Reliability testing of backsheets: Thermal analysis for comparing single and module aged films

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ABSTRACT

The main objective of this study was to evaluate the suitability of thermal analysis for characterizing the stage of hydrolytic degradation of PV backsheets containing polyethylene terephthalate (PET) as a core layer. Additionally, the ageing behaviour of single backsheets was compared with that of backsheets incorporated within PV modules. Test modules using identical components (glass, encapsulant, solar cells, etc.), varying only in the type of backsheet used, were fabricated and artificially aged (damp heat: 85°C / 85% relative humidity storage up to 2000h). The material characteristics of the single backsheets and module-incorporated backsheets before and after artificial ageing were determined by thermal analysis. It was shown that the most significant changes between unaged and aged sheets can be observed in the cooling curve of the differential scanning calorimetry (DSC) runs. For all materials, a significant increase in the crystallization temperature was found. Furthermore, the results revealed no influence of the PV module lamination procedure on the thermal characteristics of the polymeric backsheets. Even after artificial ageing under damp-heat conditions, differences between single and module-incorporated laminated backsheets were negligible. The ageing-induced degradation effects of PET could be detected by DSC for all the aged sheets. It is therefore proposed that the testing of single PET-based backsheets under accelerated ageing conditions may be a practicable way to investigate the applicability of a new backsheet material for use in reliable PV modules.

Introduction

In the PV industry, discussions about reliability testing of materials and modules are still ongoing, with a particular focus on the ageing behaviour of backsheet films and their influence on PV module reliability. Among the reported failures of backsheets are delamination within the multilayer laminate, and embrittlement, leading to cracks, yellowing etc. [1–7]. Yellowing of backsheets, however, is reported to have no effect on the electrical performance of the modules [1]. The worst failures within backsheets are cracks and delaminations, because they allow enhanced water vapour and oxygen ingress into the PV module. Water vapour is known to have a critical impact on various degradation phenomena, such as corrosion of metal cell parts, potential induced degradation (PID) of PV modules, and encapsulant degradation [5–6]. As a consequence, these failure modes can impair the performance of a PV module and shorten its lifetime [4].

To fulfil all requirements, most backsheet films for PV modules are multilayer composites comprising three or more polymer layers. The outer layers have to be resistant to various weathering impact factors (irradiance, humidity, etc.). Fluoropolymers – for example polyvinylfluoride (PVF), polyamide (PA) or specially stabilized polyethylene terephthalate (PET) – are often used as protection layers. The main purposes of the core layer are to offer mechanical stability, act as a barrier against water vapour and oxygen, and provide electrical isolation; the most frequently used polymer for this purpose is PET. In some cases barrier layers – for example aluminium or silicon oxide (SiO_x) – are additionally incorporated between the protection and core layers in order to improve the barrier properties of the backsheet [7].

"Should the individual components and materials be tested in isolation or when laminated within a PV module?"

Of particular interest is the question: should the individual components and materials be tested in isolation or when laminated within a PV module? On the one hand, individual component testing would simplify sample preparation and reduce costs; moreover, destructive tests methods – such as tensile tests or dynamic mechanical analysis (DMA) – can also be employed, which are very sensitive in detecting chemical and physical ageing processes. On the other hand, there remains the important question of material (in)compatibility and synergistic effects, and thus how the results of single materials and components correlate with those of specimens aged within PV modules. In the case of solar cell encapsulants, the testing of whole modules is preferred, since some interactions (PID, snail tracks, corrosion, yellowing, etc.) cannot be reproduced by ageing of the individual materials. Only the main applicability, the pre-selection or process unit improvements can be determined by the testing of an encapsulant material on its own. Backsheet films, however, when subjected to accelerated ageing and testing, seem to be less critical with respect to the installation situation, as fewer failure/degradation cases occur when they are combined with other PV module components.

