Assessment of the cross-linking degree of EVA PV encapsulants

Manuel Hidalgo & **Dominique Thil**, Arkema, Sollia Laboratory at INES-LMPV, Le Bourget du Lac, &
Chistophe Dugué, Photowatt, Bourgoin-Jallieu, France

ABSTRACT
This paper presents a comparison of different characterization methods used for determining the relative degree of cross-linking of samples of PV-type EVA films, obtained under three different process conditions in a vacuum PV laminator. The methods investigated are gel content measurements, rheological measurements and differential scanning calorimetry (DSC). For the latter, two distinct procedures are employed – the residual enthalpy method and the melt/freeze method.

Introduction

Hidalgo et al. [1] introduced a new characterization method for assessing the cross-linking degree of EVA encapsulant films used in the PV industry. That work presented the basis of the so-called Sollia method, which employs differential scanning calorimetry (DSC) and, in particular, the crystallization transition of EVA during a DSC melting and freezing type of experiment. In the last two years a great deal of work has been done on optimizing the test conditions (the test duration is now only 20 minutes per sample) and gathering experimental data for a significant number of industrial EVA encapsulant films. As a result, the Sollia method has now joined with another DSC method, proposed by Xia et al. [2] and based upon a completely different thermal transition (heat release during cross-linking), in an IEC international standard proposal for the characterization of the cross-linking degree of EVA encapsulant films [3]. The two DSC methods, referred to now as the melt/freeze (M/F) method (based upon the work of Hidalgo et al.) and the residual enthalpy (RE) method (based upon the work of Xia et al.), are complementary and offer the possibility of double-checking the cross-linking degree of a given sample.

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This study uses both of these DSC methods, as described in the standard proposal, to determine the relative degree of cross-linking of a commonly used PV encapsulant film, under three different process conditions that might be used for the industrial lamination of PV modules. In order to check the consistency of the information thus obtained, the same samples were characterized using two different reference methods: 1) the well-known gel content method, widely used for the assessment of the cross-linking degree of EVA polymers; and 2) rheological measurements, carried out in the way initially described in Hidalgo et al. [1].

Experimental conditions: materials and methods

The PV encapsulant film was one that had been stored for several months, and the purpose of using three different process conditions was to allow the set point of the vacuum laminator’s temperature to be varied, as would be done in an industrial facility when attempting to optimize this temperature parameter for a given EVA film.

The EVA film was provided by STR (reference Photocap 15420P/UF) and was received in September 2012, with a 6-month lifetime guarantee. The lamination of samples for cross-linking degree characterization was carried out in June 2013, meaning that the film was already regarded as ‘old’, although the storage conditions (cool chamber at 10°C, aluminized sealed packaging) were such that the use of this film for comparative purposes (testing of three different lamination temperatures) was considered acceptable.

The lamination of the EVA encapsulant films was carried out by stacking, downside up, a 15cm × 15cm, 3.2mm-thick glass plate, a thin Teflon non-adherent sheet to prevent the EVA/glass adhesion, two EVA sheets to be cross-linked, and one more Teflon non-adherent sheet. In this stack the two EVA sheets to be cross-linked were placed in the position that they would normally occupy in the lamination stack of a typical glass/EVA/cells/EVA/backsheet PV module. The stacks were laminated at three different set-point temperatures of 145, 150 and 160°C in an industrial-type 3S laminator (model S1815E), following a standard lamination procedure including degassing and cross-linking stages. The degassing step was set for a duration of 4 minutes, and the actual lamination time for a duration of 8 minutes, under approximately 900mbar of differential pressure.

The DSC measurements were carried out on the same samples at two different places (different operators, different equipment). The calorimeter used at the first location was a TA INSTRUMENTS DSC model Q 10, equipped with an RCS 90 cooling device, and at the other, a Netzsch DSC model 200F3. The samples weighed between 5 and 9mg, and the measurements were conducted under a continuous nitrogen flow of 50ml/min. No sample conditioning was applied before the DSC measurements. To generate the necessary data for the analysis with both the RE and the M/F methods, the DSC programme used was as follows:

1. Heat to 100°C at 10°C/min, which melts the sample and erases thermal history.
2. Cool to –20°C at 10°C/min, which ‘freezes’ the sample, making it crystallize. The crystallization peak is then analyzed according to the M/F method.
3. Heat to 225°C at 10°C/min, which makes the residual peroxide of the sample react. The enthalpy peak between 100 and 200°C, or between its two onset temperatures, is then analyzed according to the RE method.

