

A new method for measuring cross-link density in ethylene vinyl acetate-based encapsulant

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ABSTRACT

Among the different packaging materials used in photovoltaic solar modules, ethylene vinyl acetate-based (EVA) encapsulants play an important role during the lifespan of the module assembly. Prior to lamination, EVA is a thermoplastics polymer containing a number of additives. During the lamination process, EVA cross-links into a three-dimensional network structure, i.e., a thermoset, which provides protection for solar cells against detrimental environmental conditions. Since EVA has a very low glass transition temperature and melting points, proper cross-link density has to be achieved through the lamination process to prevent the EVA from cold flowing in the field. As a result, module manufacturers constantly monitor the cross-link density or gel content of EVA after lamination. This paper proposes a new method of measuring the EVA cross-link density value while avoiding many of the pitfalls associated with conventional cross-link density test method.

Introduction

Many of today's commercial photovoltaic solar modules carry a 25-year warranty. Significant efforts have been dedicated to understanding and improving the reliability and durability of the whole module assembly [1], the majority of these modules use ethylene vinyl acetate (EVA) as an encapsulation material. Evidence suggests that among the different module components, the encapsulant plays a critical role in ensuring the lifetime performance of the solar module [2-3].

The EVA encapsulant serves several key functions including: 1) holding/bonding the module components together; 2) optically coupling the glass and the solar cell; 3) providing the required barrier between the solar cells and the environment; and 4) maintaining electrical isolation. The most commonly used EVA encapsulant for PV modules is a block copolymer of ethylene and vinyl acetate (VA) with a VA content of about 33% by weight. The high VA content guarantees a greater than 90% light transmission onto the solar cells. Fig. 1 is the chemical structure of an EVA block copolymer.

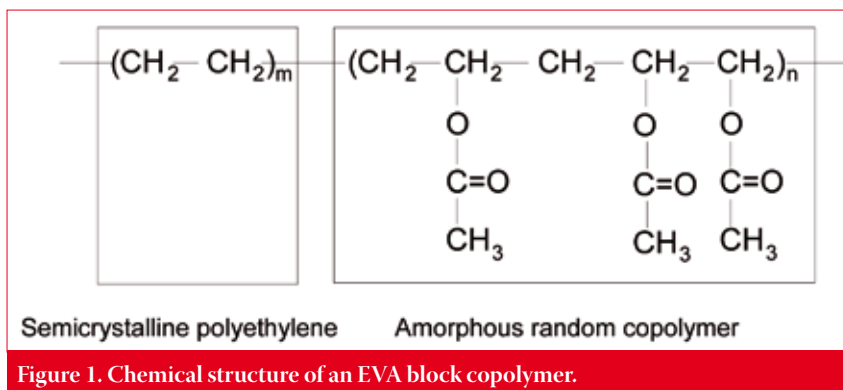
Uncured EVA is a thermoplastics polymer that has a low glass transition temperature and low melting points. In order to be suited to PV module applications, EVA must be cross-linked (or cured) into a three-dimensional network structure such as a thermoset polymer. The curing is typically achieved through the application of cross-link agents activated during the module lamination process. Cross-link agents that are generally used to cure EVA are peroxides, such as 2,5-dimethyl-2,5-di-tert-butylperoxy hexane (Lupersol 101) and tert-butyl 2-ethylhexyl percarbonate (TBEC) [4].

During the standard module lamination process, the peroxide will decompose homolytically to generate a pair of oxy radicals. Each of these radicals can abstract a hydrogen atom from the EVA molecule and initiate the cross-linking in EVA. Research carried out at Jet Propulsion Lab [5] showed that the presence of VA functional groups is critical to the cross-linking of EVA, and that polyethylene without VA groups could not be cured at all with these peroxides under normal lamination conditions.

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Since EVA is an elastomer, achieving a proper cross-link density in EVA is essential to overcome the 'cold flow' of EVA and thus make the module durable for field applications. As a result, module manufacturers should constantly check the cross-link density of cured EVA. The most widely accepted way of measuring the EVA cross-link density is through solvent extraction [5], which must be operated at elevated temperatures for better solubility of EVA in the solvent. Some common solvents that have been used to extract EVA include toluene, tetrahydrofuran and xylene.

