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A new DSC method for the quality control of PV modules: Simple and quick determination of the degree of crosslinking of EVA encapsulants

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ABSTRACT

This paper presents a new differential scanning calorimetry (DSC) method that allows the determination of the degree, or level, of crosslinking of ethylene-vinyl acetate (EVA) copolymers, including EVA films used as encapsulants for photovoltaic (PV) applications. This method can also determine additional characteristics of EVA, such as its weight per cent (wt %) vinyl acetate (VA) content and its fluidity. The paper describes the procedure and its application to EVA film samples laminated at 145°C, for different lengths of time in an industrial-type laminator for PV modules, as well as to EVA uncrosslinked samples of different composition and fluidity. The scope of the method compared to other characterization methods for the degree of crosslinking of EVA is discussed. An experimental comparison is also made to rheological and gel content methods.

Introduction

A large majority of PV modules need a support or back sheet, a front cover or front sheet, and, in between, a layer of encapsulated, conveniently interconnected, PV cells which must be protected against environmental exposure, including mechanical loading, impacts, moisture, oxidation and other possible causes of damage or deterioration [1,2]. The most common way of creating this multi-layered structure is a lamination process, during which all the layers are stacked and thermally sealed in a laminator.

The encapsulant is a transparent polymeric material responsible for the protection of the strings of interconnected PV cells. Most module manufacturers still prefer a crosslinkable ethylene-vinyl acetate (EVA) copolymer. A typical EVA film for cell encapsulation is 300 to 500 microns thick and comprises a VA-rich EVA base (e.g. a 33 wt % VA content), a crosslinking system (mainly a peroxide or a peroxide mixture), an adhesion promoter (e.g. silanes), and a cocktail of conveniently chosen UV-stabilizers and antioxidants [2]. In the case of EVA encapsulants, good processability in the lamination step is achieved by regulating the flow properties of uncrosslinked EVA and adjusting its crosslinking kinetics, so that the material presents an optimized rheological behaviour, i.e. becoming liquid enough during the first stages of the lamination for a complete encapsulation of the cells

to take place, and crosslinking fast enough during the last stages for the encapsulant to become a thermoset solid.

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The actual properties of the EVA encapsulant after the lamination step depend, to an important extent, on its degree (or level) of crosslinking. This paper introduces a new characterization method for this property, which retains the simplicity of the most popular industrial quality control techniques while extending the range of potential applications.

Determination of the degree of crosslinking of EVA encapsulants

Swelling experiments and mechanical measurements are two possible techniques for directly determining the crosslinking densities of polymer networks. However, they are seldom used in quality control, because of the complex underlying physics, the need for careful sample preparation and measurement, and the long time required to obtain reliable data.

Industrial companies use indirect, simpler techniques, among which the so-called 'gel content' technique is by far the most widely used. Measuring the gel content implies carrying out the solvent extraction of the soluble fraction of the crosslinked polymer. The remaining insoluble fraction of the original dry sample is considered to be composed of the crosslinked polymer network. The results are expressed either in terms of per cent 'insolubles' (% gel content) or in terms of the complementary per cent 'solubles' (% extracted material). High gel contents correspond to densely crosslinked networks. The method is fairly simple and easy to perform. On the other hand, the extraction experiments must be carried out at relatively high temperatures (over 70°C) for 12 to 24 hours. Another important drawback is the need to handle (and dispose of) organic solvents. There is certainly a need for efficient ventilation systems, good management of fire and explosion hazards, and responsible disposal of used solvents.

