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Aging mechanisms of polymeric films for PV encapsulation

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Abstract

This paper focuses on the description and evaluation of aging mechanisms in multi-layer films that are used for encapsulation of photovoltaic (PV) cells. The materials investigated include polyethylene terephthalate (PET), polyvinyl fluoride (PVF) and polyvinylidene fluoride (PVDF). The materials were exposed to a relative humidity of 85% at 85 °C ("damp heat test"). To describe the aging mechanisms, materials were characterized by infrared spectroscopy in attenuated total reflection mode (ATR), by differential scanning calorimetry (DSC) and by mechanical tensile tests. The damp heat test resulted in significant hydrolysis of PET and post-crystallization of materials. Tensile tests showed a significant embrittlement and thus chemical degradation of PVDF and PET caused by the damp heat test. The strain at break value proved to be a very sensitive indicator of global aging.
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1. Introduction

Currently PV cells are mainly embedded in soft EVA sheets and encapsulated either by glass/glass or glass/plastic technology. With increasing demand in quality and quantity the glass/plastic encapsulation laminate structure has been increasingly promoted (Plessing, 2003). In case of the glass/plastic encapsulation there are several advantages. The encapsulation process is faster and simpler, the use of plastic reduces the weight of a module and thus the installation becomes easier.

The glass front cover works as a protection against all environmental influences. It weakens the UV fraction of the incoming sunlight and it provides mechanical strength and it is a barrier against oxygen and humidity. Backsheet materials have to provide similar properties, except for UV protection. To fulfil these requirements multi-layer films are used. While fluoropolymers such as polyvinyl fluoride (PVF) and polyvinylidene fluoride (PVDF) act as a protection against weathering influences, polyesters such as polyethylene terephthalate (PET) provide mechanical strength. To improve the barrier properties, usually an additional alumina or aluminium layer is used. Recently also thin silicon oxide layers have been applied. A silicon oxide barrier layer reduces the permeability of humidity by a factor of 10 (Barber et al., 2002).

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For PV modules a total lifetime of at least 20 years is intended. The modules are exposed to various stresses (e.g. UV radiation, temperature, atmospheric gases and pollutants, the diurnal and the annual thermal cycles), which may decrease module stability and performance. Additional losses in performance may be caused by rain, dust, wind, hail, condensation and evaporation of water, and thermal expansion mismatches (Czanderna and Pern, 1995).

Due to the multi layer build up of PV encapsulation materials aging can occur at the surface, in the bulk of single layers or within the interfaces of layers, which are usually adhesively bonded. The problem of delamination, which is a specific failure mechanism of multi layer films, is described elsewhere (Oreski and Wallner, 2004; Jorgensen et al., 2003). While in various papers the aging mechanisms of soft PV embedding materials are discussed (Czanderna and Pern, 1995; Klemchuk et al., 1996), it is the objective of this paper to describe the aging mechanisms of PV backsheet materials at standardized testing conditions.

2. Experimental

Various thermoplastic films with different thicknesses for PV backsheet application were investigated: polyethylene terephthalate (PET, 75 μm), polyethylene terephthalate with an evaporated 80 nm silicon oxide barrier layer (PET-SiO$_x$, 100 μm), poly vinyl fluoride (PVF, 45 μm) and poly vinylidene fluoride (PVDF, 37 μm, with 10–20% poly methyl methacrylate (PMMA) copolymer fraction). Both PET films were transparent, whereas the PVF film was dark grey and the PVDF film was white. All films were provided by ISOVOLTA AG (Werndorf, Austria).

Tensile test specimens with a width of 10 mm and a length of 100 mm were subjected to 85 °C and 85% relative humidity for 1000 and 2000 h (damp heat test according to IEC 61215). The aging behaviour was characterized by infrared spectroscopy in attenuated total reflection mode (ATR), by differential scanning calorimetry (DSC) and by tensile tests.

The ATR measurements were carried out using a spectrometer of the type Bruker FTIR Vector 22MIR (Karlsruhe, D). The absorption spectra were recorded over the IR range from 4500 to 650 cm^{-1} (2.2–15.4 μm).