During the extraction process, the uncured EVA will be dissolved in the hot solvent, while the cured EVA will remain solid. The samples are weighed before and after the extraction with the ratio between the two weights representing the gel content. However, this solvent extraction method poses several drawbacks including health, safety and environment issues resulting from dealing with chemicals, long turnaround time, high test variability, and the potential for built-in inaccuracies as will be discussed later in this paper.



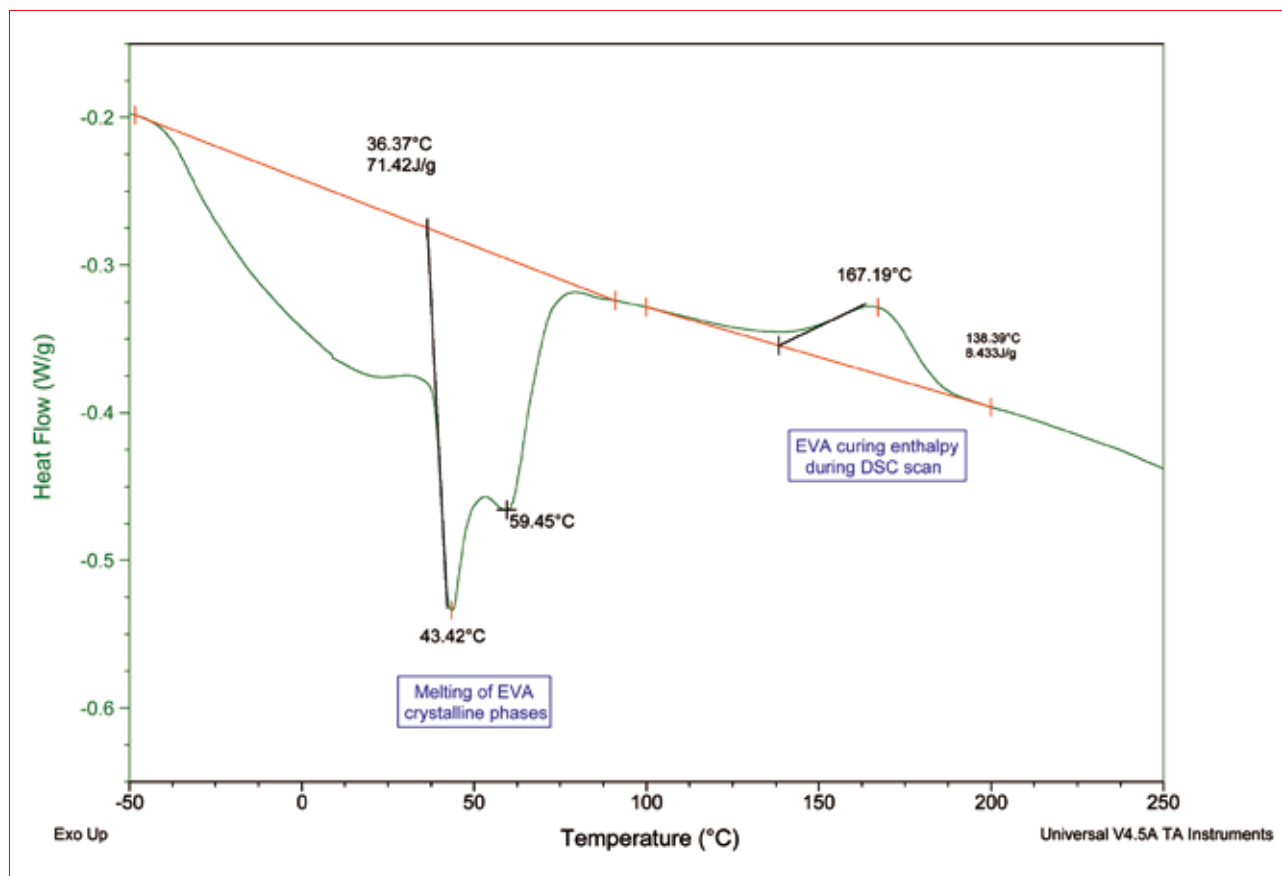


Figure 2. DSC trace of a partially cured EVA heated from -60°C to 300°C at $10^{\circ}\text{C}/\text{min}$.

