

XPS analysis of photovoltaic EVA encapsulants and interfacial damp heat degradation products

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Abstract

The lifetime of a photovoltaic module depends significantly on the used polymeric encapsulant [1]. Ethylene vinyl acetate copolymer grades (EVA) are still dominating the market. The main objective of this study is to evaluate various EVA grades, to establish structure-property correlations and to elucidate the degradation products at the EVA/solar glass interface. While well-established characterization methods such as infrared spectroscopy (IR) or differential scanning calorimetry (DSC) were also used, special attention was given to advanced X-ray photoelectron spectroscopy (XPS). The XPS results were systematically compared to IR and DSC data.

EVA copolymer structure and property correlations

In Table 1 the nominal VA content of various unaged EVA copolymer grades is compared to characteristic values of IR, DSC and XPS data. Regarding IR analysis, the absorbance of the C=O band at 1730 cm⁻¹ was related to the band of the C-H methyl band at 2920 cm⁻¹. The C=O absorbance increased with vinyl acetate comonomer (VA) content. Moreover, the crystallization T_c deduced from DSC thermograms revealed a linear correlation with the VA content. While both DSC and FTIR are often employed to characterize EVA encapsulants [2–4], XPS is rarely used despite its excellent potential to characterize polymers and detection of chemical changes [5–7]. Furthermore, the clear advantage of XPS compared to FTIR and DSC is that the VA comonomer fraction can be determined directly, without the need of reference samples and calibration routines. As depicted in Table 1, XPS also allowed to establish a linear correlation between the VA content and XPS peak intensity ratios. Interestingly, the XPS data indicated a slightly higher VA content within the first few nanometers of the surface of the sample. Presumably, this could be attributed to a higher concentration of the VA-rich amorphous phase fraction on the surface of the semi-crystalline EVA material.

Table 1. Nominal VA content compared to the measured values.

Nominal VA (wt%)	A ₁₇₃₀ /A ₂₉₂₀	T _c (°C)	VA (wt%) by XPS
9.0	0.32	80.5	10.9
14.0	0.54	70.4	16.5
26.0	0.93	52.4	27.0
28.0	0.96	49.4	29.6
40.0	1.56	28.8	41.3

Damp heat degradation products at the EVA/glass interface

Furthermore, to elucidate the degradation mechanisms, a commercial, UV-transparent, peroxide-crosslinking EVA encapsulant with a VA content of 30.2 wt% (as determined by XPS) was used for lamination of double solar glass laminates, which were exposed to damp heat (85°C, 85%rh) and fractured by compressive shear testing. The delaminated surfaces of the double glass laminates were investigated by IR and XPS. By IR, a new peak at 1560 cm⁻¹ is clearly discernible. This peak is attributed to carboxylates which were formed upon damp heat exposure close to the glass/EVA interface in agreement with other studies [8,9]. By visual inspection the laminates were classified as failed at the interface.

Regarding XPS, a comprehensive analysis was carried out in the middle of the fractured compressive shear specimen. The changes of concentration of Na, Ca and Si are depicted in Figure 1. The interface-near failure of the aged specimens is clearly confirmed by the significant Si concentration just for the aged fractured specimens. Moreover, the Na and Ca concentration is increasing upon damp heat ageing. This is attributed to the migration of Na from the glass substrate to the fracture process zone. The Ca signatures are most likely related to the accumulation of Ca stearate acid scavengers, enriching also close to the glass surface.

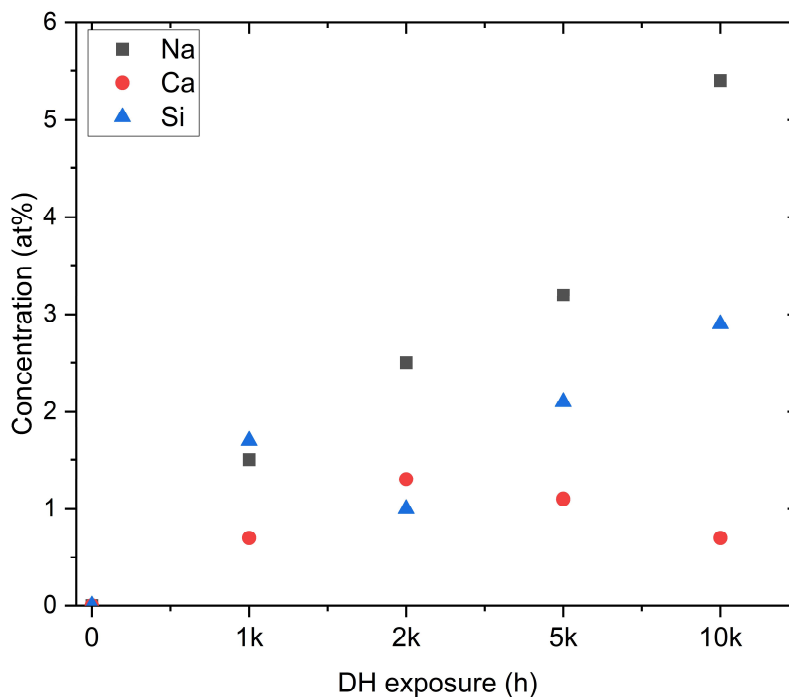


Figure 1. Changes of the elemental concentration of Na, Si and Ca of the fractured surfaces of damp heat (DH) exposed and compressive shear tested specimens by XPS.

Additionally, high resolution (HR) XPS spectra of the C1s peak of the fractured double glass samples show that the O-C=O functionality increased significantly. The data hints at diffusion of acetic acid degradation products to the interface, their reaction with Na ions from glass and the formation of Na acetates. Furthermore, the binding energy of the O-C=O decreased by 0.5 eV. Due to delocalization of the negative charge, the binding energy of Na acetate is slightly lower than for vinyl acetate. After 10.000 h of damp heat exposure, the relative fraction of O-C=O increased significantly. This rise follows a linear relationship with damp heat ageing time.

Overall, the investigations have clearly shown that XPS is a highly sensitive and reliable tool for the quantification of the comonomer content in EVA. An excellent correlation with IR and DSC data and the nominal VA fraction was deduced. Moreover, the results indicate a slightly higher amorphous phase fraction at the surface of the EVA material.

The damp heat ageing study for up to 10.000 h on double glass laminates encapsulated with an UV-transparent, peroxide crosslinking EVA confirmed an interfacial failure along with the enrichment of acetic acid moieties and the formation of acetic acid salts within the fracture process zone. This phenomenon is in good agreement with in-field ageing studies on photovoltaic modules with silicon solar cells [9].

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