Previous studies have shown that hydrolysis is the dominant ageing mechanism of PET, whereas the other materials used within the backsheets, such as fluoropolymers or polyamides, are not affected significantly by exposure to high humidity at elevated temperatures; in most cases the failure of the backsheet was caused by the

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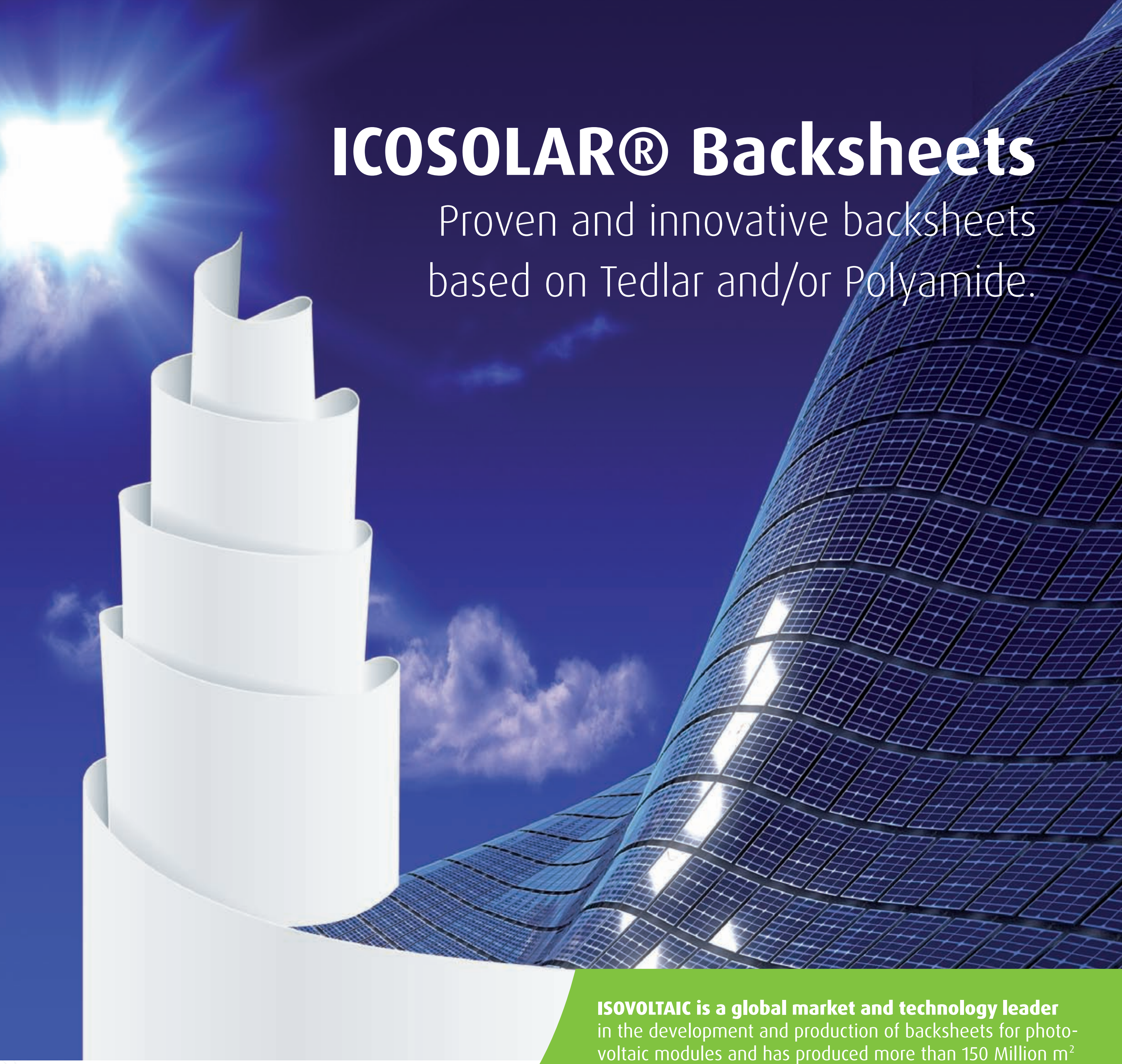

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failure of the PET core layer [7–9]. Therefore, this paper focuses on the description of the ageing behaviour of the PET core layer of various polymeric multilayer backsheets, as the stability of this layer defines the reliability of the backsheet as a whole. Hydrolysis of PET results in polymer chain scission, leading not only to embrittlement, but also to physical ageing processes, such as post-crystallization or a decrease in free volume. Both embrittlement and physical ageing may result in a significant stiffening accompanied by crack formation in backsheets, and can be detected very well using destructive methods such as tensile testing [10].