Thus it is of great interest to the PV industry to develop an alternative method for measuring the cross-link density in cured EVA that can overcome the aforementioned shortcomings associated with the solvent extraction method. In this work, the feasibility of using differential scanning calorimetry (DSC) as an alternative method of measuring EVA cross-link density was evaluated. Compared with the solvent extraction method, DSC is a thermo-physical method, and can also provide structural information about the EVA formulation.

Experimental

The EVA used in this study was a standard fast cure EVA with 33 wt% vinyl acetate. The EVA was laminated under different conditions, after which process all samples were conditioned at approximately 23°C and 50% relative humidity for 48 hours prior to the DSC or solvent extraction test.

DSC tests were performed on a Q2000 modulated DSC equipped with an auto-sampler and Tzero aluminum sample pans with standard lids. During the DSC scan, an N_2 purge at 50ml/min was used to protect the sample from oxidation. The temperature range for the test was from -60°C to 300°C , with a heating rate of $10^{\circ}\text{C}/\text{min}$, which was chosen because the heating rate of EVA during lamination in this study was also around that range. The integration range for measuring the curing enthalpy was from 100°C to 200°C , and the samples weighed approximately 5mg.

Toluene solvent extractions were performed on the same set of samples that were analyzed by DSC. The extractions were carried out at 60°C for 24 hours. Samples were weighed before and after the extraction. The gel content was then calculated using the following formula:

$$\text{gel content} = \frac{\text{final weight}}{\text{initial weight}}$$

Key assumptions involved in this method are that uncured EVA dissolves 100% in hot toluene, and anything that is not soluble after the extraction will be counted as gel content. As will be shown in the results and discussion section, this method poses some key drawbacks, including over-predicting the EVA gel level if the solvent extraction is performed at temperatures lower than the high end of the EVA melting range.

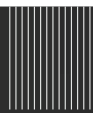
Results and discussion

As discussed earlier, cross-linking of EVA is through the reaction between peroxide and EVA. However, under normal module lamination conditions, not all of the peroxide will be consumed in cross-linking EVA due to a number of factors including limitations in EVA-curing kinetics, the presence of antioxidants in the formulation, absorbed oxygen, ethylene chain branching, and un-saturation of the polyethylene backbone [6]. According to the research carried out by Ezrin et al. [7],

there remains about 30% unused peroxide in a typical EVA module immediately after lamination. These residual peroxides will either further react with EVA in the field and/or decompose into by-products as a result of outdoor aging [7].

Differential scanning calorimetry technique

The residual peroxide within the partially cured EVA can be further reacted in a controlled manner using a continuous temperature scan. DSC is an ideal technique for this application. In a standard DSC set-up, there are two heating stages inside a furnace. During the test, two aluminium pans are placed on the two heating stages. One pan holds the test sample, while the other is empty and used as a reference. The furnace is heated and the temperature of each pan is monitored. If the test sample undergoes a thermal transition, a difference in temperature between the two pans will ensue. The DSC instrument converts the temperature difference into exothermic or endothermic heat flow data. Since the curing reaction of EVA gives off heat, when there is residual peroxide, an exothermic peak will appear in the DSC trace. By comparing the size of the exothermic peak in the uncured and the partially cured EVA, the relative amount of residual peroxide in the partially cured EVA can be quantified. In other words, the larger the exothermic peak, the more residual peroxide is left in the partially cured EVA, meaning less



