

CHANGES OF MORPHOLOGY AND MATERIAL PROPERTIES OF THIN ETHYLENE-VINYL ACETATE-FILMS UNDER DIFFERENT AGING CONDITIONS

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ABSTRACT: The influence of photochemical and thermal aging on the morphology and material properties of EVA was investigated by means of Atomic Force Microscopy (AFM) and Raman spectroscopy.

The encapsulation, for which EVA is used in most c-Si PV modules, is of great importance for the long-term stability of PV modules. Delamination between the encapsulation and the solar cell or the glass may occur whilst outdoor exposition. In order to understand the processes which take place at the EVA/Silicon and EVA/Air interface during exposure to UV radiation and elevated temperature, thin non-cross-linked EVA films, spin coated onto silicon substrates to a thickness of 80 and 95 nm, were made from commercial EVA foils and from EVA pellets without stabilizing agents. The samples were aged at different temperatures (23°C and 85°C) with and without UV radiation for 200 h. The topography and the material properties of the surface were measured every 40 hours by Tapping Mode AFM and Raman Spectroscopy. Thus, the temporal evolution of morphology changes could be examined. Surface crystallization was observed, especially for the irradiated samples. EVA films which were exposed to UV light at room temperature did not show any morphological changes, indicating the necessity of a certain temperature to trigger crystallization processes. The samples with non-stabilized EVA degraded faster than the samples with additives. The Raman Spectra of the non-stabilized EVA sample gave evidence for changes in the chemical structure of the material. This finding could explain the different surface structures observed in the AFM images.

Keywords: Ethylene-vinyl acetate, degradation, aging, Atomic Force Microscopy, Raman Spectroscopy

1 Introduction

Degradation of polymeric materials usually starts at the surface due to higher absorption and the presence of oxygen and proceeds into the bulk material. Thus changes at the surface indicate degradation and can affect the mechanical properties of the material. For c-Si PV modules Ethylene-vinyl acetate (EVA) is mostly used as the encapsulation material. To maintain a high electrical yield of the PV module under different aging conditions it is important that the encapsulation material provides optical and mechanical stability. EVA foils show a decrease of elongation at break after aging with UV radiation and elevated temperature [1]. It is assumed that surface crystallization processes and inhomogeneous degradation in the crystalline and amorphous phase cause micro cracks and lead the EVA surface to become more brittle. Until now this assumption was made by means of measurements of EVA foils with DSC, DMA or tensile tests. Morphological changes could not be examined directly on the surface. By using Atomic Force Microscopy (AFM) rearrangement processes of the polymer chains can be observed down to the low nanometer scale. The EVA surface in PV modules is connected to the other module components like the solar cell, the front side glass or the backsheet. Consequently, quality of the interface of EVA with other materials is given by the EVA surface. Mechanical changes of EVA can therefore induce delamination. To understand the processes at the EVA surface, a model system consisting of thin EVA films with thicknesses of 80 and 95 nm, spin coated on silicon substrates, was investigated by means of AFM. Chemical changes in the material were examined by Raman spectroscopy [2]. To determine the influence of stabilizing agents two different EVA formulation, a commercially available and one without stabilizing agents, were used for the model system. The samples were aged under UV radiation and elevated temperature. They were measured regularly to investigate

the temporal evolution of the morphological changes.

2 Materials and Techniques

2.1 EVA

Two different EVA formulations were used. The vinyl acetate content of both samples was 28 w%. The EVA without stabilizing agents will be named EVA0, the EVA sample with stabilizing agents will be named EVA1 in the following. The melting temperatures, determined by DSC measurements, of EVA0 and EVA1 were 45°C and 43°C, respectively.

2.2 Preparation of the thin EVA films

Small pieces of EVA foils (EVA1) and EVA pellets (EVA0) were solved in toluene. The velocity during spin coating was 2000 rpm. The concentration c of EVA in toluene and the resulting film thicknesses t of the EVA films are shown in Table I.

Table I: Concentration and thickness of thin EVA films

	c [mg/ml]	t [nm]
EVA0	17.5	95
EVA1	15.8	80

2.3 Aging of the thin EVA films

The samples were aged in a climatic cabinet (Horstmann HS 220 K 45 L). The intensity of the UV radiation in the wavelength range of 315 and 400 nm was 128 W/m² and 1 W/m² for wavelengths below 315 nm.