The DSC measurements were carried out using a Mettler Toledo DSC831 (Schwerzenbach, CH). Thermograms were recorded under static air. The heating rate was 10 K/min. Glass transition temperature (T_G), melting point and melting enthalpy were evaluated according to ISO 11257-2 and ISO 11257-3. The degree of crystallinity was determined as the ratio between the melting enthalpy of the sample and the melting enthalpy of the 100% crystalline polymer. The data for 100% crystalline PET, PVF and PVDF was taken from ATHAS Data Bank (ATHAS Data Bank, 1994).

For the tensile tests rectangular strips with a width of 10 mm and a length of 100 mm were used. The tensile tests were carried out with an Instron 4505 (High Wycombe, UK) tensile testing machine at 23 °C and a crosshead speed of 10 mm/min.

3. Results and discussion

3.1. Spectroscopic investigations

Infrared absorption spectra are shown in Figs. 1–3 for the investigated materials in the unaged condition and after damp heat test (aged). The absorption spectra of PET exhibit two significant changes in the range between 4000 and 2500 cm^{-1} due to damp heat testing (Fig. 1). The aged material exhibits an additional peak between 3500 and 3000 cm^{-1}. This peak refers to a stretching vibration of hydroxyl groups. The hydroxyl groups are related to hydrolysis, which occurs in humid climate and which is accelerated above PET's glass transition temperature (approx. 80 °C). The broad band indicates a strong hydrogen bond network. The changes in the stretching vibration region of the methylene group (CH$_2$) between 3000 and 2840 cm^{-1} are attributed to chain scission due to hydrolysis. The ratio of the number of terminal ethylene glycol groups relative to the number of bulk polymer ethylene glycol groups is changed (Sammon et al., 2000).

Damp heat testing did not have any effects on the characteristic peaks of PVF (Fig. 2). However, an additional broad band between 1700 and 1500 cm^{-1} appears for the aged specimen. This region can be attributed to the stretching vibration of a carbon double bond. Presumably, gaseous hydrofluoric acid was separated and conjugated double bonds were formed (Wentink et al., 1961).
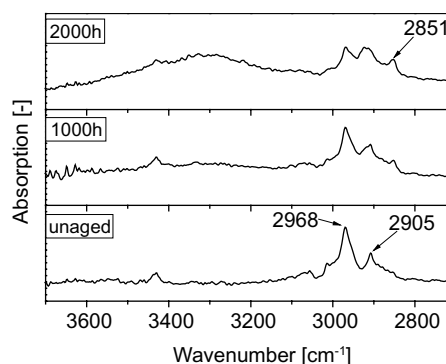

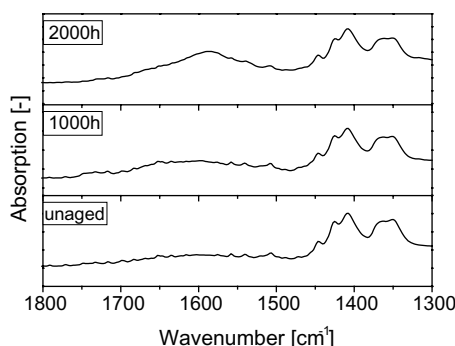Fig. 1. ATR absorption spectra for unaged and aged PET samples.

Fig. 2. ATR absorption spectra for unaged and aged PVF samples.
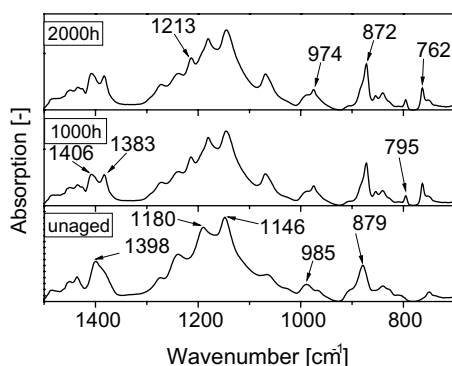

Fig. 3. ATR absorption spectra for unaged and aged PVDF copolymer samples.

The spectra of the PVDF copolymer exhibit the typical peaks of PVDF and PMMA (Fig. 3). In comparison to PET and PVF there are significant distinctions in the characteristic peaks between unaged and aged materials. New peaks appear at 1213, 795 and 762 cm^{-1}. The peak at 879 cm^{-1} shifts to 872 cm^{-1}, and the region between 1500 and 1350 cm^{-1} is altered.