Unfortunately, mechanical testing is not applicable to backsheets that have been incorporated into PV modules. Spectroscopic methods – such as Raman spectroscopy, which as a matter of principle allows the non-destructive testing of backsheet films as well as PV modules – can detect hydrolysis and other chemical ageing processes. However, a reliable assessment of the stage of hydrolysis, in other words the stage of embrittlement and crack formation, has not yet been achieved using a spectroscopic characterization of the polymers [7,10].

Although destructive, thermal analysis may be a possible approach to testing single backsheets as well as backsheets laminated within a PV module. The crystallization behaviour in particular may indicate changes in the chemical structure of a material, such as the decrease in molecular mass as a result of polymer chain scission caused by hydrolysis [11–13].

The main aim of this paper, therefore, is to evaluate the use of thermal analysis for characterizing the stage of hydrolytic degradation of PV backsheets containing PET as the core layer. In a second step, the ageing behaviours of PV backsheets with PET core layers after exposure to damp-heat (DH) conditions, both as a single film and when laminated within a PV module, are investigated and compared. The influence of material interactions on the reliability of the PET core layer within the PV module is discussed.

Experimental

In the study reported here, the ageing behaviour of four different types of backsheet, all of which contain PET core layers, from three different producers was investigated. The outer/inner layers of the backsheets were either 1) fluoropolymers (symmetric composition), or 2) stabilized PET on the outer side and ethylene vinyl acetate (EVA)/polyethylene (PE) as a primer on the inner side. Test modules consisting of a glass front sheet (float glass, 2mm), a fast cure EVA encapsulant, six polycrystalline Si cells, and polymeric backsheets were fabricated using a standard lamination process. The composition of all test modules was identical except for the type of backsheet used; a description of the backsheet films investigated is given in Table 1. Single backsheet films and one set of test modules were exposed to DH conditions at 85°C and 85% relative humidity (RH) for 1000h and 2000h. A second set of test modules and backsheets was set aside as original reference samples.

The thermal behaviour was characterized by means of differential scanning calorimetry (DSC) using a Perkin Elmer DSC 4000; the measuring programmes and parameters are listed in Table 2. Samples of the backsheets (~10mg) were cut and placed in 50µl pans with perforated lids. Samples from the modules were taken from the border regions. For each evaluation, an average was taken from at least two sample runs. Melting points, melting enthalpies and crystallization temperatures were evaluated in accordance with ISO 11357-3 [11].

Results and discussion

The results will be described and discussed by considering first the DSC curves of single backsheet films in their original state and then after ageing (DH storage). The description of the results will focus on the ageing behaviour of the PET core layer, which is mainly responsible for the mechanical stability, and thus the reliability, of the backsheets [8,9]. In the following step, single backsheets and sheets incorporated into modules in the original state will be compared. Finally, the ageing-induced (DH storage) changes at the module and component levels will be compared, and the influence of material interactions on the reliability of the PET core layer within the PV module will be discussed.

The results of the DSC runs (first heating, cooling, second heating) for backsheet B1 are shown in Fig. 1. For the first heating curve (in black) the first melting peak, T_{m} = 194°C, can be attributed to the PVF outer layers.

Abbreviation	Inner layer	Core layer	Outer layer	Thickness [µm]
B1	PVF	PET	PVF	340
B2	PVDF	PET	PVDF	325
B3	EVA/PE	PET | aluminium	PET	390
B4	EVA/PE	PET	PET	370

Table 1. Properties of backsheets used.

	Start	End	Time/ramp
Isothermal segment	20°C		5min
Segment 1	20°C	270°C	10°C/min
Isothermal segment	270°C		5min
Segment 2	270°C	20°C	10°C/min
Isothermal segment	20°C		5min
Segment 3	20°C	270°C	10°C/min

Table 2. Experimental parameters for DSC measurements (nitrogen atmosphere).

The highest melting peak with respect to temperature and area (T_m = 256°C) is attributed to the melting of the main fraction of the PET crystallites. A secondary melting peak of the PET core layer was found at 219°C, which can be attributed to small crystallites formed during exposure to elevated temperatures. This peak was not detected in the second heating run (red curve), which confirms its irreversible, ageing-induced character. Glass transitions or the thermodynamic melting of a polymer are reversible effects and will therefore be seen in each heating run, irrespective of the history of the polymer. The second heating run gives information about material-specific constants and includes only reversible effects; it plays a subordinate role in the analysis of ageing-induced changes. In the second heating run, the PVF melting peak was detected at 192°C and the PET melting peak at 248°C.

