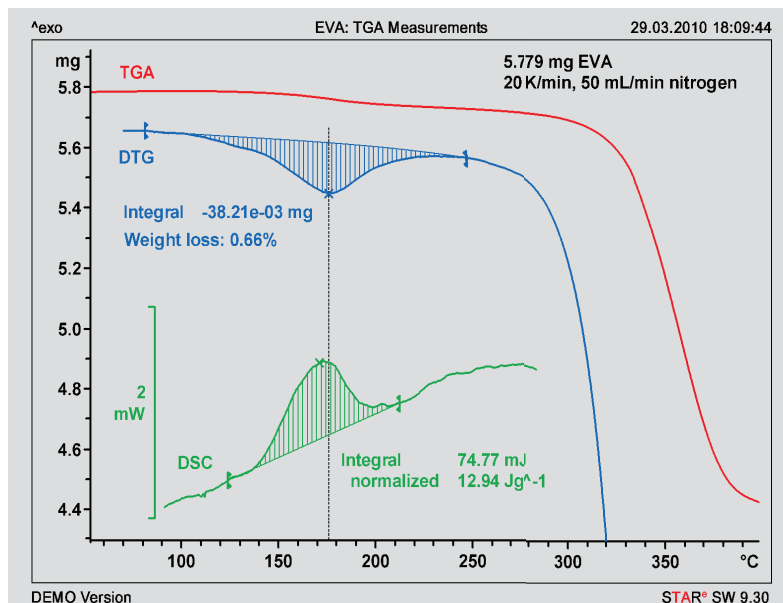

Figure 5: The TGA curve of uncured EVA shows a weight loss of about 0.66% between 100 and 250 °C.

creasing time (in an isothermal experiment) or with increasing temperature (in a dynamic experiment). For low network densities (as in this case), the modulus is proportional to the network density. The curing process can therefore be studied by measuring the modulus, for example in a suitable DMA experiment, as illustrated in Figure 6.

The DMA measurements in the range −60 °C to 200 °C show the storage modulus, G'' (the real component of the complex shear modulus), and the loss factor, tan delta, during the first and second heating runs. The first step in the storage modulus and the peak in tan delta at about −22 °C correspond to the glass transition of the vinyl acetate (VA) part. The second step in the storage modulus at about 55 °C is due to the melting of PE crystallites. During the first heating run, the sample becomes liquid at about 70 °C (tan delta > 1). From about 120 °C onward, the modulus increases and at the same time the loss factor decreases.
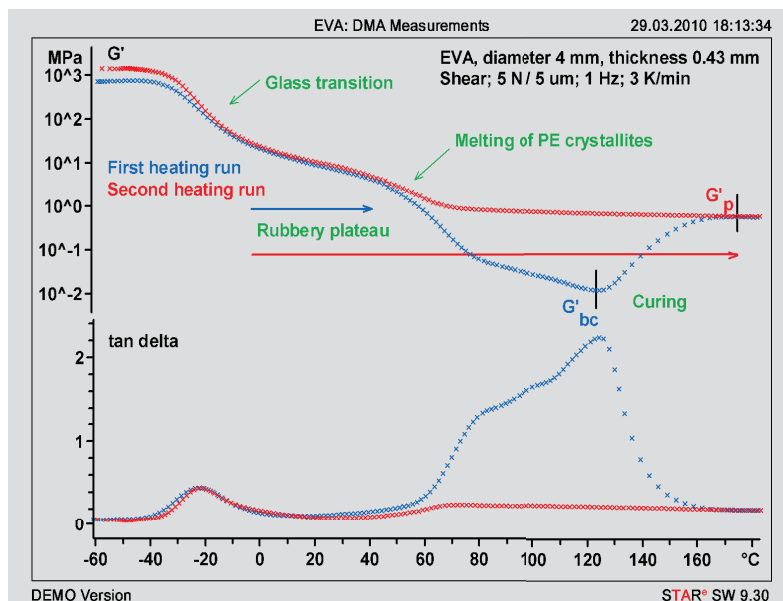

Figure 6: DMA measurements showing first (blue) and second (red) heating runs.

This indicates that the material loses its liquid-like character and becomes rubbery (tan delta << 1) as a result of the beginning of the crosslinking reaction.

In the second heating run, the PE crystallites also melt at about 55 °C. However, they are now embedded in a crosslinked VA matrix, which gives the material a certain amount of mechanical stability. After melting, the loss factor therefore remains significantly smaller than in the first heating run. The crosslinking reaction leads to a slight increase in the modulus in the glassy state. The glass transition temperature of the crosslinked VA chains shows hardly any change compared with the glass transition temperature in the uncrosslinked state. This indicates that the degree of crosslinking is relatively low.