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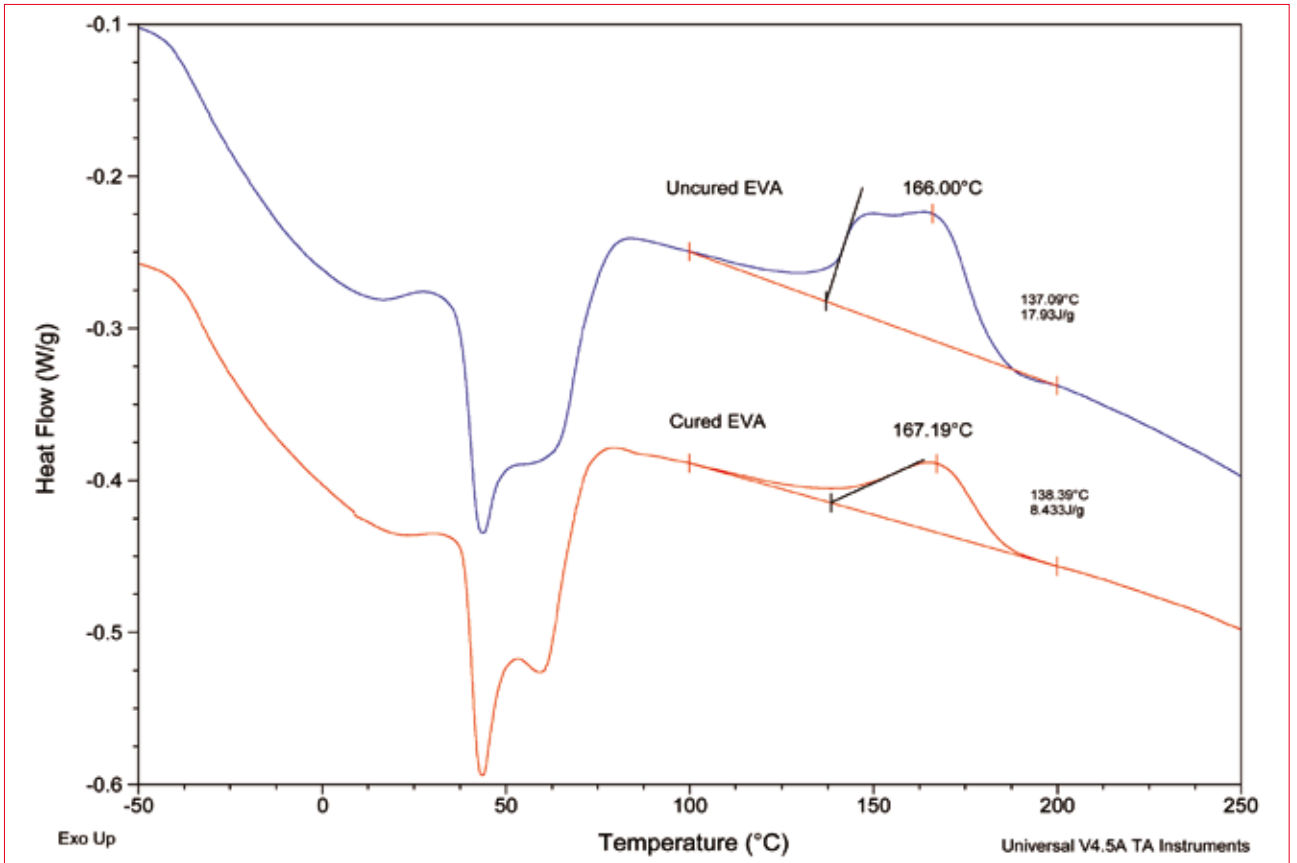


Figure 3. DSC traces of both uncured EVA (blue) and a partially cured EVA (red).

peroxide was used in cross-linking the EVA. Using the same rationale, one can also monitor the shape and position of the exothermic peak. The latter is especially useful to differentiate specific EVA curing packages.

Fig. 2 shows a DSC temperature scan for a partially cured EVA. As the sample was heated from -60°C to 300°C, a series of thermal transitions were observed. The two major endothermic peaks at 43°C and 59°C are related to the two crystal

morphologies in EVA. The peak at 43°C is due to the melting of less perfect crystals, while the peak at 59°C corresponds to the crystalline phase of the better packed polyethylene chains. This complex crystallographic structure of EVA comes