Recently a new indirect method for determining the degree of crosslinking for EVA-based encapsulants was proposed [3]. It is based on the fact that the crosslinking reaction of EVA, initiated by peroxides, is an exothermic process. This method uses differential scanning calorimetry (DSC) on small samples of EVA, whether uncrosslinked or crosslinked. DSC is a well-known technique for the thermal characterization of polymers [4]. It is



based upon a controlled heating or cooling (temperature scan) of two metallic closed crucibles containing, respectively, a small sample (usually a few milligrams) of the material to be analyzed and air (closed crucible with no sample). During the scan, the temperatures of the crucible containing the sample and the empty (containing only air) crucible (reference) are compared; if a difference arises, the calorimeter compensates immediately so that the temperatures remain equal. The amount of heat required to compensate is measured and recorded. Whenever the analyzed sample undergoes a thermal transition (understood to be any process giving rise to heat absorption or release), this event will appear in the thermogram as an upward or downward deviation of the baseline (peak or jump). With the 'Exo up' convention (meaning released heat is represented as an upward deviation of the base line, and, correspondingly, absorbed heat as a downward one), the most common thermal transitions that polymers may undergo are schematically shown in Fig. 1.

The recently proposed DSC method, hereafter referred to as the 'residual peroxide method' [3], measures the heat released by the exothermic crosslinking of EVA encapsulant film samples. When the encapsulant is uncrosslinked, a heating scan up to the temperature zone where the reaction takes place (> 100°C) will produce an exothermic signal similar to the one shown in Fig. 1 labelled 'chemical reaction.' The integral of the heat flow signal will correspond to the total maximum enthalpy that the crosslinking reaction, carried out in its entirety, will release. The residual peroxide method is based on the assumption that an already laminated EVA sample still has some heat to release when submitted to a DSC scan. By comparing it to the heat released by the uncrosslinked (no lamination) sample, a relative degree of crosslinking of the laminated sample may be determined. The method correlates well with gel content measurements [3]. On the basis of this good agreement, the new calorimetric measurement could be used for determining the degree of crosslinking of EVA encapsulants, and subsequently the crosslinking kinetics, namely the evolution of the crosslinking degree for different lamination times. The use of DSC has some important advantages over the gel content technique: it does not need any solvents, and the DSC equipment can easily be operated by the manufacturing teams. The sample needed for a measurement is very small (only a few milligrams), and the measuring time is very short (typically less than one hour) compared to the solvent extraction time. On the other hand, the residual peroxide DSC method relies on the presence of this residual additive, and is therefore not applicable to samples with complex or unknown thermal history (since, for the method to be accurate, all of the peroxide decomposition must have taken place either during the manufacturing process or during the post-lamination DSC measurement). Obviously, the method cannot be applied, or needs to be adapted, to samples being crosslinked by methods other than pure peroxide-initiated crosslinking.

Introducing a new, improved calorimetric method

This paper introduces a new DSC method which maintains the advantages of the use of DSC over other techniques such as rheology, swelling experiments or gel content measurements. Moreover, it is based upon more direct principles than the residual peroxide method (structural changes in EVA), and thus considerably improves the range of potential applications.

Materials and methods

The EVA copolymers for lamination experiments were provided either by STR Spain or by Etimex (now Solutia): the STR film reference was 15420P/UF, and the Etimex film reference was Vistasolar 486.00. All other EVA copolymers in pellet form were provided by Arkema under the references Evatane 18-150, 18-500, 24-03, 28-05, 28-150, 40-55 and 42-60.

The lamination of EVA encapsulant films was carried out by stacking, downside-up, a 16×16cm, 3.2mm-thick glass plate, a thin Teflon non-adherent sheet to prevent the EVA/glass adhesion, two EVA sheets to be crosslinked, one more Teflon non-adherent sheet, and two more EVA sheets which served as damping layers. In this stack, the two EVA sheets to be crosslinked were placed in the position that they would normally occupy in the lamination stack of a typical glass/EVA/ cells/EVA/back sheet PV module.

The stack was laminated at 145°C in an industrial-type 3S laminator (model S1815E), following a standard lamination procedure including degassing and crosslinking stages. In this procedure, the actual lamination time (after 5 minutes' degassing) was varied between 3 and 15 minutes (in the standard procedure the lamination time is usually 10 minutes). All DSC measurements were carried out in a TA Instruments DSC calorimeter (model Q 10) equipped with an RCS 90 cooling device. All samples weighed between 5 and 12mg, and the measurements were conducted under a continuous nitrogen flow of 50ml/min. No sample conditioning was applied before the DSC measurements.

