THERMOPHYSICAL AND SPECTROSCOPICAL CHARACTERIZATION OF NEW MATERIALS FOR SOLAR THERMAL APPLICATIONS

Christoph Zauner[1], Daniel Lager[1], Wolfgang Hohenauer[1]

[1] Austrian Institute of Technology, Vienna (Austria)

1. Introduction

The constant need for ever cheaper collectors is exemplified in the ongoing shift from copper to aluminum and the even more radical material change related to the introduction of polymeric materials in solar collectors [1]. Many process heat and solar cooling applications demand medium temperature collectors providing reasonable efficiencies up to 250 °C [2]. Even higher temperatures occur in concentrating solar power applications [3], while the combination of solar thermal systems with heat pumps extends the operating temperatures well below 0°C [4].

Consequently, a number of new collector designs deviating substantially from "standard flat plate collectors" are currently under investigation [5, 6, 7]. Experimental as well as theoretical development relies fundamentally on the detailed knowledge of the underlying thermophysical properties of the employed materials over the whole temperature range of interest.

However, especially when new materials are developed these properties are not known at all. Also, when standard collector materials are used for very low or high temperatures, data sheets are often not concise enough and studies of processed or materials aged in real collectors are scarce.

Thus, in this article we present the application of various thermophysical methods to different examples in the development of new solar thermal collectors to point out the importance and benefits of advanced material characterization.

2. Polymeric Collectors

The substitution of standard collector materials by polymeric ones is tempting due to potentially lower costs and ease of mass-fabrication. However, especially the maximum temperatures in stagnation as well as thermal stress during day-night cycles and shocks (cf. internal and external shock, rain penetration test according to EN12975) pose a potential threat to long term integrity of the collector.

In order to exemplify the potential of a thorough thermophysical characterization, we investigated a new solar thermal collector by Aventa AS.

We measured the properties of the as-produced absorber raw material Xtel XE4500BL from Chevron Phillips Chemicals and also of the extruded absorber after having completed the reliability tests according to EN12975 (in particular exposure, internal shock, external shock, and rain penetration test).

The thermal diffusivity, a, was measured using a NETZSCH Laser Flash Analyzer LFA 427, the specific heat, c_p, using a NETZCH Dynamic Scanning Calorimeter DSC 404 C, the coefficient of thermal expansion, *CTE*, using a NETZSCH pushrod dilatometer DIL 402 C. Change of mass is measured with a NETZSCH Simultaneous Thermal Analyzer STA 449 F1 Jupiter. Equipment is operated at ambient pressure conditions using synthetic air. Thermal density, ρ, is examined from initial density, ρ_0, at room temperature and thermal expansion data. From these quantities, the thermal conductivity, λ, is calculated by

$$\lambda(T) = a(T) \cdot c_p(T) \cdot \rho(T) . \quad (1)$$

Figure 1 shows the corresponding curves for the as-produced raw material and Figure 2 depicts the curves for the aged absorber.

