Qualification of new polymeric materials for solar thermal applications

Michael Köhl, Cornelia Peike, Karl-Anders Weiss

Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstrasse 2, 79110 Freiburg, Germany

Abstract

Polymers can offer additional degrees of freedom for collector design and access to cost-effective mass-production technologies for solar thermal applications, like collectors for example. But they have to stand harsh operational conditions. They are exposed to high temperatures, humidity and UV-irradiation.

We exposed different types of polymeric materials to accelerated ageing tests. Samples were based on commodity plastics like poly-propylene (PP) with different stabilization systems, technical polymers like polyamide (PA) and cyclic olefin copolymers (COC), some with nano-fillers like glass-fiber (GF) or carbon-nano-tubes (CNT). Different compounds of high-performance polymers like polyphenylene sulfide (PPS) have been exposed, too. Some of the materials have been coated with optical selective coatings.

The ageing conditions were different levels of high temperatures, high humidity and high UV-irradiation as well as combined tests.

Optical, non-destructive methods like FFT-IR spectroscopy and Raman microscopy have been used for the characterization of the samples as well as atomic force microscopy (AFM). The results show a very strong influence of humidity at high temperatures on the degradation while UV exposure didn't lead to significant changes of the surfaces.

1. Introduction

Almost all technical devices and components experience different kinds of influence of the ambient climate during their service life. Especially if they are used outdoors, e.g. in solar energy or automotive applications, they have to withstand considerable UV-irradiation, high temperatures and humidity. In case of the factors temperature and humidity not only the high levels are demanding for the materials, but the regular changes of them lead to additional stress accelerating the degradation processes further more. Especially polymeric materials are sensitive to these influences which can lead to a decrease of durability and a shorter service life. Therefore they are usually stabilized by a combination of different additives to prevent or retard degradation. Unfortunately, only little data about systematic outdoor tests is available and also a better data correlation between accelerated indoor ageing tests and outdoor exposition is required. Knowledge about the degradation behaviour of materials with different stabilisation systems under different exposure conditions is mandatory for service life prediction.

Combinations of new analytical methods like Raman-microscopy and AFM, together with established methods like FFT-IR spectroscopy improve the understanding of material degradation processes.

2. Samples

The investigated PP samples contain two different amounts of phenolic antioxidant (AO) and three different levels of a hindered amine light stabilizer (HALS). Further tests were carried out on PPS samples and PPO with poly styrene (PPO/PS), on PA samples filled with 1% CNT as well as glass fiber and 0,5 % CNT, with and without an optical selective (AZO) coating, respectively. The analyzed COC samples contained both, CNT and an optical selective coating.

3. Ageing test conditions

PP samples have been exposed at an outdoor test site in Arizona, USA. Samples have been removed for analytical purposes after every tenth week. Additional accelerated indoor ageing tests have been performed under systematic variation of temperature and irradiation at three temperature levels (45, 65 and 85°C) and at three irradiation levels (48, 60 and 72W/m²). PA and COC samples have been aged indoors under damp heat conditions (85°C, 85% r.h.), irradiated with up to 60 W/m^2 and weathered in a combined UV and damp heat test for up to 1000 h. Several different thermal (85 and 120°C), photothermal (85°C, 362W/m^2), combined UV/damp heat (85°C, 75% r.h., 362 W/m^2) as well as pure damp heat aging procedures have been carried out with the PPS and PPO/PS samples.

4. Results

4.1. Polypropylene (PP)

The microscopic analysis of highly stabilized PP samples after up to 60 weeks of outdoor exposure in Arizona and after indoor UV aging is shown in fig.1. First significant cracks appear after an ageing time of 40 weeks, intensifying after 50 and 60 weeks. The indoor aging with an irradiation of 20,4kWh/m^2 seems to be comparable to an outdoor treatment of 30 weeks since no surface embrittlement is visible.
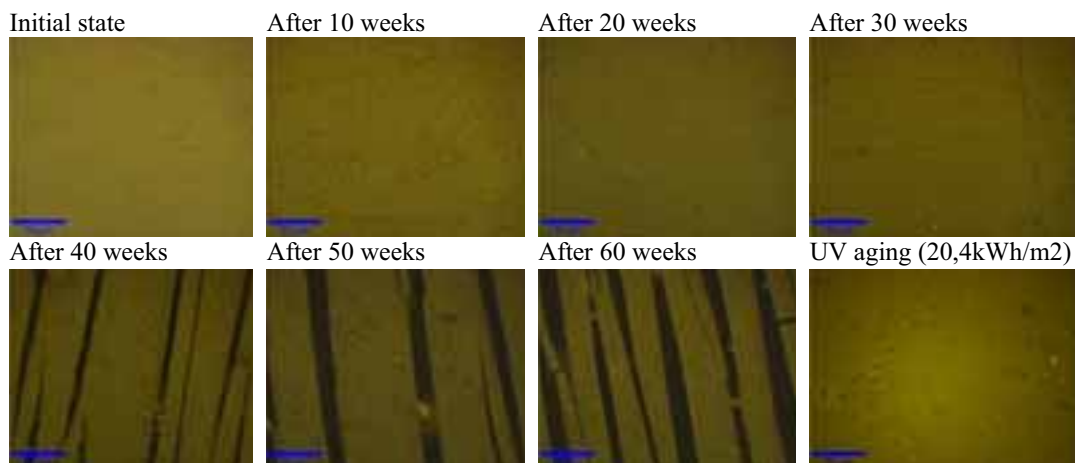