Three heating scans covering a temperature range from -70°C to 100°C were carried out with a heating rate of 10°C/min. After each heating scan, a cooling scan was applied from 100°C to -70°C, except for the third cooling scan, for which the lower temperature limit was -20°C. Before each heating scan the temperature was equilibrated at -70°C for 5 minutes; no equilibration time was applied at 100°C before the cooling scans. The upper temperature limit (100°C) was designed to prevent the samples from continuing to crosslink during the DSC experiment, in contrast to the residual peroxide method.

The rheological measurements were carried out using an Anton Paar Physica MCR 301 rheometer under a parallel-plates configuration, in the shear (oscillatory) mode. After a period of testing, the experimental temperature was set to 100°C,



Figure 2. (a) Typical DSC thermogram obtained by applying the procedure described in this paper. (b) First heating scan (from −70°C to 100°C) of this specific DSC experiment. (c) DSC thermogram in (a) without the first heating scan in (b), and without the final return from −20°C to room temperature.

and frequency sweeps from 0.01 to 10Hz were conducted. The elastic, G' and viscous, G", components of the complex shear modulus were measured, and their ratio, tan $\delta = G''/G'$, was determined (the lower this ratio, the more elastic the material, i.e. the better the crosslinking).

The gel content measurements were carried out through solvent extraction in xylene (Rectapur, three isomers mixture) at reflux temperature for 12 hours, by adapting ASTM D-2765-95 standard. The gel content was calculated by (% gel content) = 100 - (% extracted).

Results and discussion

Reproducible thermal transitions of EVA by DSC analysis

The sample crucibles were weighed before and after the DSC characterization, in order to check for any possible weight loss. No weight losses were detected when using the DSC procedure (three heating– cooling scans) described above. A typical heat flow vs. temperature plot is shown in Fig. 2(a); the first heating scan from -70°C to 100°C at 10°C/min is shown in Fig. 2(b). Fig. 2(c) shows the same plot as in Fig. 2(a), but without the first heating scan, and without the last return to room temperature. By comparing Figs. 2(a)-(c), it is clear that only the first heating scan is not reproducible. Indeed, the plot in Fig. 2(c) shows three neat, very reproducible thermal transitions for the EVA copolymer, corresponding to: the glass transition region (at around -40° C), the melting region (with a single endothermic peak at around 70° C of peak minimum), and the recrystallization region (with a maximum peak at around 40° C during cooling).

Several authors have shown and sometimes discussed [3,5-8] the double endotherm in the melting region from the first heating scan in DSC of EVA copolymers. Imperfect crystalline regions of different sizes and metastable states may explain this kind of melting behaviour, leading to a first DSC scan of EVA copolymers which is dependent on the thermal history of the sample. Fig. 2(c) shows that, after the first scan, subsequent heating scans lead to a very reproducible melting behaviour for EVA; the same is true for the glass transition. One important aspect of this characteristic behaviour of EVA copolymers, when using DSC to follow crosslinking evolutions (according to the method proposed herein), is that the elimination of the very first heating scan allows the nonreproducible component of the thermal history of the samples to be erased, and this, in turn, allows the characterization measurements by DSC to be performed without any requirement concerning previous conditioning of the samples.

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Regarding the recrystallization behaviour, it is clear from Fig. 2(c) that all three cooling scans superimpose very well. This means that, if only the recrystallization region is to be analyzed for the EVA characterization (discussed later), the experiment can be stopped after only the first or, at most, the second cooling scan, making it possible to reduce the measurement time per sample considerably. If, again, only the recrystallization region is used for data analysis, further optimization is possible by using a lower temperature limit much higher than -70° C. We believe that quality control measurements could be carried out in about 30 to 45 minutes per sample.

Analysis of the glass transition and melting regions

It is well known that the glass transition temperature, T_{g} of polymers may increase

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Figure 3. (a) Zoom-in on the melting zone for EVA encapsulating films after lamination times of 3 to 15 minutes. The melting temperatures corresponding to the minimum heat flow are also shown. (b) Melting temperature as a function of lamination time.

when they are crosslinked [9]. Although we did verify this effect in our work, the shift appears too small for $T_{\rm g}$ measurements to be used to follow crosslinking kinetics, and the results will not be discussed here.