4. Cool to −20°C at 10°C/min, which is only necessary if no highly cross-linked sample (near 100% gel content) is available. This cooling step will generate a second crystallization peak after all the residual peroxide of the sample has reacted. The second peak corresponds to a highly cross-linked sample which has continued to cross-link in the calorimeter during step 3.

5. Return to room temperature, which allows the sample to be unloaded from the calorimeter.

The rheological measurements were carried out using an Anton Paar Physica MCR 302 rheometer in a parallel-plates configuration and in the shear oscillatory mode. As described in Hidalgo et al. [1], carrying out a frequency sweep at 100°C has been found to be a good compromise for EVA encapsulants, whether uncross-linked or cross-linked. The elastic, G', and viscous, G'', components of the complex shear modulus were therefore measured at 100°C for a frequency sweep between 0.1 and 100Hz. The method described by Hidalgo et al., which consists of using a value of $\tan\delta = G''/G'$ at 1Hz to characterize the degree of cross-linking, was applied herein.

The gel content measurements were carried out through solvent extraction in toluene at a soaking temperature of 60°C for at least 18 hours. Samples of size 1g were weighed and immersed in 100ml beakers with toluene and 0.1g of butylated hydroxytoluene (BHT) as an antioxidant. The beakers were covered with aluminium foils and kept in the oven at 60±5°C for at least 18 hours. The samples were subsequently paper filtered, and the residual material was dried at 105±5°C for four hours. Once cooled down to room temperature, the dried samples were weighed again, and the gel content was calculated using Equation 1.

$$\%\ \text{gel content} = \frac{\text{Residual EVA weight after 18 hours soaking at 60°C, and subsequent drying}}{\text{Initial EVA sample weight}} \times 100$$

Equation 1.

Results and discussion

DSC analysis

Fig. 1 shows a typical DSC plot obtained using the five-step programme mentioned above. After steps 1 and 2, a crystallization peak corresponding to the actual state of the sample is obtained; from this peak, the three parameters of the M/F method (see below) may be determined. After step 3, the exothermic peak corresponding to the decomposition of residual peroxide, and further cross-linking of the sample in the calorimeter, is obtained; the surface under the curve (enthalpy) is used in applying the RE method. After step 4, a new crystallization peak for the sample which has been cross-linked further in the calorimeter is obtained. In the case where no highly cross-linked samples are available, the peaks obtained after step 4 may be used to determine the M/F parameters of highly cross-linked samples, as will be explained below.

Melt/freeze method

Fig. 2 shows the crystallization peaks corresponding to the three set-point temperatures for which every parameter of the M/F method has been calculated or graphically determined. The three M/F parameters are: 1) the maximum crystallization temperature, or peak