Fig.1.Micrographs (50x lens) of PP plates with an high amount of UV-absorber and AO after up to 60 weeks of outdoor exposure compared to an indoor UV aging with 20,4 kWh^2 showing surface degradation.
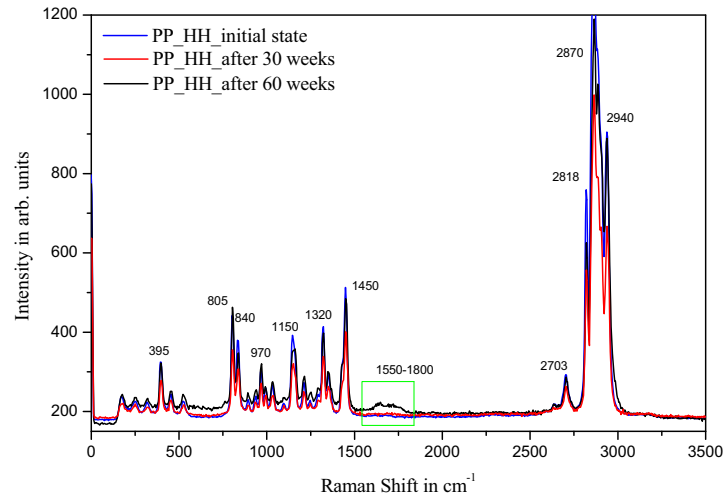
Fig. 2. Raman spectra of a PP sample with a high amount of UV-absorber and antioxidant (HH) in the initial state and after 30 and 60 weeks outdoor exposure in Arizona, respectively.

Raman image and depth scans, consisting of 80 x 80 full Raman spectra, were measured on areas of 30 x 30 μm^2 on the surface of the sample and in near-surface areas. Fig. 2 shows near-surface Raman Spectra before aging and after 30 and 60 weeks outdoor exposure in Arizona. The analysis of the spectra shows that some bands significantly change over time which can be accentuated with sum filters in the range of the interesting bands. Pictures calculated with a sum filter in the range 1562 – 1788 cm^{-1} show a significant increase of the signal at the surface of the samples beginning after 30 to 40 weeks of outdoor exposition (fig.3).
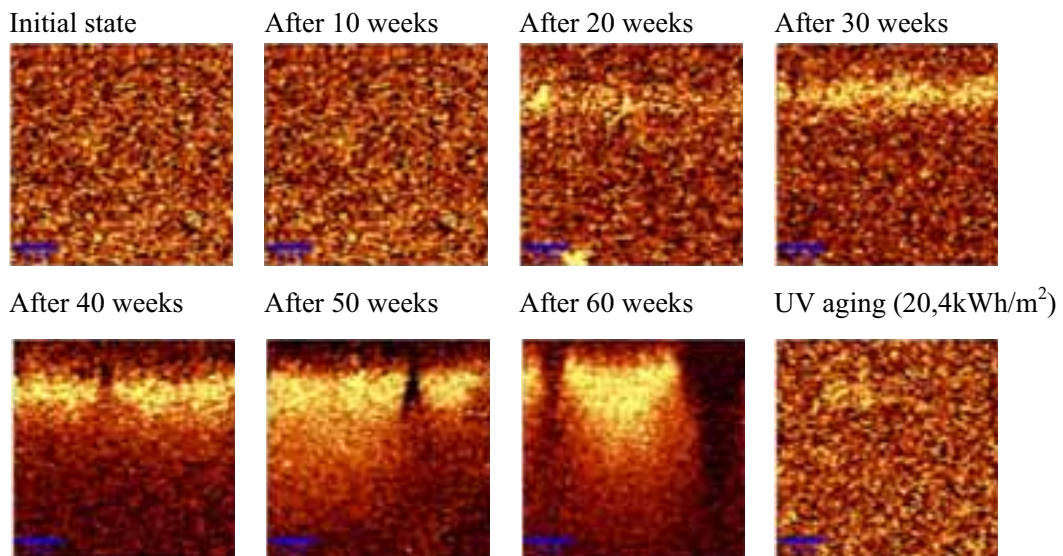