EVA copolymers present a broad melting region, possibly due to the imperfect crystallization of ethylenederived moieties caused by the insertion of VA-derived groups into the polymer chains [4,7,8], as may be concluded from the fact that increasing the vinyl acetate content reduces the total crystallinity of EVA copolymers. As shown in Fig. 2, the first heating scan in DSC produces multiple (at least two) melting peaks related to the thermal history of the sample. From the second heating scan onwards, the melting transition appears as a very reproducible, broad endothermic deviation from the DSC baseline, with a part of the melting taking place in the form of a large endothermic peak. Fig. 3(a) shows a zoomin on the melting region from the second heating scan, for samples undergoing different lamination times; a clear shift towards lower temperatures of the large

peak can be observed. Fig. 3(b) shows the variation of the melting temperature, taken at the lowest value of the heat flow signal, *q*, of Fig. 3(a), as a function of the lamination time. The melting temperature initially decreases very sharply with lamination time, and then tends towards a stable value at high degrees of crosslinking. By following the evolution of the melting temperature, obtained as described above (second or subsequent heating scans), it is possible to differentiate samples with different degrees of crosslinking, up to reasonably high crosslinking levels.

Analysis of the recrystallization region

Fig. 4(a) shows the plots of the first cooling scan and the second heating scan, for the five samples at different lamination times described earlier. For clarity, the curves were shifted downwards with respect to the sample of 3 minutes' lamination time (blue curve). The recrystallization region is, by a large margin, the transition region which undergoes the biggest change with crosslinking: not only does the recrystallization peak shift to lower temperatures, as for the melting region, but also the shape or form of the peak is significantly changed. Fig. 4(b) shows a zoom-in on the recrystallization region, corresponding to the three cooling scans carried out on each sample. It can be seen from this figure that the DSC scans lead to extremely reproducible results. Indeed, only the less crosslinked sample (3 minutes' lamination time) reveals the fact that three cooling scans have been plotted; for all the other lamination times, the results are so reproducible that the three scans superimpose very well, as if only one curve were plotted. It is also apparent from Fig. 4(b) that the shape of the peak changes with crosslinking (increasing lamination time), mostly at the lower temperature side of the peak.

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In order to characterize the temperature shift of the recrystallization peak, we have selected two parameters, as illustrated in Fig. 5(a): the temperature of the recrystallization peak's maximum, T_{c} , and the extrapolated temperature of the onset of crystallization, T_{onset} . In order to characterize the change of the peak's shape, different parameters may



Figure 4. (a) DSC plots for all the samples at different lamination times. A downward shift of 0.05W/g has been applied to the curves for lamination times of 7 to 15 minutes. (b) Zoom-in on the recrystallization region of the DSC plots for all the different samples.



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Figure 5. (a) Determination of the temperature shift parameters T_c and T_{onset} . (b) Calculation of the shape factor $SF = 100 \times red$ area / (red + grey area).

be used. After trying several possibilities, we chose a graphical method, related to the concavity of the lower temperature side of the crystallization peak, specifically the temperature region contained between T_c and T_c -20°C. In fact, the graphical method is similar to the calculation of fill

factors from characteristic plots of current (I) vs. voltage (V), well known in the PV community. In order to do this, the steps below are followed:

- 1. Selection of heat flow (q) data between T_c and T_c -20°C.
- 2. Inversion of the *q* values by taking their inverse function, 1/q (the plot of 1/q vs. *T* between the limits T_c -20°C and T_c then looks much like a plot of *I* vs. *V*).
- 3. Determination of the maximum value of the product $1/q \times T$ (in the



Figure 6. Labview graphical display of the plots needed to calculate the shape factor. The computed value of the shape factor and its correlated gel content (see text) are also indicated (top left). The green bar on the left reflects the final result: the sample with 12 minutes' lamination time is well crosslinked (> 80%).