The differences in the region between 1500 and 1350 cm^{-1} can be assigned to different crystal structures. The spectrum of unaged PVDF is typical for PVDF in the β-crystalline phase (β-PVDF), which exhibits an all trans conformation (TTT). γ-PVDF is in comparison to β-PVDF an intermediate form consisting of three trans bonds separated by one gauche bond. To separate them usually the peaks at 1269 cm^{-1} (β-PVDF) and 1236 cm^{-1} (γ-PVDF) fit best. However, the stretching vibration of the carboxylic group of MMA superposes this region. Because of the characteristic band at 1433 cm^{-1} the unaged reference material can be identified as β-PVDF. The additional and shifted peaks noted before are characteristic for α-PVDF, which exhibits a trans gauche structure (TGTG) (Bormashenko et al., 2004). Thermodynamic investigations showed, that

α-PVDF is kinetically favoured, while β-PVDF is thermodynamically favoured. α-PVDF is formed by direct crystallization from melt, β-PVDF by stretching of α-PVDF (Boccaccio et al., 2002). The additional peaks indicate post-crystallization of α-PVDF during damp heat test. While the absorption spectra for PVDF (Fig. 3) reveal significant physical aging effects (e.g. post-crystallization), no indications of chemical degradation effects (e.g. conjugated double bond formation) could be identified.

Differences in the intensities of the peaks at all measurements are caused by problems of reproducibility. The most critical factor of quantitative reproducibility is the physical contact of the specimen with the internal reflection element of the ATR unit. The contact force must be sufficient and reproducible (Mirabella, 1982). This was not possible for the ATR device used.

3.2. Thermoanalytical investigations

The DSC thermograms are displayed in Figs. 4–6 for the different unaged and aged materials. For PET a melting peak between 170 and 270 °C, with a maximum at 256 °C (Fig. 4) is observable. The melting energy for the unaged and aged materials varies between 57 and 68 J/g, the degree of crystallinity between 41% and 49%. For the unaged material a glass transition at 76 °C is found. The aged materials exhibit an additional, weak endothermic peak at about 125 °C. This peak can be attributed to post crystallized structures located in the highly extended amorphous phase (Chartoff, 1997). Due to the fact that the aging time does not have any effect on the size of the weak endothermic peak, post-crystallization takes place during the initial stage of damp heat test. As shown in a previous publication (Wallner et al., 2004), post-crystallization occurs in PET annealed in air at 80 °C and annealed in water at 80 °C. That means, post-crystallization effects are not depending on the environmental media.
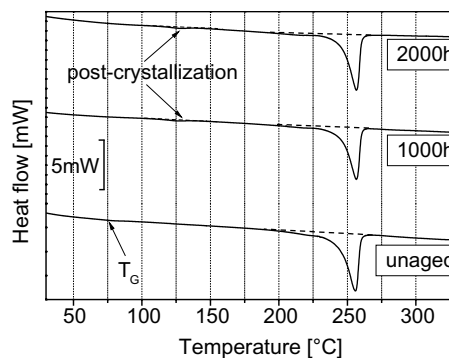

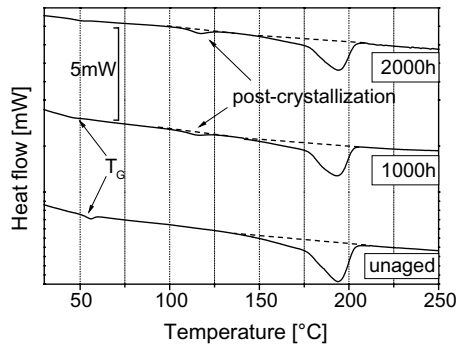Fig. 4. DSC plots for unaged and aged PET samples.
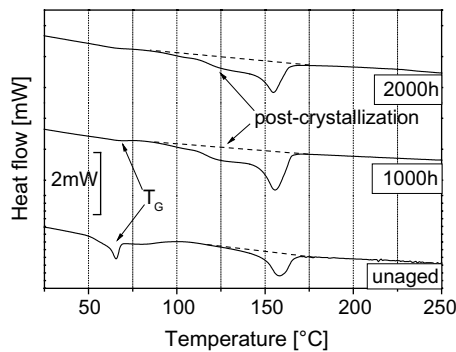
Fig. 5. DSC plots for unaged and aged PVF samples.

Fig. 6. DSC plots for unaged and aged PVDF copolymer samples.