The first crystallization peak (T_c) on the cooling curve is attributed to PET (205°C) and the second to PVF (169°C). The information obtainable from the crystallization behaviour (i.e. cooling run) is rarely discussed in standard literature. However, it bears evidence of changes in the chemical structure of a material, such as the decrease in molecular mass because of polymer chain scission, etc. [12–13].

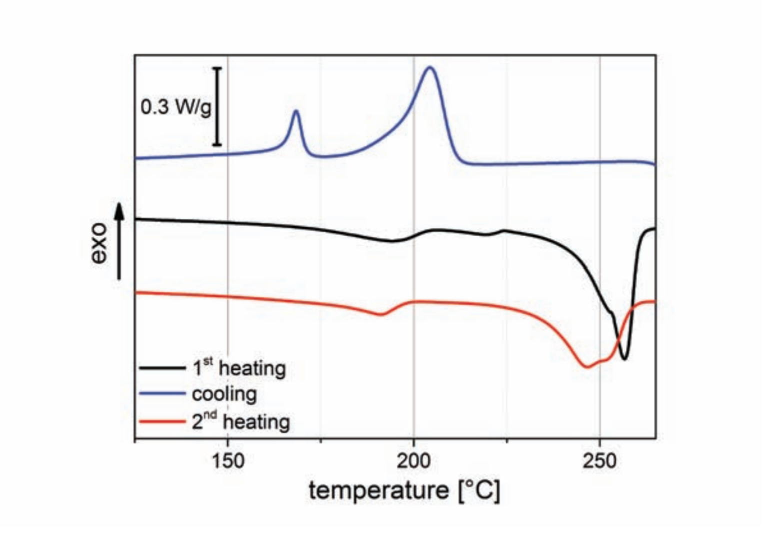
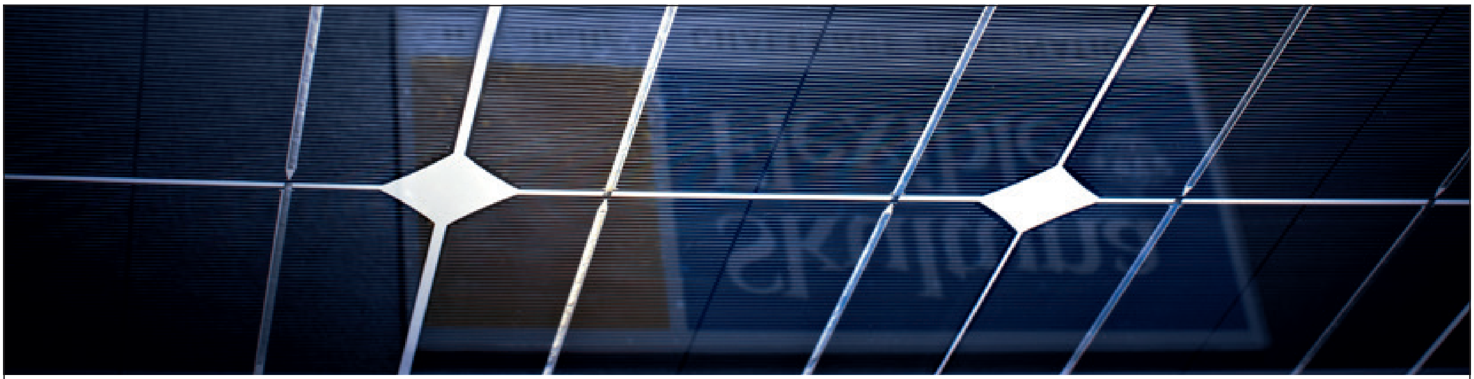


Figure 1. DSC curves for the initial state of single backsheet B1.

Post-crystallization of polymers results in an increase in the melting enthalpy as well as a shift to higher melting temperatures. Hydrolysis induces polymer chain scission, leading to a decrease in molecular mass and to a shift in the crystallization temperature to higher values as well as to an increase in the crystallization enthalpy [12].