Fig. 3. Pictures showing near-surface degradation of PP plates with an high amount of UV-absorber and AO after several outdoor aging steps compared to an indoor UV aging with 20,4 kWh^{-2}. Pictures are calculated from Raman depth scans with a sum filter at 1562-1788cm^{-1}

This increase of the signal can be explained by an increasing amount of degradation products due to longer exposition times of the samples (fig. 3). After longer ageing periods, this effect is intensifying, reaching up to 10 µm into the sample. The change of material properties goes along with the appearance of cracks on the surface which are another indicator for significant material degradation. Samples show no significant changes in the analyzed spectra after Weather-O-Meter indoor ageing with 20,4kWh/m^2 at 65°C. This accelerated test causes less degradation than 40 weeks of outdoor exposition in Arizona.

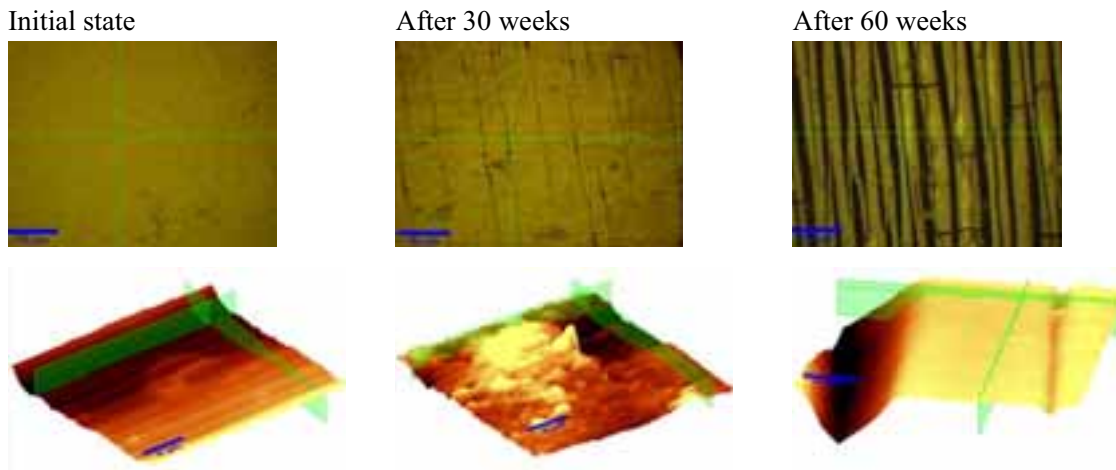| Initial state	After 30 weeks	After 60 weeks

Fig.4. Micrographs and AFM topography pictures of PP plates with a high amount of UV-absorber and AO after several outdoor aging steps compared to an indoor UV aging with 20,4 kWh^{-2}.

AFM measurements ware carried out before and after several aging steps, for a better understanding of the surface properties of the samples. Fig.4 reports AFM topography pictures as well as the corresponding micrographs of a highly stabilized PP sample before and after outdoor aging. First cracks in the surface appear after 30 weeks of outdoor exposure and after another 30 weeks of outdoor exposure, cracks with a depth of up to 5 µm are detectable by AFM.