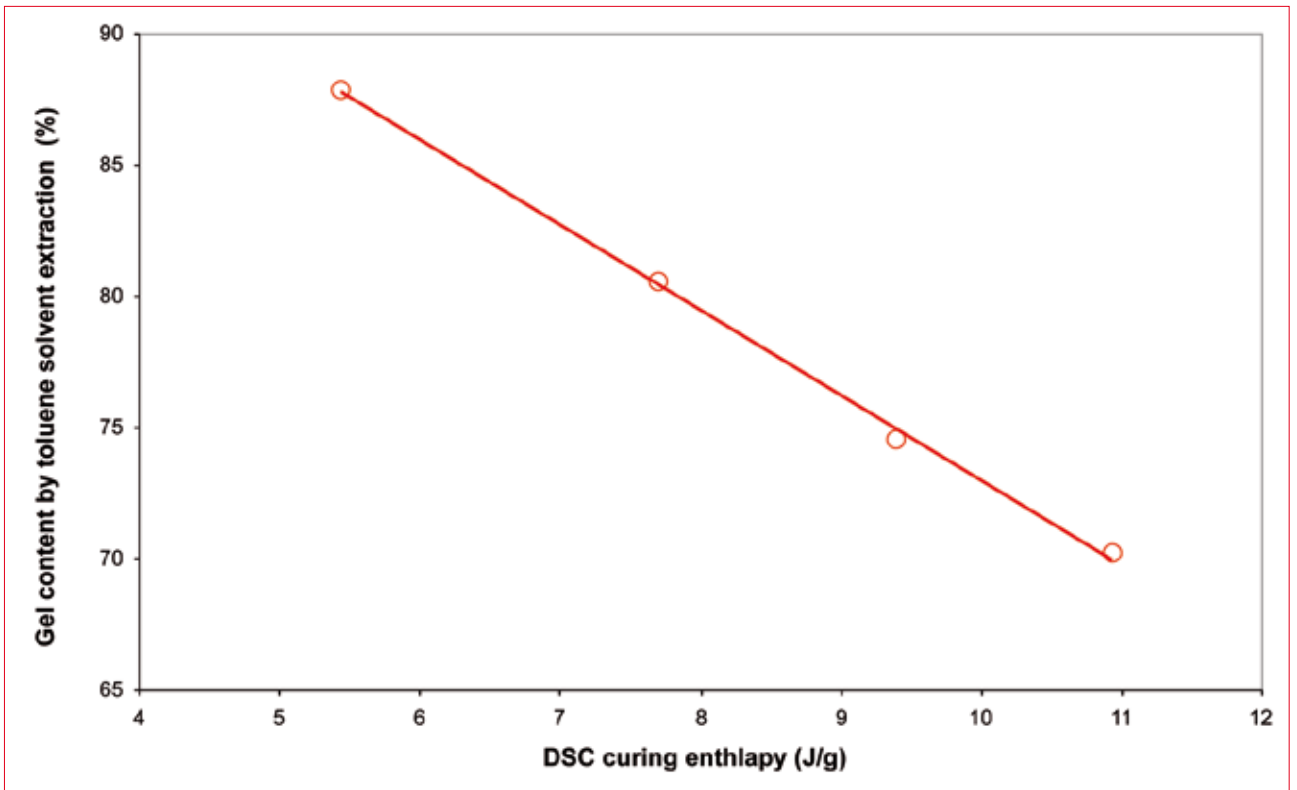


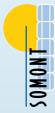
Figure 4. Correlation between DSC curing enthalpy and gel content measured by solvent extraction.



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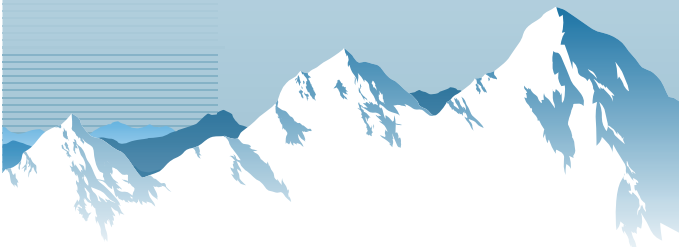