For all backsheets the melting region of PET was found to be rather broad (230–270°C), although the maximum of the peak was highly reproducible in a very narrow temperature range, between 256 and 258°C. The maxima of PET on the crystallization curves varied between 204 and 214°C. For backsheets B3 and B4, a double peak of PET on the crystallization curves was seen, which can be attributed to the two PET layers (core and outer layer), which vary in composition. The outer PET layer is claimed to be hydrolysis- and UV-resistant: a different additive formulation, molecular mass distribution and/or crystallinity of the



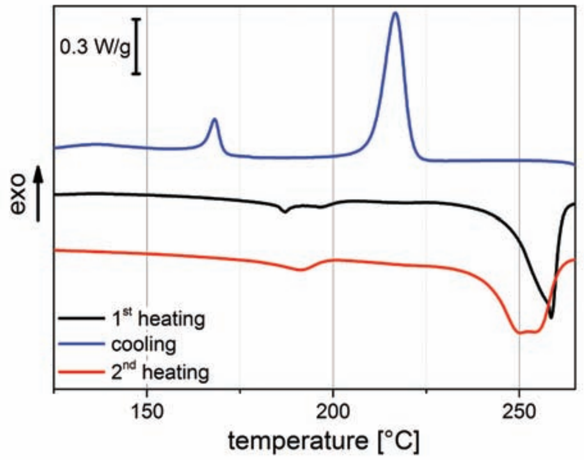


Figure 2. DSC curves after 2000h DH exposure of single backsheet B1.

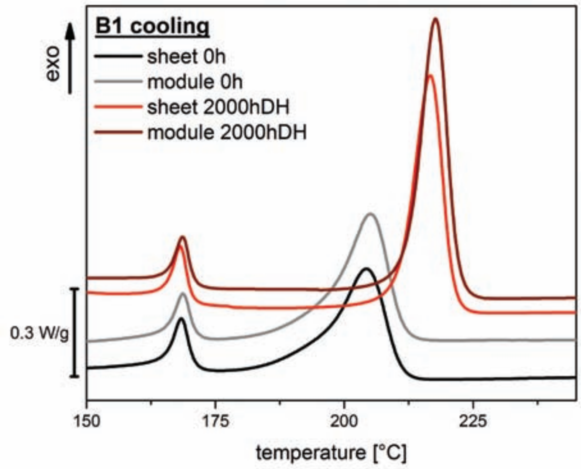


Figure 3. DSC cooling curves for the initial state and aged (2000h DH) samples of backsheet B1.

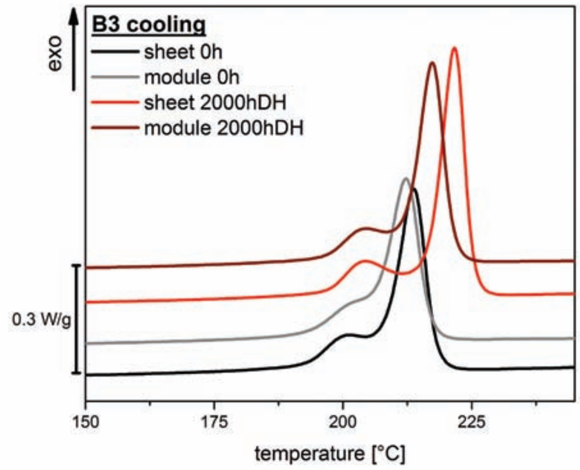


Figure 4. DSC cooling curves for the initial state and aged (2000h DH) samples of backsheet B3.

material is therefore expected.

The DSC runs (first heating, cooling, second heating) of backsheet B1 after 2000h of damp-heat testing are shown in Fig. 2. The maxima of the melting peaks of the PET materials lie between 258 and 259°C, with a standard deviation of less than 0.3°C; in comparison to the initial state samples, this means a small increase of ~1–2°C in the melting temperature. The melting enthalpies, on the other hand, show a significant increase. Both of these factors indicate a post-crystallization, which generally appears as a result of the ageing of PET at elevated temperatures [12]. The mechanism is enhanced because of the exposure of PET over the glass transition temperature (~80°C).

> "Compared with the unaged samples, the aged samples exhibited an increase of ~5–13°C in the crystallization temperature."

The most significant differences between unaged and aged sheets can be seen in the cooling curve of the DSC runs. The maxima of the PET crystallization peaks of the various backsheet materials were found between 217 and 222°C, with a standard deviation of less than 0.4°C; compared with the unaged samples, the aged samples exhibited an increase of ~5–13°C in the crystallization temperature. Changes in the DSC cooling curve are related to chemical changes in the polymers. Polycondensation polymers are susceptible to hydrolysis, which in the case of PET is the cleavage of the ester groups in the polymer chain by the addition of water. This reaction therefore leads to chain scission and thus a reduction in average molecular weight. Crystalline parts of the polymer can be regarded as being impermeable to water vapour, so hydrolysis occurs solely in amorphous parts of the polymer or in imperfections in the crystalline zones [14,15]. All terminal groups produced during artificial ageing act as a nucleating agent for new crystals: as a consequence, smaller crystals, but with broader lamellae sizes, are formed, which is known to enhance crystallization temperatures [12,13].