4.1. Polyamide (PA)

FFT-IR spectroscopic measurements were carried out on the samples after up to 60 kWh UV exposure, 1000 h damp heat aging (85°C and 65°C, 85% r.h.), as well as after a combined UV and damp heat aging (75°C, 75 % r.h.). The results show a strong decrease of reflectivity of coated samples in the IR range after aging at high humidity and high temperature (Fig.5a).
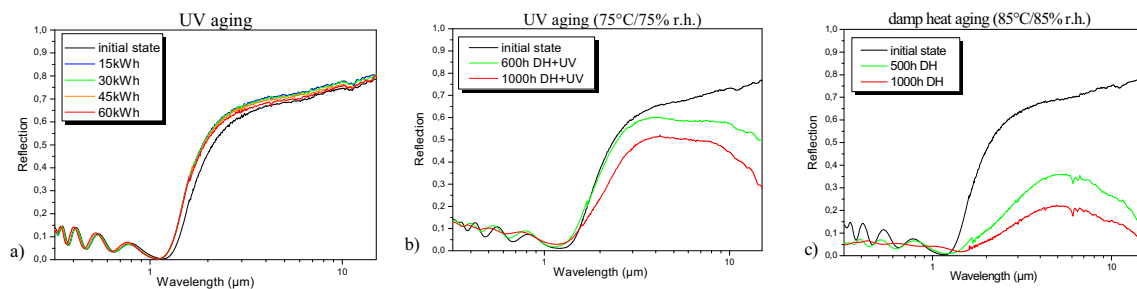

Fig.5. FFT-IR Spectra of AZO coated PA samples with 0,5% CNT and glass fiber after UV aging (a), combined UV / damp heat aging (75°C, 75% r.h.) (b) and after pure damp heat aging (c).

After 1000 h damp heat aging at 85°C and 85 % r.h. the reflectivity at 5 µm decreased to about 30% of the initial value (Fig.5, middle). In contrast, UV exposure seems to have no influence on the reflectivity of the samples (fig.5c).

The dependency of the reflection at 5 µm on aging time and irradiation is shown in fig. 6. For the coated PA samples with CNT and glass fiber, the most effective degradation acceleration factor appears to be the simultaneous occurrence of high temperature and high humidity. UV irradiation seems to have a minor effect on the aging of the coating.
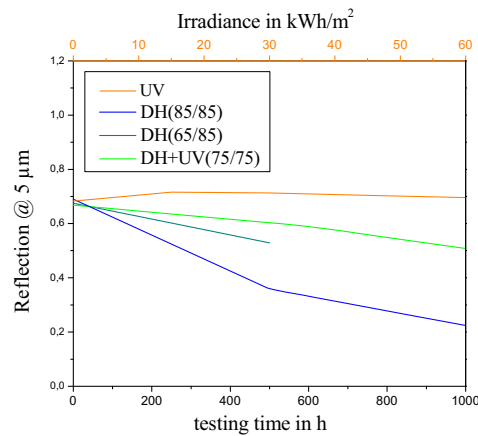

Fig.6. Influence of different aging conditions on the reflection of coated PA samples with 0,5 % CNT.

4.3. Cyclic olefin Copolymer (COC)

Raman Spectra of the non-aged coated COC samples with CNT show bands which can be attributed to the AZO coating, CNT G and D band as well as COC vibrations (fig.7). A weakening of the polymeric valence vibrations as well as an absence of the vibrations of the coating is detectable in several areas of the sample surface after 550 h damp heat (85°C, 85% r.h.) exposure (fig. 2).
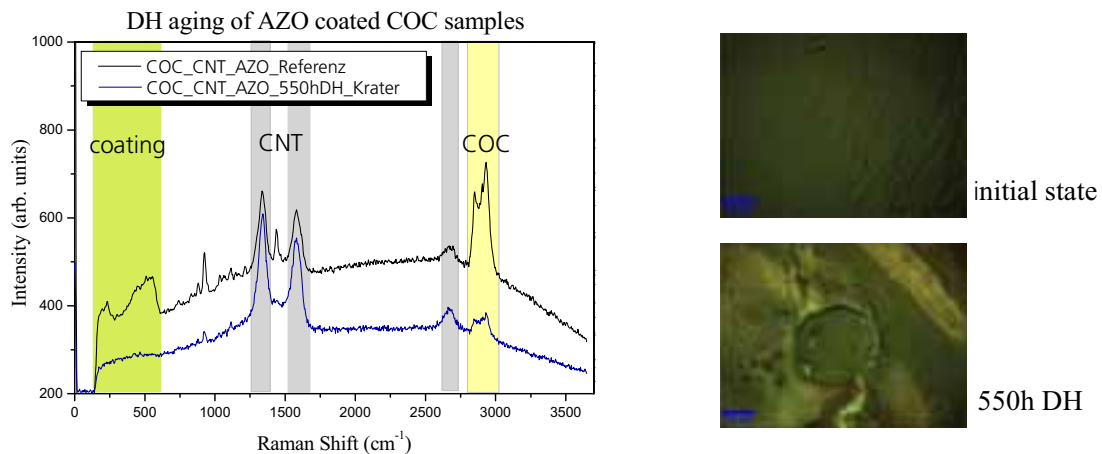

Fig.7. Raman spectra and micrographs (50x lens) of COC samples with CNT and coating, before and after damp heat aging (85°C, 85% r.h.).