2.3 Atomic Force Microscopy

The measurements were carried out using a WITec Alpha 500 combined AFM and Raman microscope. For Tapping mode AFM Nanoworld Arrow-NCR cantilever

with a force constant of 42 N/m and a resonance frequency of 285 kHz were used. Tapping mode images with a size of $30 \times 30 \mu\text{m}^2$ and $5 \times 5 \mu\text{m}^2$ were made every 40 h of aging. The resolution was 256x256 points per image with a scanning speed of 1 line/s.

2.4 Raman Spectroscopy

The samples were investigated by Raman spectroscopy every 40 h of aging. The WITec Alpha 500 with a laser wavelength of 532 nm was used. For each measurement 10 spectra with an integration time of 2s were recorded and averaged.

3 Results

3.1 Morphological changes under different aging conditions

AFM Tapping Mode measurements on the unaged samples proved that the sample surface is very even and did not show any elevated surface features in a range of a few nanometers (see Fig. 1). The surface roughness R_a with a value of 0.9 nm confirms the flatness and homogeneity of the EVA film. The average roughness R_a is defined by $R_a = 1/N \sum |z_i - z|$ at which N is the number of pixels, z the average height value and z_i the height value at position i.

After an aging of the EVA1 samples for 200 h under UV radiation and a temperature of 85°C the topography reveals elevated surface features with a diameter in the range of 1 μm and a height of 20 nm (see Fig. 2). The formerly homogenous surface became inhomogeneous and rougher.

The morphology of the thin EVA films that had been aged under UV radiation at ambient temperature (23°C) did not change and had even a flat surface after 200 h of aging (see Fig. 3). Heating the thin EVA films to a temperature of 85°C without irradiation caused an increasing roughness (see Fig. 4), but less elevated surface features than in the films with UV radiation and a temperature of 85°C were observed. The temporal evolution of the roughness stays constant for the irradiated samples at ambient temperature whereas the roughness increases if the thin EVA is heated and irradiated (see Fig. 5). The temporal evolution of the roughness clearly indicates the significance of the elevated temperature.

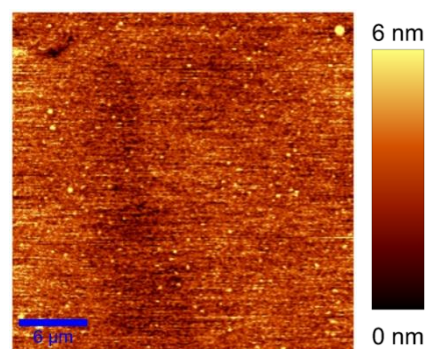


Figure 1: Topography ($30 \times 30 \mu\text{m}^2$) of EVA1 before aging

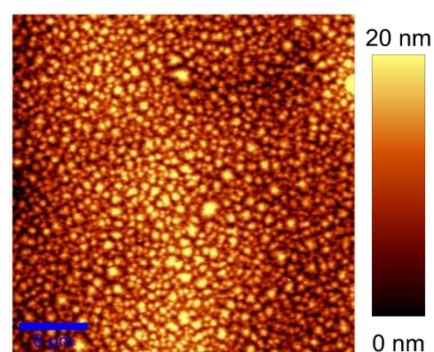


Figure 2: Topography ($30 \times 30 \mu\text{m}^2$) of EVA1 after 200 h under UV radiation and T=85°C

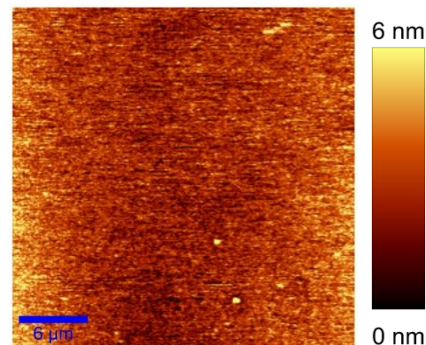


Figure 3: Topography ($30 \times 30 \mu\text{m}^2$) of EVA1 after 200 h aging under UV radiation and T=23°C