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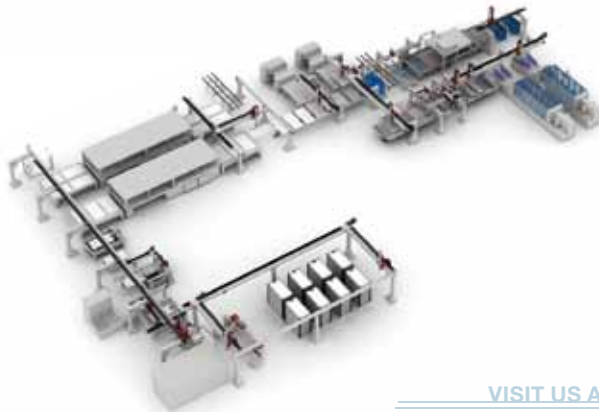
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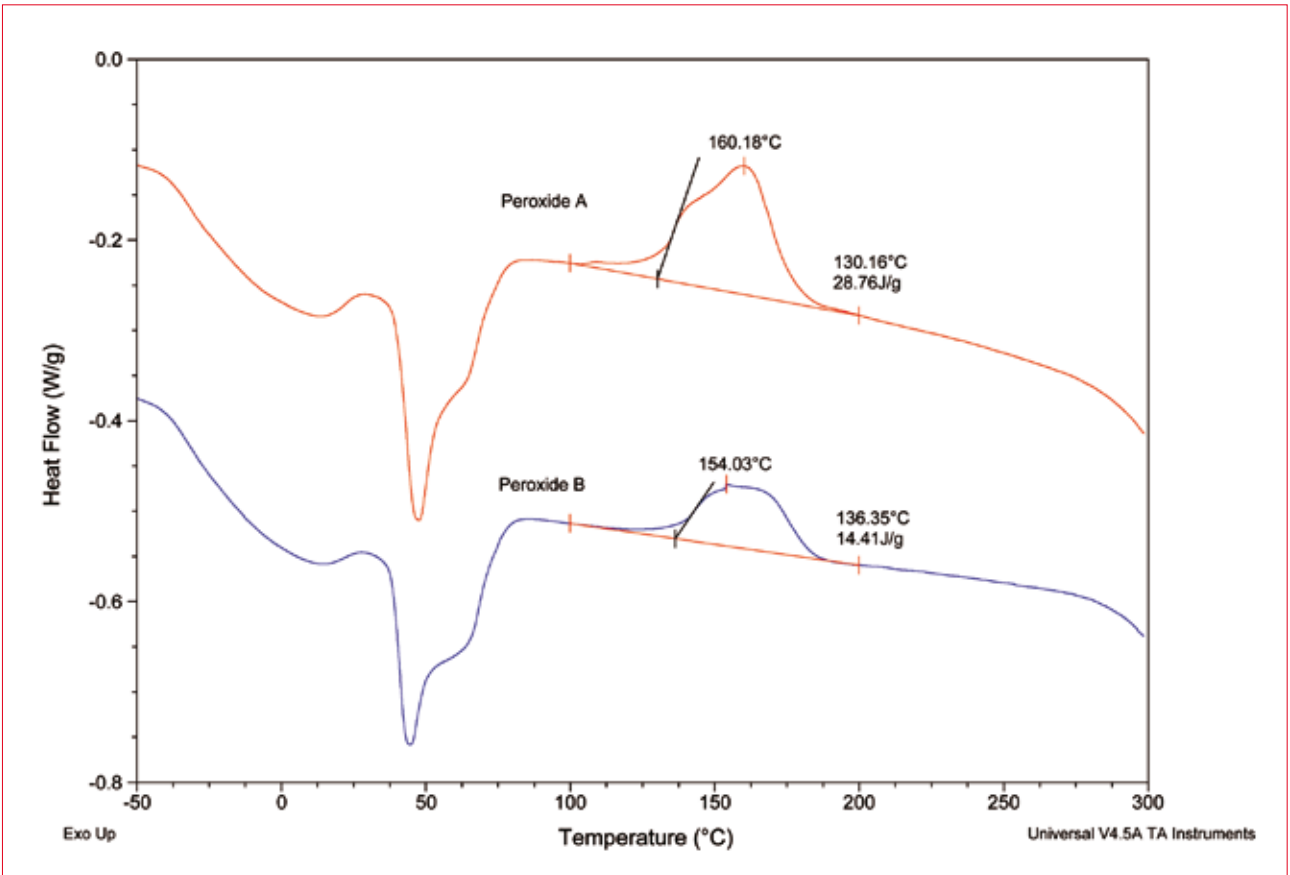


Figure 5. DSC trace of EVA samples with different peroxide types and concentrations.

from the presence of VA functional groups [8], which in turn disrupt the regularity of the polyethylene chain, which leads to poor chain packing or poor crystal

structure. The melting process continues until 75°C. It is worth noting that these melting points – which have also been reported in other studies [9] – overlap with

the glass transition temperature of EVA.