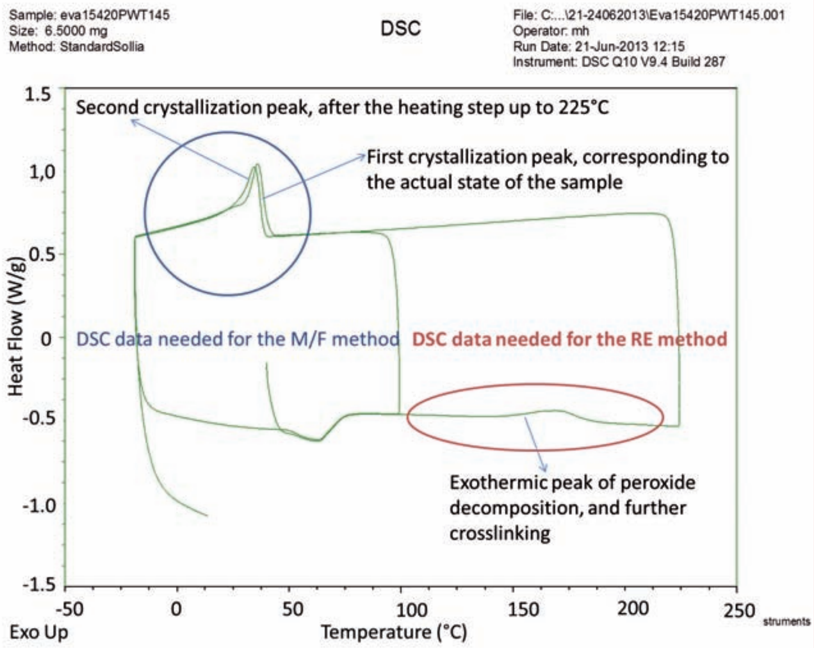

Figure 1. Specific heat flow as a function of temperature (plot produced by the five-step DSC programme).

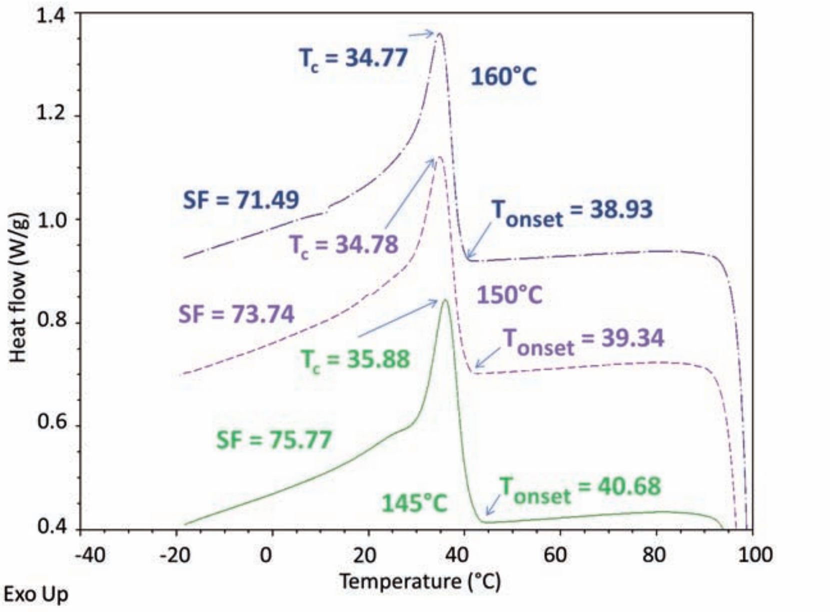

Figure 2. Crystallization peaks for each of the three samples laminated at set-point temperatures of 145, 150 and 160°C. (An offset has been applied to the heat flow curves in order to display the three peaks on the same graph.)

temperature (T_c); 2) the temperature of the onset of crystallization during cooling (T_{onset}); and 3) the shape factor (*SF*), which takes into account the concavity of the lower temperature part of the crystallization peak, i.e. between T_c and T_c – 20°C. It has been previously determined that the values of these three parameters decrease with the cross-linking level of EVA (see Hidalgo et al. [1] and Miller et al. [3] for details), and thus they constitute three different indicators of the conversion of the cross-linking reaction. The M/F method uses the values of these parameters for a given sample and compares them with those of an uncross-linked sample (giving the 0 bound of a percentage scale), as well as with those of a very highly cross-linked sample (giving the 100 bound of the percentage scale). When no highly cross-linked sample is available, the parameters from peaks obtained in step 4 of the above-mentioned DSC programme can be used. In this case, if several samples have been analyzed, different sets of parameters for step 4 peaks will be available, and the lowest values of these should be used to set the 100% bound of the scale.