The DSC traces of the PVF films show a melting peak between 135 and 210 °C with a peak temperature of 194 °C (Fig. 5). The melting enthalpy for the unaged and aged materials varies between 36 and 43 J/g, the degree of crystallinity between 22% and 26%. The glass transition of the unaged material is superposed by an endothermic irreversible relaxation effect, which does not appear anymore after aging at a temperature above glass transition temperature and slow cooling. The glass transition temperature is between 45 and 50 °C. PVF shows an additional weak endothermic peak between 100 and 125 °C with a maximum at 115 °C. The aging time does not have any effect on the size of the weak endothermic peak, which can be attributed to post-crystallization.

Fig. 6 displays the DSC plots of the investigated PVDF copolymer. The glass transition (between 55 and 65 °C) of the unaged material is superposed by an endothermic irreversible relaxation effect, which is related to processing conditions (quenching). The melting peak is between 110 and 180 °C with a maximum at 158 °C. A melting enthalpy value of 10 J/g and a degree of crystallinity of 13% was determined for the aged PVDF/MMA copolymer. The aged material shows a

more pronounced area of melting between 85 and 180 °C. The melting enthalpy increases up to more than 30 J/g, the degree of crystallinity from 13% to about 30%. The DSC data confirm the results of the ATR measurements, from which significant post-crystallization of α-PVDF was concluded.

3.3. Mechanical investigations

Typical stress–strain curves from tensile tests on unaged and aged specimens are shown in Figs. 7–10. The investigated unaged materials exhibit a ductile behaviour with yield strains between 1.7% and 3.5%. For PET elastic modulus values of about 4000 MPa were obtained. In contrast, the fluoropolymers PVF and PVDF exhibit significantly lower elastic modulus values, ranging from 1500 to about 2000 MPa.

The influence of overall aging in PET, PET-SiO$_x$ and PVF on the mechanical properties is shown in Figs. 7–9, respectively. Because of the high embrittlement, the tensile properties of aged PVDF could not be measured. As shown in Figs. 7–9 and in agreement with findings in the literature (Struik, 1978), annealing at elevated temperatures leads to an increase in yield stress of the aged materials. The significance of physical aging is supported by the fact that the increase of yield stress is nearly independent of annealing time.

To illustrate irreversible damp heat test related degradation effects, the most sensitive parameter, which is the strain at break, is depicted in Fig. 11 as a function of aging time. For PET a significant embrittlement after damp heat testing was observed (Fig. 11). The strain at break decreases significantly. After 2000 h of aging the 75 μm PET film breaks before yield stress is reached. The 100 μm PET-SiO$_x$ film exhibits better ultimate mechanical properties after damp heat testing, as the yield stress is reached after 2000 h damp heat testing. The silicon oxide layer or the film thickness seems to reduce the rate of hydrolysis in the first stage of damp heat
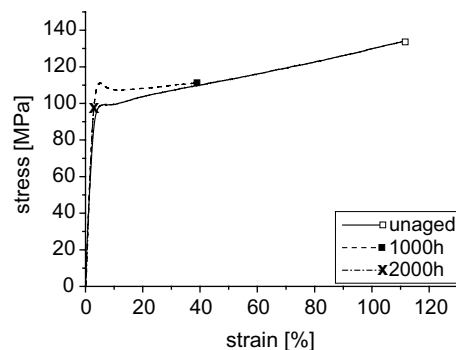

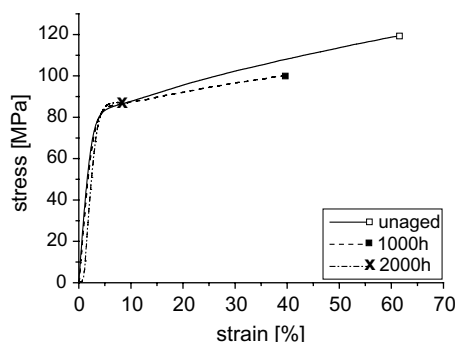Fig. 7. Stress–strain curves for unaged and aged PET specimens.