As the temperature of EVA increases to greater than 100°C, a major exothermic peak becomes visible – a result of the

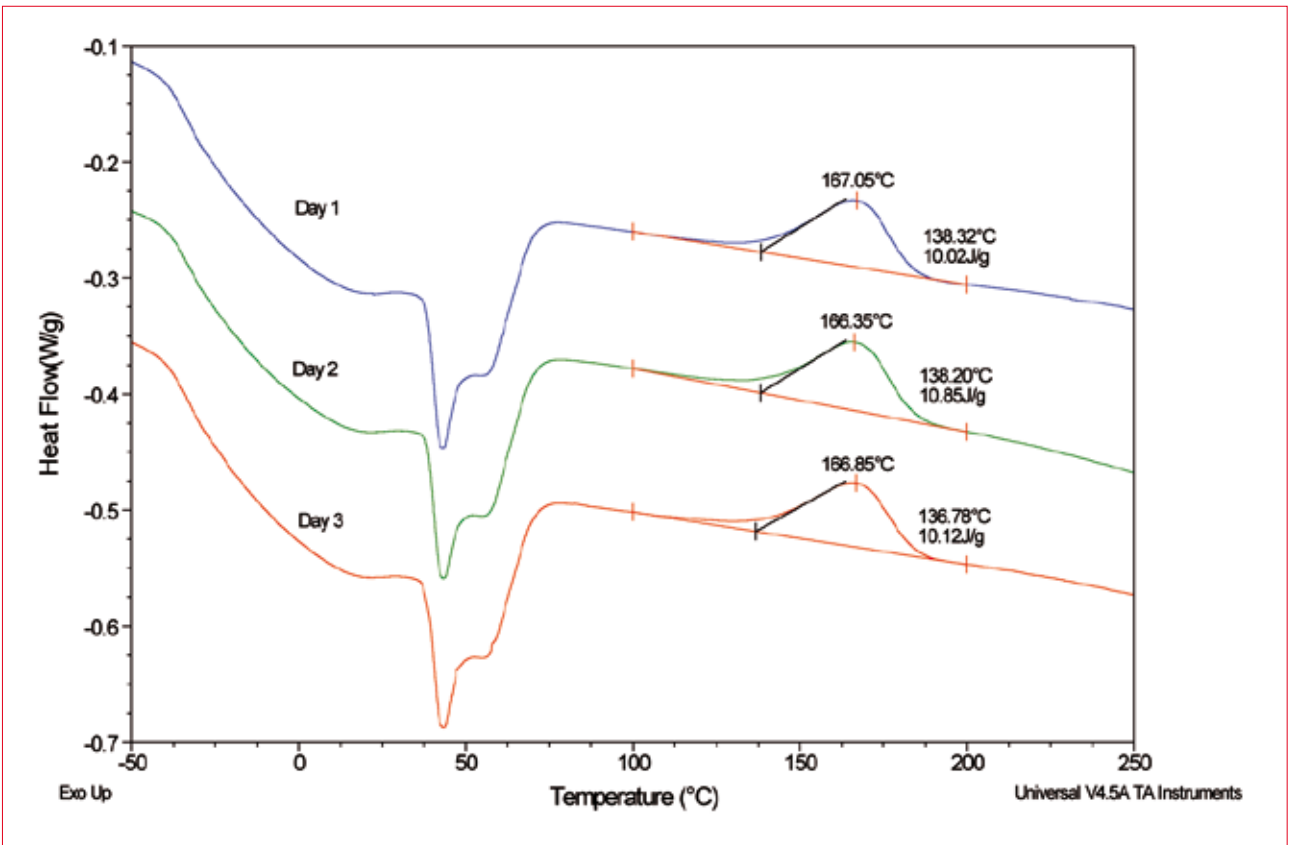


Figure 6. Repeatability check for DSC.