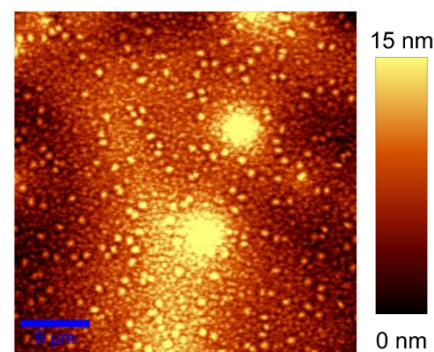


Figure 4: Topography ($30 \times 30 \mu\text{m}^2$) of EVA1 after 200 h at T=85°C

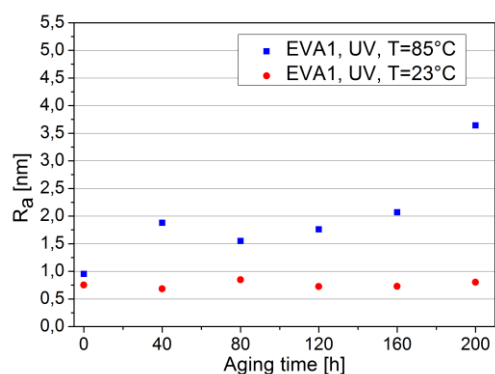


Figure 5: Average roughness of height images ($30 \times 30 \mu\text{m}^2$) of EVA1 after 200 h aging under UV radiation at $T=85^\circ\text{C}$ and $T=23^\circ\text{C}$

3.2 Influence of stabilizers to morphological changes after aging

The aged thin films of EVA without stabilizers showed the same morphological changes under UV radiation and elevated temperature as described above for the samples with stabilizing agents (see Fig. 1-4). Measurements with a higher resolution on smaller areas showed dendritic structures in the corresponding phase images (see Fig. 7). These structures could be found at the positions of the higher surface features in the corresponding height image (see Fig. 6). The roughness value for the thin films of EVA0 rises from 0.7 nm in the initial state before aging to 4.0 nm after 80 h of aging under UV radiation and a temperature of 85°C . Thus the roughness of the thin EVA films without stabilizing agents is higher after only 80 h of aging compared to the value of EVA1 after 200 h.

3.3 Chemical changes due to aging

Raman Spectra at three different positions on the thin films were measured. To examine chemical changes in the thin films, Raman Spectra were evaluated by regarding the intensities of the symmetric stretching mode of the methylene group ($2832 \text{ rel. cm}^{-1}$) and the asymmetric stretching mode of the methyl group ($2861 \text{ rel. cm}^{-1}$). The latter is part of the acetate group of EVA and is related to the amount of acetate groups in the thin films. These stretching modes were chosen to evaluate the Raman Spectra because they have high intensities and can be well detected even if the film thickness is in the nanometer range. The intensities were determined by fitting the Spectra with Lorentzian Fits in the range of 2800 and $2950 \text{ rel. cm}^{-1}$. Calculating the intensity ratios of these two modes reveal a decrease of acetate groups in the films without stabilizing agents after 120 h (see Fig.8 and Fig.9). The Raman Spectra of the thin films of EVA with additives did not reveal any changes after the whole duration of aging.

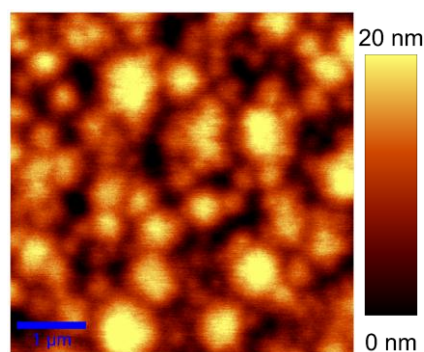


Figure 6: Topography of EVA0 ($5 \times 5 \mu\text{m}^2$) after 80h of aging under UV radiation at $T=85^\circ$

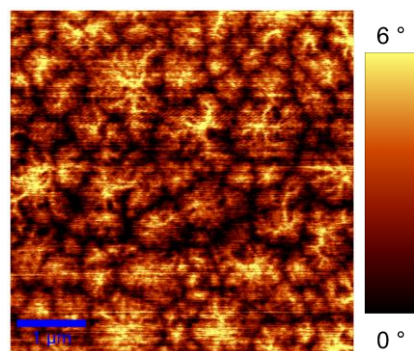


Figure 7: Phase image corresponding to the topography in Fig.6 ($5 \times 5 \mu\text{m}^2$) of EVA0 after 80 h aging under UV radiation at $T=85^\circ\text{C}$