Although a simple comparison of the raw values of the three M/F parameters for different samples already allows those that are more cross-linked than others to be distinguished, the M/F method features a more quantitative approach through the calculation of percentage cross-link (%XL) estimates for each parameter (T_c, T_{onset} and *SF*) by applying the formulas in Equations 2–4:

$$\%XL_{T_c} = \frac{T_c^{\text{uXL}} - T_c^{\text{sample}}}{T_c^{\text{uXL}} - T_c^{\text{min}}} \times 100 \qquad (2)$$

$$\%XL_{T_{\text{onset}}} = \frac{T_{\text{onset}}^{\text{uXL}} - T_{\text{onset}}^{\text{sample}}}{T_{\text{onset}}^{\text{uXL}} - T_{\text{onset}}^{\text{min}}} \times 100 \qquad (3)$$

$$\%XL_{\text{SF}} = \frac{SF^{\text{uXL}} - SF^{\text{sample}}}{SF^{\text{uXL}} - SF^{\text{min}}} \times 100 \qquad (4)$$

where the superscripts 'uXL', 'sample' and 'min' correspond to the values obtained from the crystallization peaks of the uncross-linked sample, the actual sample under investigation and a highly cross-linked sample respectively.

In order to characterize, according to the M/F method, a given sample using a single estimate of its cross-linking degree, an arithmetic average of the three estimates given by Equations 2–4 has been empirically determined to be a good global estimate for a wide variety of commercial EVA encapsulants, and one which correlates well with the results obtained using other methods. Thus, the degree of cross-linking as determined by the M/F method may be obtained using Equation 5.

Residual enthalpy method

Fig. 3 shows the residual enthalpy peaks for the samples at the three set-point temperatures. The RE method, initially described in Xia et al. [2], uses the area under the enthalpy peak which appears in the temperature range 100–225°C. All DSC calorimeters are supplied with the appropriate software for determining the integral of heat flow vs. temperature curves, which results in the desired areas under the residual enthalpy peaks.

In Miller et al. [3] it is recommended, whenever possible, to integrate enthalpy peak curves in the temperature range of 100–200°C. At Arkema and Photowatt, recent findings indicate that for some commercial EVA encapsulant films, the upper integration limit must be slightly shifted to temperatures higher than 200°C. This is the reason why the authors consider it to be more generally applicable to integrate the residual

$$\%XL_{\text{average}}^{\text{M/F}} = \frac{(\%XL_{T_c} + \%XL_{T_{\text{onset}}} + \%XL_{\text{SF}})}{3}$$

Equation 5.

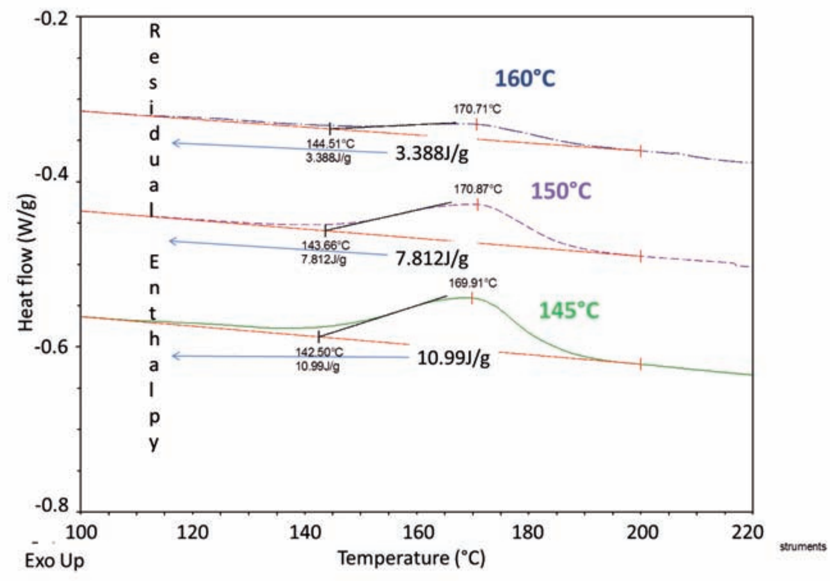

Figure 3. Residual enthalpy peaks for each of the three samples laminated at set-point temperatures of 145, 150 and 160°C. (An offset has been applied to the heat flow curves in order to display the three peaks on the same graph.)