	DSC	Solvent extraction
Pros	Fast turnaround time	More historic data
	Can provide curing kinetics	Widely used
	Physical process/no chemicals needed	
Cons	Relies on residual peroxide	Could over-predict EVA gel content
	Not applicable to EVA with no residual peroxide, or with unknown thermal history	Long turnaround time
		High variability
		Chemical solvent required

Table 1. Comparison of DSC and solvent extraction.

reaction between EVA and peroxide during the DSC heating process. The peak temperature centres around 167°C, and continues to about 190°C. Integration of this peak shows that the amount of curing enthalpy is 8.433J/g for this sample.

“By comparing the size of the exothermic peak in the uncured and the partially cured EVA, the relative amount of residual peroxide in the partially cured EVA can be quantified. In other words, the larger the exothermic peak, the more residual peroxide is left in the partially cured EVA.”

In order to further understand the change in curing enthalpy during lamination, an as-received EVA sample (uncured EVA) was analyzed using the DSC method, the results of which analysis are depicted in Fig. 3. For comparison purposes, the partially cured sample in Fig. 2 is also plotted in Fig. 3. To determine the extent of cure, the total energy released under the curve is determined as J/g. In the case illustrated, the uncured EVA has a total curing enthalpy of 17.93J/g versus 8.433J/g for the partially cured sample. Based on these data, about 50% of the original peroxide still remains in the partially cured EVA, while the other 50% of the peroxide has been consumed in cross-linking EVA during lamination.

To get a direct relationship between the DSC curing enthalpy and the solvent extraction gel content values, EVA samples with different levels of cross-link density were prepared using different lamination conditions (time/temperature). The cured EVA samples were then analyzed by both DSC and toluene solvent extraction, the results of which are shown in Fig. 4. This illustrates that a good correlation has

been established between the DSC curing enthalpy and the gel content measured by the conventional solvent extraction method.

A DSC dynamic temperature scan can also be used to determine the type and the amount of peroxide in EVA. Fig. 5 shows the DSC traces for two uncured EVA samples with different peroxide types and concentrations. The EVA with peroxide A (red line) shows a higher curing enthalpy than that with peroxide B (blue line). In addition, peroxide A begins to cure EVA at a lower temperature than peroxide B. Based on the DSC analysis, EVA with peroxide A will generate higher cross-link density than peroxide B if laminated under the same conditions.

To check the repeatability of DSC, three identical EVA samples were cured with the same lamination conditions but on different days and analyzed by DSC. Overall, very consistent DSC traces were obtained, as shown in Fig. 6. It was found that curing enthalpies for all three samples were not statistically different from each other, from which we can conclude that DSC has an excellent repeatability.

“In order to further understand the change in curing enthalpy during lamination, an as-received EVA sample (uncured EVA) was analyzed using the DSC method.”

As Fig. 2 showed, the upper range of EVA melting extends all the way up to 75°C. Therefore, if the solvent extraction is performed at a temperature lower than 75°C, part of the EVA crystalline phase will not fully melt and will be mistakenly counted as EVA gels. This will over-predict the true gel content in partially cured EVA.

Of course, the DSC method has limitations too. Since the measurement is

based on the residual peroxide continuing to cure EVA, this method is not applicable to samples with unknown thermal history, such as field return samples, where residual peroxides may not be even present anymore. Also, for filled EVA materials, the filler level needs to be determined first for accurate measurement of the curing enthalpy or the gel content by solvent extraction. Table 1 summarizes the comparison between the DSC and the solvent extraction methods.

Summary

DSC has been proved to be a fast and reliable method of measuring the cross-link density of EVA. Given the nature of the analysis, no chemicals are involved in the process. DSC takes a much shorter time than the solvent extraction method. Furthermore, with a well-controlled lamination process, it is actually a more accurate way of measuring EVA cross-link density. Compared with solvent extraction, DSC is not only able to predict cross-link density, but also is capable of determining the curing kinetics of different peroxides.

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