To apply model free kinetics to DMA data, the DMA measurements also have to be performed at different heating rates (see Figure 7, above left). Conversion curves for the curing reaction are then calculated from the DMA curves. This can be done by calculating the difference between the storage modulus at a particular temperature, $G'(T)$, and the modulus value before curing, G'_{bc}, (123 °C at a heating rate of 3 K/min) normalized to the difference between the plateau modulus, G'_p, (170 °C at a heating rate of 3 K/min) and the modulus before curing:

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

The conversion curves determined from the dynamic measurement curves are shown in Figure 7 (below left). These curves were used to calculate the conversion-dependent activation energy (see Figure 7, above right). From this, isothermal predictions were derived for 130 and 135 °C (Figure 7, below right). For comparison, the diagram also shows the conversion curves obtained from isothermal experiments performed at the same two temperatures. The measured curves are shown in Figure 7, above left. The measured and calculated conversion curves again show excellent agreement.
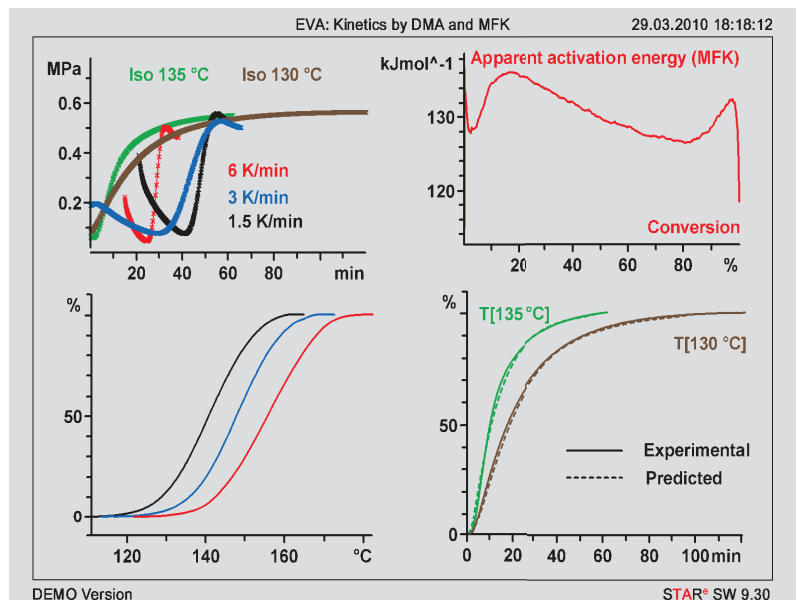

Figure 7: DMA/MFK evaluation. Above left: dynamic and isothermal DMA curves. Below left: conversion curves. Above right: the apparent activation energy. Below right: predictions for isothermal curing at 130 °C and 135 °C and the corresponding experimental measurements.

Figure 8 compares the results obtained from DSC kinetics with those from DMA kinetics. The figure shows that the calculated activation energy is of the same order of magnitude for both techniques. Furthermore, for curing times longer than 10 min, it is apparent that the degree of cure determined by DMA is higher than the values obtained from the DSC measurements.

The reason for this is that we have assumed that the plateau modulus is independent of temperature (the modulus is needed for the calculation of the DMA conversion curve).

However, Figure 6 shows that G' decreases slightly with increasing temperature in the rubbery plateau and the calculated degree of cure is therefore somewhat too large (see the G' curve in the second heating run). Quantitative estimates show that this effect overestimates the degree of cure determined from the DMA measurements by not more than 10%.
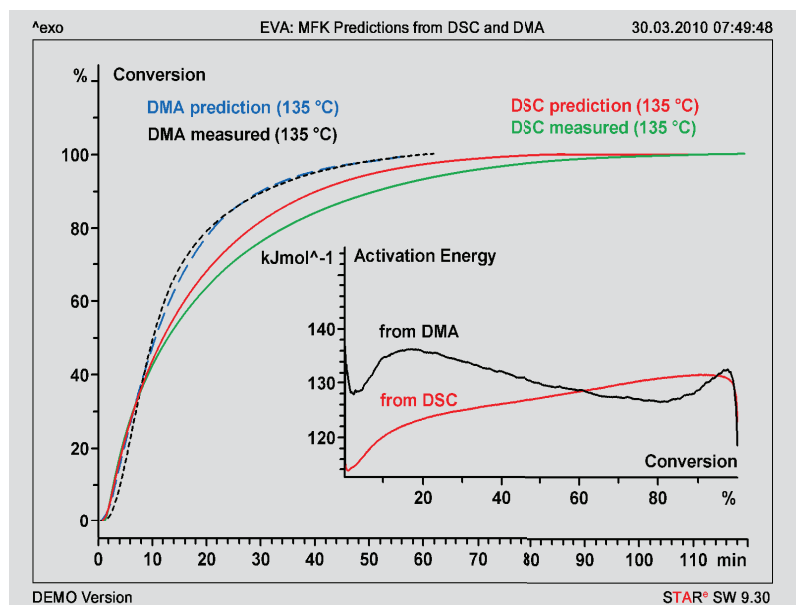

Figure 8: Comparison of DMA and DSC results and MFK evaluation. Activation energy and predictions for isothermal temperatures and comparison with isothermal measurements.

Conclusions

The kinetics of the curing reaction of EVA that occurs during the lamination of photovoltaic modules can be investigated using DSC and DMA measurements. This is done by performing measurements at different heating rates and evaluating the results using the model free kinetics method. The results show that both techniques can be used to describe the curing process of EVA. The predictions made from model free kinetics about the isothermal curing behavior were confirmed experimentally. Both DSC and DMA measurements are suitable for the optimization of process parameters for the lamination of photovoltaic modules.

DMA yields additional information with regard to the viscoelastic behavior of the EVA film in the finished photovoltaic modules.

The two techniques can be equally well used for the quality control of laminated photovoltaic modules.

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