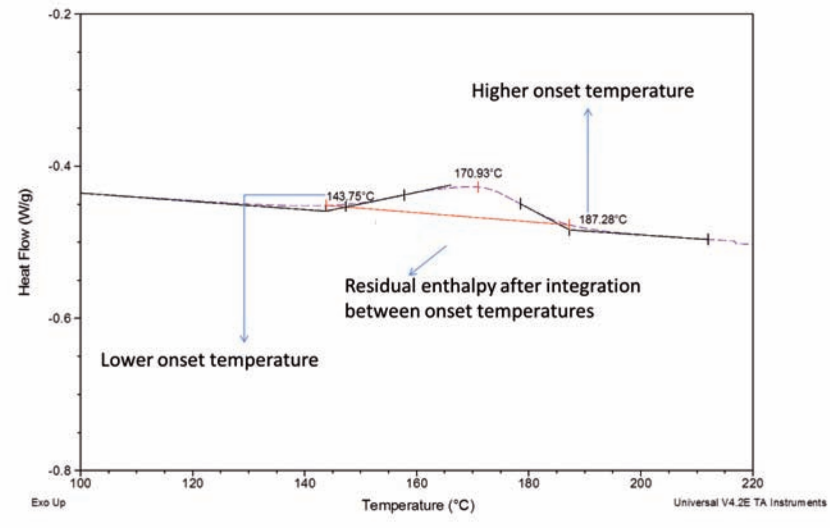

Figure 4. Determination of the integration limits for a residual enthalpy peak, from the peak's lower and higher onset temperatures.

enthalpy peak between its onset temperatures (lower and upper onsets), which can also be easily determined by commercial DSC software packages. Fig. 4 shows an example of integration between onset temperatures, instead of between the fixed 100–200°C limits as in Fig. 3. Whether the fixed 100–200°C limits, the onset temperatures limits, or any other temperature limits are used for integrating the enthalpy peaks, the important thing is that the same set of limits are used when comparing different samples.

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As in the case of the M/F method, the RE method provides a quantitative estimate of the degree of cross-linking by comparing the residual enthalpy of the sample under study with that for a sample of the same EVA in its uncross-linked (as-received) state. The degree of cross-linking as determined by the RE method may be obtained using Equation 6:

$$\%XL^{RE} = \frac{H_1 - H_2}{H_1 - 0} \times 100 \qquad (6)$$

where H_1 corresponds to the residual enthalpy of an uncross-linked sample and H_2 corresponds to the residual enthalpy for the actual sample under analysis.

As with the M/F method, the residual enthalpy is a distinctive parameter of the DSC plot of a sample (obtained through programme step 3 of the above-mentioned procedure), which decreases with the increasing degree of cross-linking of EVA. The form of Equations 2–4 is very much like that of Equation 6, which includes the assumption that for the upper bound (100%) of the %XL estimate from the RE method, the residual enthalpy is zero.

Rheological measurements

Rheology of molten or soft solid samples may be carried out in the shear mode with most conventional rotational rheometers. Among the many types of experiments that can be useful in determining the mechanical state of samples, and thus their cross-linking level, it was decided to carry out dynamic (oscillatory) experiments in the form of frequency sweeps at a constant temperature. The fixed temperature was selected so that the samples were beyond the end of the fusion of the crystalline part of EVA, while still at a sufficiently low temperature to avoid, or at least reduce to a minimum, the cross-linking of samples during the experiment.