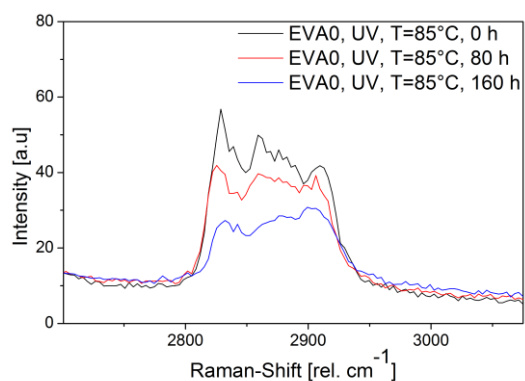


Figure 8: Raman-Spectra of EVA0 after 0, 80 and 160 h under UV radiation and $T=85^\circ\text{C}$

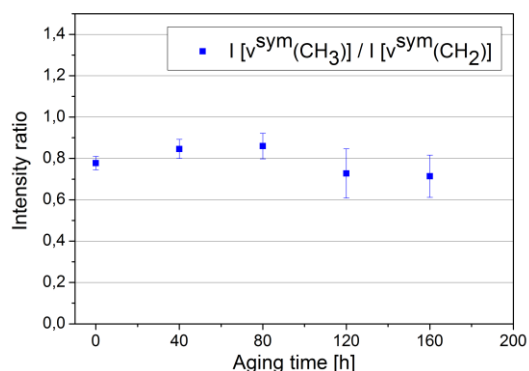


Figure 9: Intensity ratio of asymmetric CH_3 -stretching mode and symmetric CH_2 -stretching mode for EVA0 samples

4 Discussion

The topography of the aged thin films change compared to the initial topography before aging. By comparing the results it is evident that only high temperature leads to the formation of elevated surface features. This process is favored if the sample is additionally irradiated by UV light. The elevated surface features show a contrast in the phase image. This contrast is due to different mechanical properties of the crystalline and amorphous phase in a semicrystalline polymer like EVA. Thus the dendritic structures observed correspond to the crystalline phase that is spherulithic like in bulk EVA. Since the phase contrast corresponds with a higher topography the calculated roughness describes to increasing crystallinity of the sample with UV radiation at 85°C . The stabilizing agents could attenuate the crystallization process so that the roughness further increases only after 160 h of aging. The thin EVA films without stabilizers displayed higher roughness values than the films with additives. Consequently it can be assumed that the additives slow down the crystallization by protecting the EVA chains. Chain scissions caused by UV radiation decrease the chain length of the polymer chains and lead to higher mobility of these sequences. Without an elevated temperature the mobility of the chain segments is not high enough to be transported to crystallite. By heating the sample up to 85°C crystallization is triggered. The decreasing intensity ratio of the asymmetric CH_3 -stretching mode compared to the symmetric CH_2 -stretching mode indicates a loss of acetate due to formation of acetate acid. Acetate acid is volatilized in open systems like the thin EVA films. The correlation between the decreasing acetate and the increasing crystallinity give evidence for the assumption that deacetylation of EVA facilitates crystallization processes.

5 Conclusion

AFM measurements revealed morphological changes in the model system of thin EVA films due to crystallization processes. Thereby segregation between the crystalline and amorphous phase occurred. Further aging of samples with crystallized and amorphous areas can cause an inhomogeneous degradation since oxidation

can only take place in the amorphous phase. Consequently the inhomogeneity of the surface of the thin films is further increased. In this way the processes in the model system can describe changes at the surface of EVA foils. Crystallization and degradation of the amorphous phase can cause embrittlement of the surface and thus can deteriorate the mechanical properties of the foil. In a PV module laminate the change of surface properties can affect the stability of the adhesion between EVA and other components by formation of local defects like cracks and delamination. If EVA changes its mechanical properties, also the protection of the cells against mechanical and thermo-mechanical loads can be reduced.

To connect the results of the model system of nanometer thin films to the foil surface further research has to be done. Perfectly smooth surfaces of EVA foil could be examined by means of AFM to compare the degradation processes to the model system. By using bulk EVA other experimental techniques like DSC and DMA could be applied.

6 References

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