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same way that a maximum power is obtained from *I* vs. *V* plots).

- 4. Calculation of the area of the rectangle defined by the coordinates of this maximum, i.e. T and 1/q at which the product $(T \times 1/q)$ reaches a maximum.
- 5. Calculation of the area of the rectangle defined by the limits of data, i.e. T_c on the one hand, and (1/q) at T_c -20°C on the other.

The shape factor is then obtained as the ratio given by the first rectangle area (step 4) divided by the second rectangle area (step 5); a more practical form can be used by multiplying this ratio by 100, in order to use it as a per cent scale.

Fig. 5(b) illustrates the shape factor (SF) calculation. Although more complicated to obtain than the parameters which describe the shift towards lower temperatures of the crystallization peak (i.e. T_{c} and T_{onset}), the shape factor may be easily programmed for automatic calculation from the DSC data between the temperature limits of T_c and a lower limit, defined here as $T_{\rm c}$ –20°C. This single numerical parameter represents a modification of the shape of the crystallization peak, and could be particularly useful as a graphical method that is less dependent than the temperature shift parameters on quality of the baseline and calibration issues.

A Labview program displaying the calculation of the shape factor is shown in Fig. 6. The plots in the main window correspond to: the raw DSC data at the crystallization region, q vs. T (top); the inverse function of the selected data, 1/q vs. T in the T_c -20°C to T_c interval (centre); and the product $1/q \times T$ vs. T in the same interval (bottom). The maximum in the last plot $(1/q \times T \text{ vs. } T)$ defines the coordinates needed to calculate the red rectangular area in Fig. 5(b). The current criterion for what the gel content should be for an EVA encapsulant to be acceptably crosslinked is roughly > 75-80% [2]. Fig. 6 considers the sample for 12 minutes of lamination time. The green bar on the left is a graphical expression of the final result: according to the method described here, using the shape factor of the recrystallization peak and its correlation with gel content measurements (see below), the sample is well crosslinked (correlated gel content > 80%).

Fig. 7(a) shows the evolution of the three parameters – T_c , T_{onset} and SF – which characterize the crystallization region as a function of the lamination time for the EVA encapsulant films considered in this work. It can be seen from this figure that the trend is the same as for the melting temperature in Fig. 3(b).

Two other methods – rheology and solvent extraction – have been used for





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comparison with the new DSC method described in this paper. The experimental details for both are given in the materials and methods section. Fig. 7(b) shows the values of tan δ at 1Hz and 100°C, from rheological measurements as a function of the lamination time; the trend is very similar to that for the DSC characteristic parameters (melting temperature, T_{cr} T_{onset} , *SF*).

Solvent extraction experiments were carried out on the same EVA samples as before, laminated at different times. Fig. 7(c)shows the results in the form of both the % extracted material and, its counterpart, the % gel content (see materials and methods section). The same type of trend as for the DSC parameters and the rheological measurements is found for the % extracted material. Moreover, the solvent extraction measurements confirm that the sample at 3 minutes is not crosslinked. As can be seen from Fig. 7(d), the DSC parameters (obtained from the recrystallization region) and the rheological data correlate very well with gel content measurements. The correlation between the melting temperature (not shown) and the gel content is less satisfactory.

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We can conclude that, with the use of this new DSC method (referred to hereafter as the 'Sollia method'), the degree of crosslinking of EVA encapsulant films can be determined from DSC parameters obtained from the melting, and, even better, from the recrystallization zones of thermograms conducted under conditions where the samples do not crosslink in the DSC calorimeter. This new DSC method offers the advantages of DSC over rheology or gel content measurements, while avoiding the drawbacks of the recently reported residual peroxide DSC method. Indeed, the Sollia method could be considered to be an upgraded DSC method because:

- it relies on structural changes in EVA copolymers, caused by crosslinking, rather than on the residual peroxide content of the EVA formulation;
- being independent of residual peroxide, it may be applied to EVA samples with any thermal history, including returnfrom-the-field samples;
- it does not require any sample conditioning;
- it can be applied to EVA samples crosslinked by processes other than peroxide reactions;
- besides the degree of crosslinking, it yields other types of valuable information about EVA, as will be shown in the following sections.