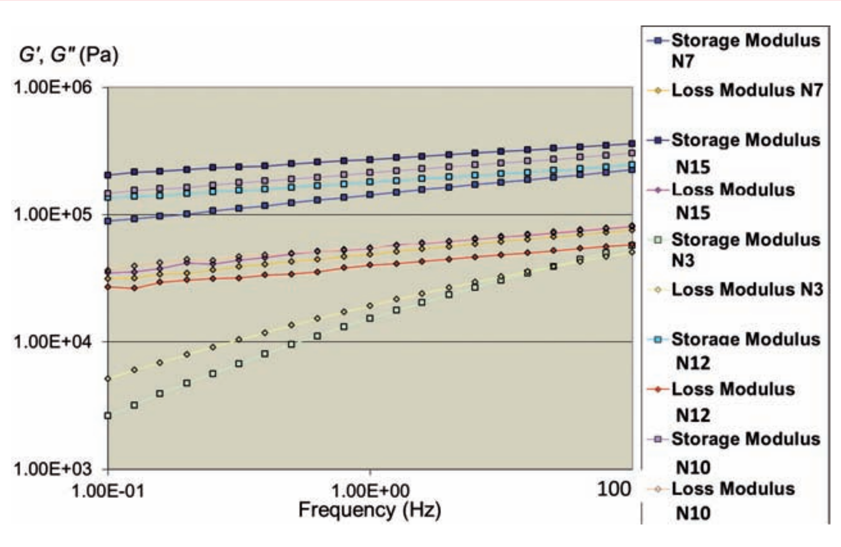

Figure 5. Elastic shear modulus (*G'*) and viscous shear modulus (*G"*) as a function of frequency for samples in a previous study. The numbers 3, 7, 10, 12 and 15 represent the times taken for lamination using the same method as described in this study, for a hot-plate set temperature of 145°C in the PV laminator.

As reported in Hidalgo et al. [1], DSC experiments helped to establish that fixing the temperature at 100°C offered a good compromise. Dynamic experiments in isothermal conditions provide the values of the elastic and viscous (*G'* and *G"*) components of the complex shear modulus at different frequencies, as demonstrated in Fig. 5 for samples from previous work in which the set-point temperature for lamination was kept constant, and the lamination time was varied from 3 to 15 minutes. The value of *G'*, when accurately known, can be directly related to a cross-linking density [4,5]. The accurate measurement of *G'*, however, may be a delicate task. The approach taken here (and in Hidalgo et al. [1]) was to determine the ratio G"/G' of the viscous and elastic components of the complex shear modulus, alternatively known as tan δ. This method has been found to compensate for some of the errors introduced, for example through the geometry of the sample, which may lead to inaccurate values of *G'* [1]. Values of tan δ, at a given frequency, may thus be compared with one another, to obtain the relative degree of cross-linking of EVA samples. The values at 1Hz, for example, have been found to lead to systematic trends in EVA samples laminated for different times [1,6]. In the work reported in this paper, all samples are assumed to be, at least, fairly cross-linked, and the relative value of tan δ is expected to reflect the differences (however slight) in cross-linking degrees.

Solvent extraction (gel content method)

The solubility of EVA samples in good solvents depends strongly on their degree of cross-linking. For many years, solvent extraction methods have been used as quality control techniques by industrial polymer suppliers when there has been a need to determine the degree of cross-linking of EVA and other rubbery materials. Although various solvent extraction methods and operating conditions are used by EVA resin suppliers, as well as EVA PV film suppliers and PV module manufacturers, the gel content (or insoluble part) on a 0–100% scale is considered to be a useful specification in that it allows the comparison of samples having different degrees of cross-linking. In this study, the above-mentioned operating conditions (see ‘Experimental conditions: materials and methods’) were used to determine the gel content of the samples at three different set points for the lamination temperature.

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Cross-linking degrees from the different methods

Table 1 presents all the results for the different methods employed in this study. The gel content method, used as a reference by the PV industry and

Temperature set point (lamination)	%XL gel content method (toluene)	%XL M/F method (Netzsch)	%XL M/F method (TA Instruments)	%XL RE method (Netzsch)	%XL RE method (TA Instruments)	Rheology: tan δ @ 1Hz and 100°C
145°C	77	60	67	51	45	0.207
150°C	83	74	70	57	54	0.192
160°C	87	76	75	85	84	0.168

Table 1. Numerical values obtained for each of the three samples laminated at set-point temperatures of 145, 150 and 160°C, by using each of the four different methods discussed.

other polymer-related industries, yields a % gel content (insoluble fraction after solvent extraction), which is a direct weight percentage, and which is often considered to be an 'absolute' measurement of the cross-linking degree of a sample. It is important to note that this is not a measurement of the cross-linking density as defined in Flory [4], but it is believed to be related to it.