4.4. Polyphenylene sulfide (PPS)

Raman spectra of the thermal (120°C), photothermal (85°C, 362 W/m^2), combined UV/ damp heat (85°C, 75% r.h., 362 W/m^2) and pure damp heat (85°C, 85% r.h.) aged PPS samples are reported in fig.8. After thermal and damp heat aging for up to 500 h, no significant change of the spectra is detectable. The presence of UV radiation while aging leads to the formation of a drastic fluorescence background, most likely due the fluorescence of degradation products of PPS. The fluorescence backgrounds of PPS samples after pure UV irradiation differ in shape and intensity after the different ageing steps and are more intensive then fluorescence backgrounds after combined UV/damp heat.
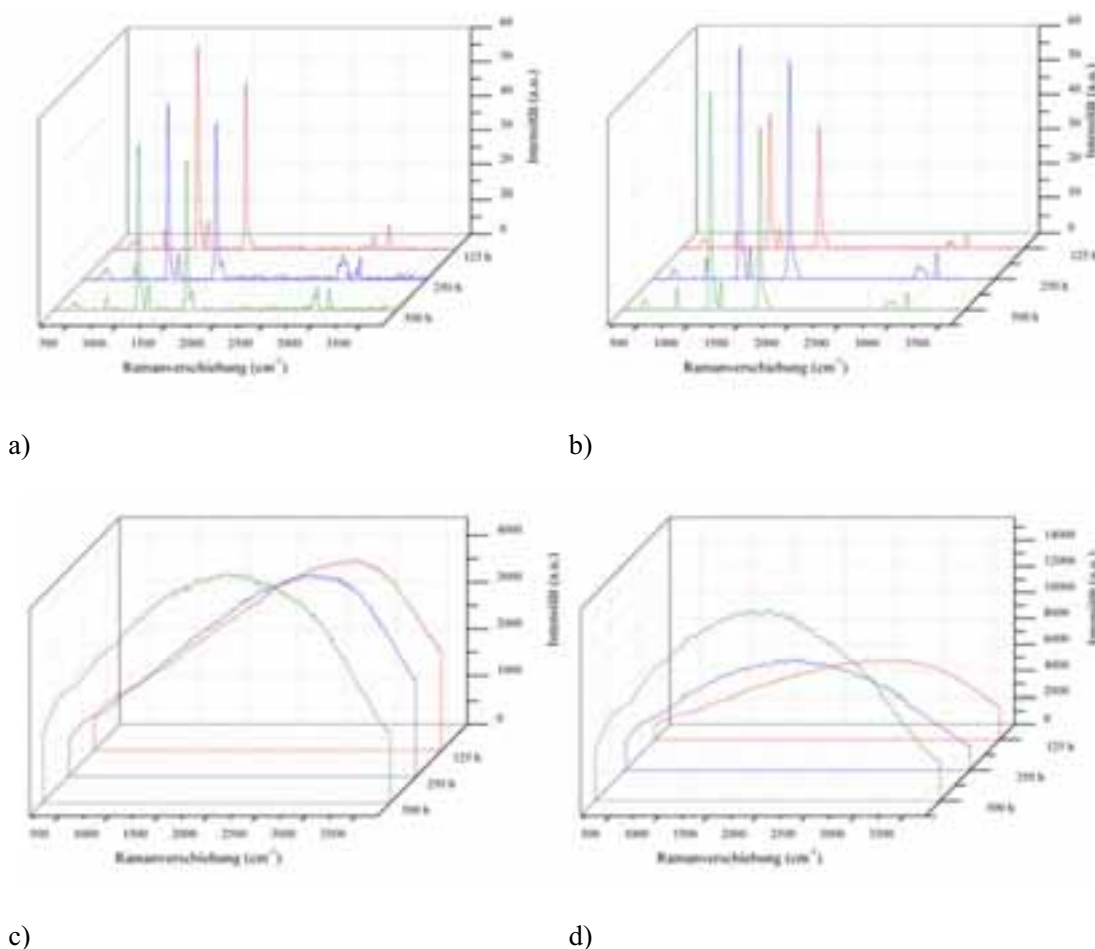

a) b)

c) d)

Fig.8. PPS- Raman Spectra after thermal aging @120°C (a), damp heat aging (b), combined UV/damp heat tests (c) and after UV irradiation (d).