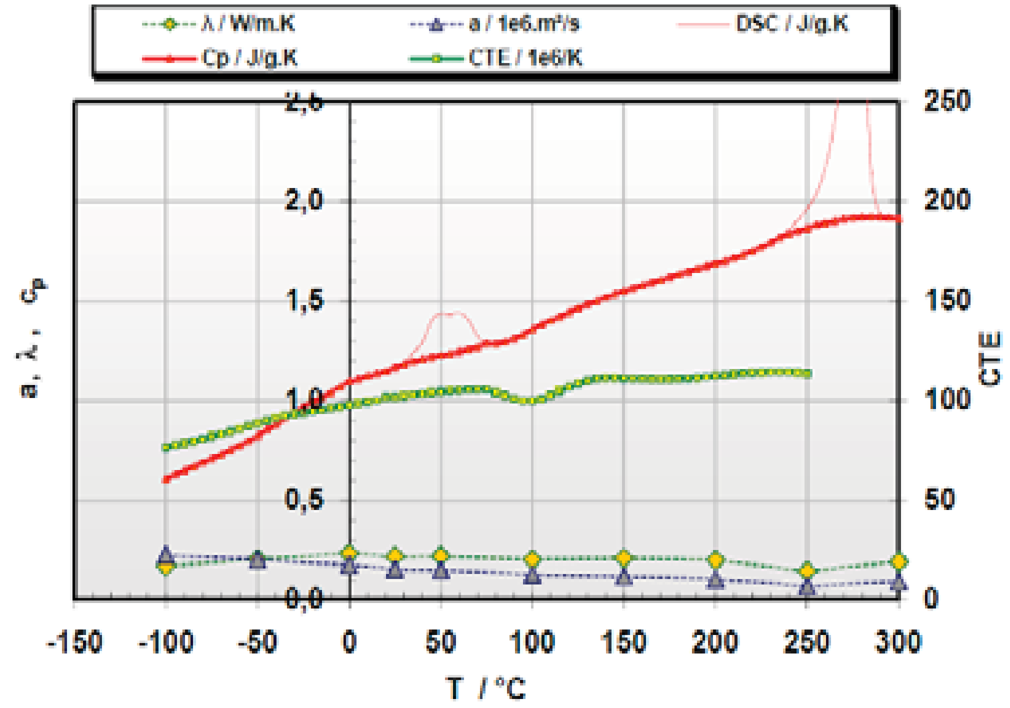

Figure 1: Thermophysical properties of the raw material for an all polymeric absorber

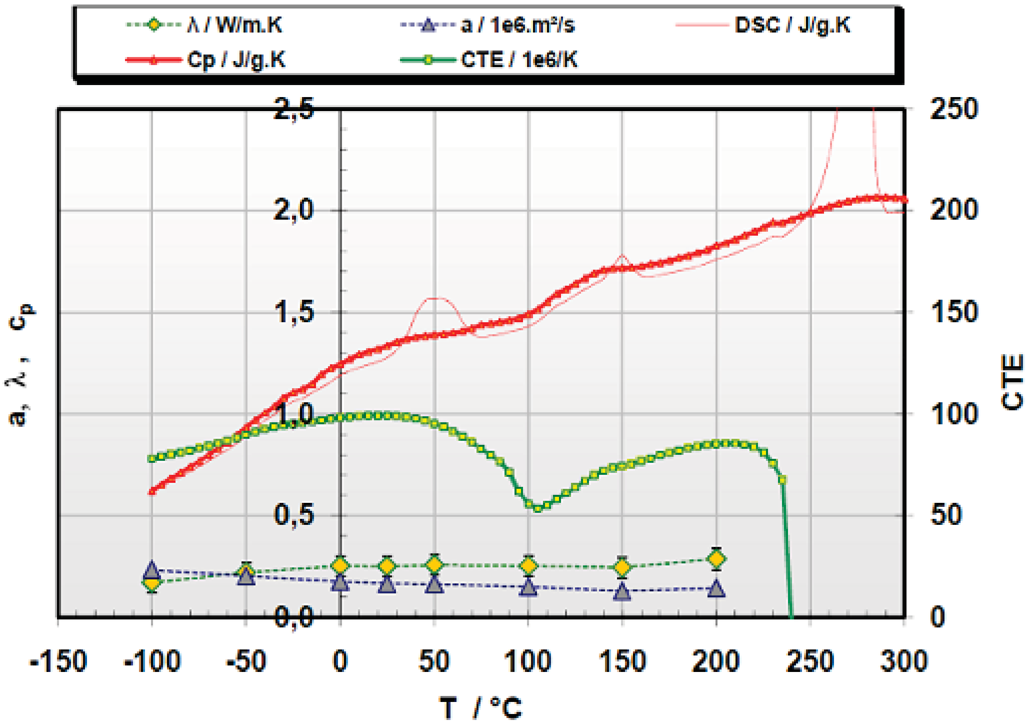

Figure 2: Thermophysical properties of the extruded polymeric absorber after having completed reliabiltiy tests according to EN12975

The thermal conductivity is magnitudes lower than for standard absorber materials (copper, aluminum), which has to be compensated for by a special absorber design. No significant change is observed in the aged sample.