For both the M/F and RE DSC methods, Equations 2–6 allow the results to be expressed in a percentage scale. The percentage scale for these two DSC methods, however, is not comparable, in terms of absolute values, to the percentage scale of the gel content method: the %XL estimates yield relative values, therefore only allowing the comparison of samples from the same roll or grade of EVA film, with respect, for example, to different lamination conditions (time, temperature, pressure). In order to translate %XL values from the DSC methods into their equivalent % gel content values, a correlation analysis must be performed, preferably with a significant number of samples having different cross-linking degrees. It can be seen from Table 1 that all the methods reveal a consistent trend: the %XL estimates increase with set-point (lamination) temperatures, and the tan δ values decrease (more elastic, less viscous) as a function of these temperatures.

One of the trickiest questions when determining cross-linking degrees using any method is whether or not a given sample corresponds to a sufficiently cross-linked film. This question is of major importance and will be answered in terms of pass/fail criteria, as discussed in the next section.

Pass/fail criteria

A three-colour code has been adopted to account for empiric pass/fail criteria for each method. This code is indicated in Table 1 and has the following meaning:

- **Red:** insufficient cross-linking degree or level. It is risky to regard this level as satisfactory.
- **Orange:** the cross-linking degree may be sufficient. This level might be safe enough, but the method requires special attention, such as the user's skill and field experience, to determine if it can be used for production.
- **Green:** the cross-linking degree is good. This level is considered to be highly reliable.

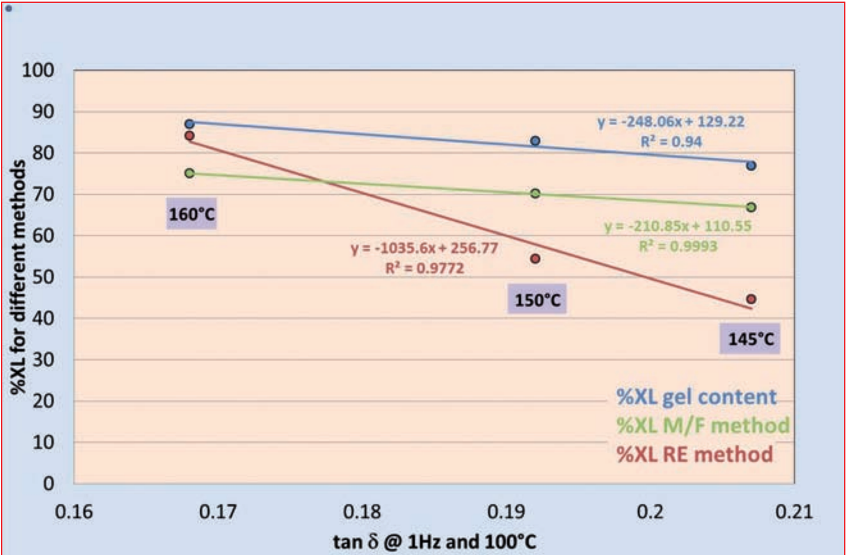

Figure 6. Correlation between %XL estimates from the gel content method and the two DSC methods (M/F and RE) with respect to the rheological parameter tan δ at 100°C and 1Hz.

The way these pass/fail criteria have been used in this study will now be described for each of the different methods.

For the *gel content method*, the current widely accepted pass/fail criterion states that suitable cross-linking is obtained if samples yield a gel content of higher than 75–80% [7] (the gel content minimum was only 65% in the early years of the use of EVA as a PV encapsulant in the 1980s [8]). For this study a gel content of below 75% is therefore regarded as insufficient (red), while a gel content of 80% or above is regarded as good (green); a value in between (75–79%) is considered to be probably sufficient (orange).

For the *melt/freeze method*, the pass/fail criteria depend on the EVA (supplier, grade) that is used. Thorough experimentation with the commercial STR Photocap 15420 P/UF used here has allowed us to consider values lower than 65% as insufficient (red), higher than 74% as good (green), and in between (65–74%) as probably acceptable, but with a careful follow-up necessary. These pass/fail criteria include close links with PV tests, such as damp-heat cycling.

For the *residual enthalpy method*, to the authors' knowledge there are no well-established pass/fail criteria, so those criteria described above for the gel content method were used.