Fig. 8. Stress–strain curves for unaged and aged silicon oxide coated PET (PET-SiO$_x$) specimens.
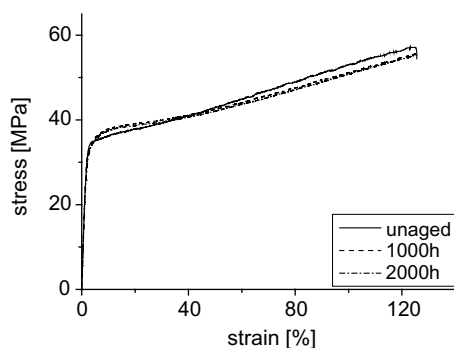

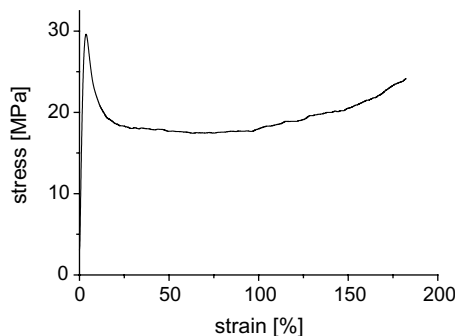Fig. 9. Stress–strain curves for unaged and aged PVF specimens.

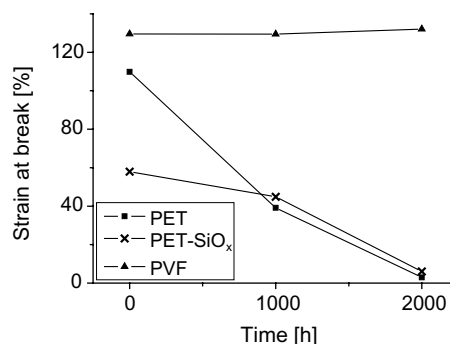Fig. 10. Stress–strain curve for unaged PVDF copolymer specimen.

Fig. 11. Strain at break versus damp heat testing time for PET, PET-SiO$_x$ and PVF.
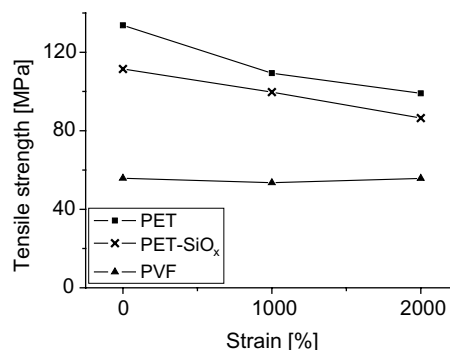

Fig. 12. Tensile strength versus damp heat testing time for PET, PET-SiO$_x$ and PVF.

with increasing time of damp heat testing. Again for PVF the tensile strength values remain unchanged. The tensile strength values also reflect degradation effects. However, compared to strain at break, tensile strength is a less sensitive indicator of overall aging.

Tensile properties of aged PVDF could not be measured due to high embrittlement of the material (Fig. 10).

4. Summary and conclusions

The aging behaviour in air at elevated temperature (85 °C) and humidity (85% RH) (damp heat test) of different PV backsheet layers was characterized by infrared spectroscopy in attenuated total reflection mode (ATR), by differential scanning calorimetry (DSC) and by mechanical tensile tests. For all investigated semi-crystalline polymers the exposition temperature was above the glass transition temperature of 75 °C for PET, 50 °C for PVF and 60 °C for the PVDF copolymer. Using ATR the influence of the damp heat testing on the polymer morphology could be detected. Significant

exposure. The best damp heat stability was demonstrated by PVF. The stress–strain curves are only affected by physical aging that results in an increase of yield stress. As shown in Fig. 11 the strain at break values remain unchanged during damp heat testing. The ultimate tensile strength values are plotted in Fig. 12 for the unaged and aged materials. It can be seen that for PET and PET-SiO$_x$ the tensile strength decreases

hydrolysis of PET was proved. For PVF formation of conjugated carbon double bonds was observed. Several characteristic peaks could be found in the absorption spectra of PVDF. The unaged sample could be identified as PVDF in the β-crystalline phase. Damp heat testing causes significant post-crystallization. Based on the characteristic peak at $795\,cm^{-1}$ it was shown that post-crystallization leads to PVDF in α-crystalline phase.

Thermoanalysis revealed that damp heat testing causes secondary melting peaks. For PET and PVF the secondary melting peaks were weak. In contrast, a significant increase of the degree of crystallinity was observed in the case of PVDF.

For aged PVDF and PET films significant embrittlement was found and described by mechanical investigations. This embrittlement can be attributed to global aging and degradation of the investigated PVDF and PET films. For the investigated PVF film excellent damp heat test stability was obtained. The ultimate strain and stress values, which are a very sensitive indicator for degradation effects, remained unchanged.

Acknowledgements

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