However, it is clearly visible that a DSC-peak arises in the aged sample around 120°C. This is accompanied by a considerable dip in the CTE-curve around 100°C, which is either related to the extrusion process itself or to the reliability tests.

The situation becomes even clearer, when one considers the linear thermal expansion of the samples (Figure 3). Up to some 50°C, the as-produced and aged samples are identical, while at higher temperatures, the expansion is lower for the absorber. In addition, one observes a dip around 100°C, presumably related to the glass transition temperature of the PPS-material, which leads to an additional expansion-contraction in the course of a normal day-night cycle, where the absorber temperature changes from ambient night temperature to possibly 150°C in stagnation.

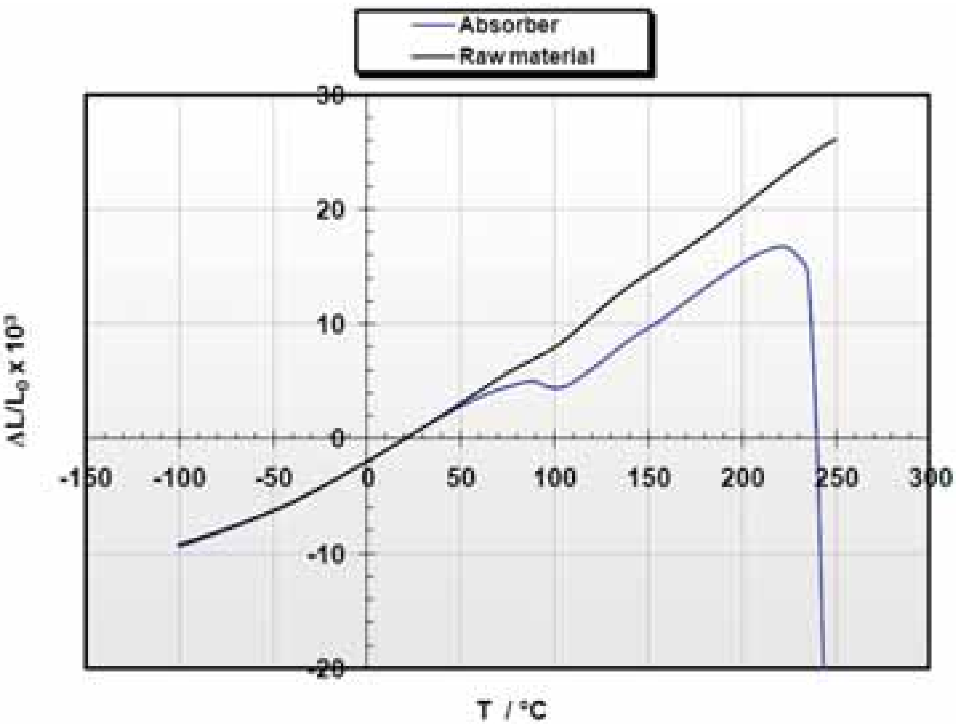

Figure 3: Linear thermal expansion of the raw material (black) and aged absorber (blue)

3. Medium Temperature Collectors

Standard flat plate collectors do not have reasonable efficiencies for a medium fluid temperature of more than 100°C. Thus, considerable effort is put into the development of various new designs, mainly relying on some kind of concentration (e.g. Fresnel, parabolic trough, compound parabolic concentrator (CPC)).

Especially CPC-collectors have the advantage that due to the very mirror design, no tracking is required. We investigated the absorber of a CPC collector in more detail and measured the thermophysical properties of as-produced copper pipes (manifold), soldered pipes (manifold) and the absorber fins (Figure 4).

Although it is well known that various grades of copper are employed in solar thermal absorbers (e.g. Cu-HCP, Cu-DHP, Cu-OFE; in our case Cu-DHP), it is not clear in advance which influence collector manufacturing steps such as soldering, brazing, welding or bending do actually have on the properties of the materials.

There is a clear trend in saving material and thus costs by continuously reducing the absorber thickness. However, below certain thickness and thermal conductivity values, the absorber itself may become a bottle neck for heat transport, which reduces collector efficiency considerably.