Finally, for *rheological measurements*, carried out in the way explained in Hidalgo et al. [1] and Hidalgo and Medlege [6], and also used in this study, it was recently found that with at least four different grades of commercial EVA PV films, values above 0.25 may reflect insufficient cross-linking (red), values below 0.2 may be regarded as good (green), and values in between (0.25–0.2) could be sufficient (orange), but a certain amount of follow-up may be necessary.

Fig. 6 shows the correlation that exists between all %XL estimates (gel content, M/F and RE) and the rheological measurements. For DSC, the values from Table 1 corresponding to the measurements with the TA Instruments calorimeter have been used. As can be seen, there is a good agreement with rheological measurements, with the M/F data yielding the best correlation.

Final comments and conclusions

The aim of this study was to show how different characterization techniques for determining relative cross-linking degrees of EVA encapsulant samples can be used in a specific example related to the optimization of a lamination process parameter (in this case the set point for the temperature of the heated plate of a vacuum laminator).

Besides the well-known gel content method and rheological measurements, which are used as references, two different DSC methods, currently being considered for the development of an international standard, were applied. These methods are easy to use, since only very small amounts (a few milligrams of unconditioned material with no particular geometrical form) of EVA film are required, and no particular sample preparation is necessary. The two DSC methods may be used either independently (two different short DSC programmes allow the gathering of the required data) or in a combined manner, with a single DSC programme generating the required data for both of them. The use of the two methods in combination results in a more reliable procedure for double-checking the outcome, since each has its advantages and drawbacks. The M/F method, for example, is considered to be more universally applicable (it can be used for 'old' as well as return-from-the-field samples, very low or very high cross-linking degrees, etc.), as it is based on a thermal transition of EVA; the RE method, on the other hand, is considered to be easier to use, as it is based on the analysis of a single parameter which can be readily obtained using standard DSC software.

> "The authors believe that it will be possible to realize a time-saving and reliability potential with the use of these new characterization methods."

The use of all these methods, including the gel content one, cannot be dissociated from the pass/fail criteria. The latter may be implemented in the follow-up process for one or more parameters, such as those obtained using the DSC methods (T_c, T_{onset}, SF, residual enthalpy), the rheological measurements (tan δ), or the solvent extraction data (% gel content). These pass/fail criteria may feature a more universal nature in the case of reference methods such as the gel content test or rheology, and may be more dependent on the type of EVA (formulation, base resin) in the case of the DSC methods. In this study, pass/fail criteria have been presented for one, widely used, grade of EVA encapsulant film. These criteria have been established to the best of the authors' knowledge for all the methods, based on their experience in working with commercial EVA films. These criteria may vary with different EVAs, especially in the case of the DSC methods, and should only be regarded as a guideline. It is expected that by applying the DSC methods, users will eventually become familiar with, and recognize the behaviour of, the EVA films that they employ, in such a way that they will ultimately be able to directly associate DSC plots with samples showing a sufficient or insufficient cross-linking degree, without even needing to calculate %XL estimates or refer to gel content characterizations. The authors believe that such a skill level can be acquired in a short time, and that it will be possible to realize a time-saving and reliability potential with the use of these new characterization methods.

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About the Authors

Manuel Hidalgo received his Ph.D. in macromolecular materials from Lyon I University. He is a senior research scientist at Arkema, and currently co-project leader at Sollia, a joint laboratory with the French Institute for Solar Energy (INES). He holds more than 50 patents and has published almost 30 papers in the polymer field.

Dominique Thil has been involved in R&D since 1990, mainly in the chemical process industry, and has two years' experience in the manufacturing of PV modules, including soldering and lamination. He currently works at the Sollia joint laboratory within INES.

Christophe Dugué is a process engineer with 22 years' experience in the field of PV energy at EDF ENR PWT (Photowatt). He is currently a co-project leader for the installation of a new production line of PV modules.

Enquiries

Dr. Manuel Hidalgo
Arkema
Sollia Laboratory at INES-LMPV
Savoie Technolac
50, avenue du Lac Léman – BP332
73377 Le Bourget du Lac Cedex
France

Tel: +33 (0) 4 79 60 14 53
+33 (0) 6 78 03 98 06
Email: Manuel.HIDALGO@cea.fr
manuel.hidalgo@arkema.com