AFM topography pictures of non-aged and combined UV/damp heat aged PPS samples are presented in fig.9. The pictures show the same area on the surface before and after aging. For better visualization, the lower pictures show a section of 5 x 5 μm^2 of the upper pictures (square in the upper pictures). The surface texture of the samples has changed while ageing. Certain spots on the surface are not detectable after aging anymore while the whole texture of the sample appears to be rougher.
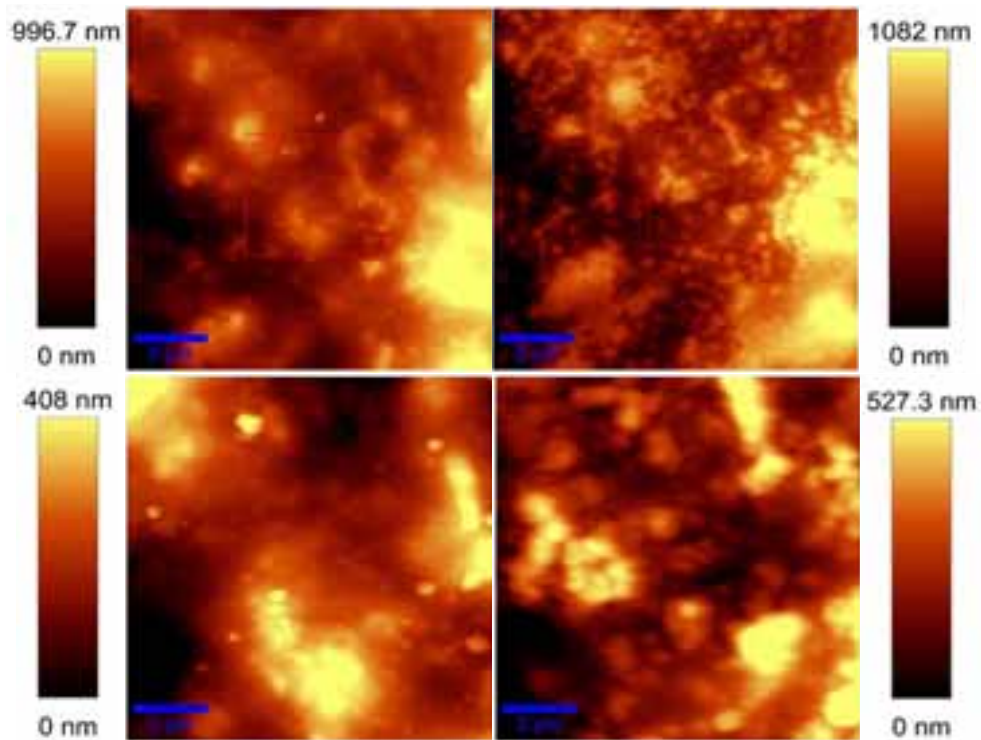
Fig.9. PPS- AFM topography pictures before aging (left) and after (right) combined UV/damp heat tests.

5. Conclusion

The presented methods for analyzing polymers cover a broad range of different material properties and seem to be suitable for the investigation of degradation processes and their effects. The results of the different methods correlate very well.

Confocal Raman microscopy allows following the ongoing degradation processes in a non-destructive way with high lateral resolution which significantly improves the information about a sample since the other methods usually analyze only the uppermost surface of the material or bulk material.

For the investigation of coated PA samples, the changes of reflectivity of the various samples after different aging conditions, measured by FFT-IR spectroscopy, give information about the aging of the optical selective coating which is mainly influenced by heat and humidity. Raman microscopy confirms these results and suggests transferability on other new polymeric materials like COC.

Raman Spectroscopic and AFM measurements on PPS samples indicate a major influence of UV-irradiation on the PPS degradation process whereas heat and humidity seem to have a minor effect.

The investigated polymeric materials seem to be principally suitable for solar thermal applications. Concerning the PP samples, formation of cracks and degradation products was already detectable after less then one year of outdoor aging in Arizona, but it has to be taken into account, that even the highest amounts of stabilizing additives used in this investigation (max. 0,2 wt%) are extremely small

compared to real-life formulations in order to be able to investigate material changes in a reasonable times. It could be shown, that the optical selective coating on PA and COC samples is very sensitive towards high temperature and humidity which certainly is a problem that has to be solved. In terms of UV stability, PPS requires stabilizing additives like already tested in PP. A stabilized PPS would probably be a very promising polymer for high-temperature solar thermal applications due to its stability against heat and humidity.

6. Acknowledgements