Vinyl acetate (VA) content

Fig. 8(a) shows a zoom-in on the recrystallization region of different EVA copolymer samples (pellets and PV encapsulant films: see materials and methods). All the samples are uncrosslinked, and three cooling scans are shown in each case. It can be seen from this figure that the recrystallization peaks shift to lower temperatures with increasing VA content. This trend is also evident in Fig. 8(b), where the selected DSC parameter T_c has been plotted against the wt % VA content of the EVA copolymer samples. The values of the characteristic parameter $T_{\rm c}$ for two EVA encapsulant films from two different manufacturers, with a stated wt % VA content of 33%, are also plotted. The EVA encapsulant films fit quite well between the peaks of the curves corresponding to 28 and 40 wt % VA content in Fig. 8(a) (or between the $T_{\rm c}$ values in Fig. 8b). Moreover, the plot in Fig. 8(b) is linear in the zone defined between 24 and 42 wt % VA. Thus, by using the DSC method described here, it should be possible to accurately predict the wt % VA content of an unknown EVA sample.

Fluidity (molecular weight distribution)

Fig. 9 shows the recrystallization peaks of the 18 and 28% VA content samples in Fig. 8. For each of these, two different samples were analyzed: EVA 18-150 and EVA 18-500 for 18%; EVA 28-05 and EVA 28-150 for 28%. The number after the wt % VA content represents the fluidity of the material, as measured by its melt flow index; the higher the number, the more fluid the sample. (The melt flow index is

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Figure 9. Recrystallization DSC plots for the pellet samples of 18 and 28 wt % VA content. Samples with the same wt % VA content but different melt flow indexes (MFI) are shown.

a standardized method of expressing the forced flow of a heated polymer sample through a hole; the temperature, and the pressure applied to the sample to push it through the hole, are constant. The melt flow index value corresponds to the weight of polymer that passes through the hole during a fixed time interval.)

It can be seen from Fig. 9 that higher melt flow indexes, corresponding to more fluid

polymers, present recrystallization peaks at lower temperatures. This temperature shift can easily be characterized by the parameters T_c and T_{onset} , as indicated in the recrystallization section analysis. The width and form of the peaks may also be considered. Given that the fluidity of the polymers is related to their molecular weight distribution, the DSC method proposed here (Sollia method) can also give

an insight into this important molecular characteristic of the copolymers.

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Conclusions and perspectives

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This paper has presented a new DSC method that can be used to determine the degree of crosslinking of EVA copolymers, which, particularly in relation to PV encapsulant applications, offers an alternative to a recently reported DSC method based upon the residual peroxide content of laminated encapsulant films. The new method is based upon changes in the microstructure of EVA copolymers. The effect of crosslinking on the thermal transitions of EVA has been discussed, and a method has been outlined for obtaining reliable, reproducible characteristic parameters, allowing the degree of



crosslinking of EVA film encapsulants to be determined. The preferred parameters for the method are those extracted from the recrystallization region of the DSC plots, such as the temperature at the peak maximum, T_{c} the temperature of the onset of recrystallization, T_{onset} and the shape factor, *SF*, reflecting the form of the lower temperature part of the recrystallization peak. The last of these is a single number which reflects a significant shape change, and should be independent of calibration or uncontrolled temperature shifts.

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The Sollia method, described here, allows the determination of the degree of crosslinking of EVA copolymers independently of their thermal history (return-from-the-field analysis becomes possible by DSC), and should be applicable to complex crosslinking mechanisms, including those without peroxides. The fact that the method proposed here is based upon intrinsic properties of EVA copolymers allows us to explore other potential applications. Two of these have been identified: 1) determination of the wt % content of VA in unknown EVA copolymer samples; and 2) characterization of the fluidity of EVA samples. In all cases, the method may be used either in a comparison to known references, or, in a relative way, in a comparison of unknown samples. However, future work is still necessary to determine the full potential of this new DSC method.

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