The next step was a comparison between single backsheets and sheets incorporated into modules. In general, the DSC curves for samples taken from single sheets were comparable to those for samples taken from modules, for initial and aged samples. Fig. 3 shows the resulting DSC cooling curves for B1 for the initial stage and aged samples. The increases in the maximum of the crystallization temperature for B1, B2 and B4 are identical for samples taken from the single backsheet and from the module.

> “The lamination process of the PV module has no influence on the thermal properties of the backsheets.”

Two main conclusions can be drawn from these results. First, the fact that the curves for single backsheets and for sheets laminated into a PV module are almost identical confirms that the lamination process of the PV module (even though enhanced temperatures of up to 150°C are involved) has no influence on the thermal properties of the backsheets. Presumably, the lamination times of a maximum of 30 minutes do not lead to significant physical changes in the PET core layer. Second, the interactions between the materials in a PV module seem to be negligible in relation to the degradation behaviour of backsheets consisting of a PET core layer.

In contrast with the other samples, for backsheet B3 a significant increase in the crystallization temperatures of the PET core layer was observed for the samples taken from the single sheets compared with those taken from the module (see Fig. 4). The likely reason for this effect is the additional aluminium barrier layer, which is the only difference between backsheets B3 and B4. In the module, with the impermeable glass front sheet on one side and the impermeable aluminium layer between the outer and core layers on the other side, the ingress of water vapour into the PET core layer is restricted and thus hydrolysis/degradation is reduced [16]. This observation reaffirms the feasibility of thermal analysis for investigating the stage of hydrolysis of PET, as it demonstrates that the limited availability of water vapour because of a barrier layer leads directly to a smaller increase in crystallization temperature.

The DSC results showed that, for the reliability testing of backsheets for PV modules, generally no significant differences between single and module-incorporated aged sheets can be found. The only exception is backsheet B3, which contains a gas-tight Al barrier layer. The interactions between materials in a PV module are negligible in relation to backsheets.

> “Generally no significant differences between single and module-incorporated aged sheets can be found.”

As described above, evidence for the reliability and long-term stability of backsheets with PET layers can be deduced from the ageing-related changes derived from the thermal analysis. The DSC results of aged backsheets taken from single and module-incorporated sheets indicated post-crystallization and hydrolysis/degradation of PET. Nevertheless, further research is warranted in order to obtain a comprehensive knowledge of the chemical ageing processes and to support the results presented here.

Summary and conclusions

This paper has presented an evaluation of the suitability of thermal analysis for characterizing the stage of hydrolytic degradation of PV backsheets containing PET as a core layer. The question as to whether meaningful reliability testing of backsheets should be performed on backsheets laminated within a photovoltaic module or on single backsheets was examined. Single and module-incorporated, unaged as well as artificially aged, backsheets were tested.

The most significant differences between unaged and aged sheets were seen in the cooling curves of the DSC runs. For all materials tested, a significant increase in the crystallization temperature was found.

Moreover, the DSC results for the reliability testing of accelerated aged backsheets of PV modules revealed no significant differences between single and module-incorporated aged sheets. In the case of backsheets with a PET core layer, the results indicate that the reliability testing for the ageing characterization of single sheets yields meaningful results which can be directly correlated to the behaviour of the backsheets laminated within a module. The interactions between the materials in a PV module seem to be negligible for the stage of hydrolysis of the PET core layer of the backsheets investigated. It can therefore be concluded that the testing of single PET-based backsheets under accelerated ageing conditions may be a practicable way of investigating the applicability of a new backsheet material for use in PV modules to ensure their reliability and stability in the long term. This would allow simplified sample preparation, reduce

costs and offer more testing options for the characterization of ageing-induced changes of the polymeric materials.

A proposed next step of the study would be to correlate the results from DSC with those from additional methods, such as tensile testing, rheology or size exclusion chromatography, which are very sensitive in characterizing the decrease in average molar mass resulting from hydrolytic chain scission.

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