Figure 4: Left: Scheme of a CPC-collector (www.solarfocus.at). Right: Absorber (top) and manifold pipes (bottom left: after brazing, bottom right: new) of the CPC collector

Figure 5 shows the results of the measurements of the absorber fin. One observes that the actual thermal conductivity is roughly ¾ of the pure copper value of 401 W/mK at 25°C.

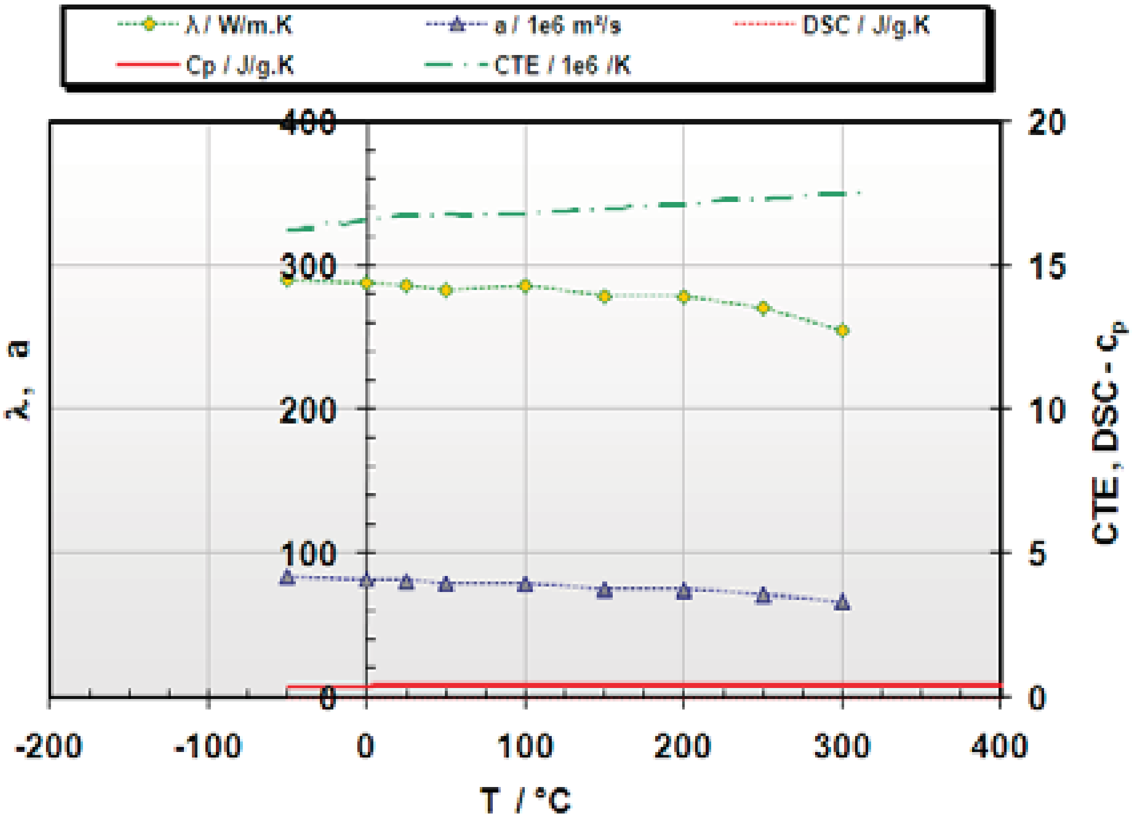

Figure 5: Thermophysical properties of a CPC-collector copper absorber

Brazing is a thermally stressful processing step (copper temperatures may reach 600-900°C) that may change the microstructure of the material itself potentially leading to different thermophysical properties. In the worst case this may cause leakages in the long run.

In Figure 6 and 7, one can observe that for the material used in the Solarfocus-CPC-collector, no considerable changes occur. Also the thermal conductivity is not altered significantly.

However in view of the envisioned pressures and temperatures in medium temperature collectors (operating pressures up to 20 bar and temperatures up to 250°C), a thorough thermomechanical analysis would be reassuring.

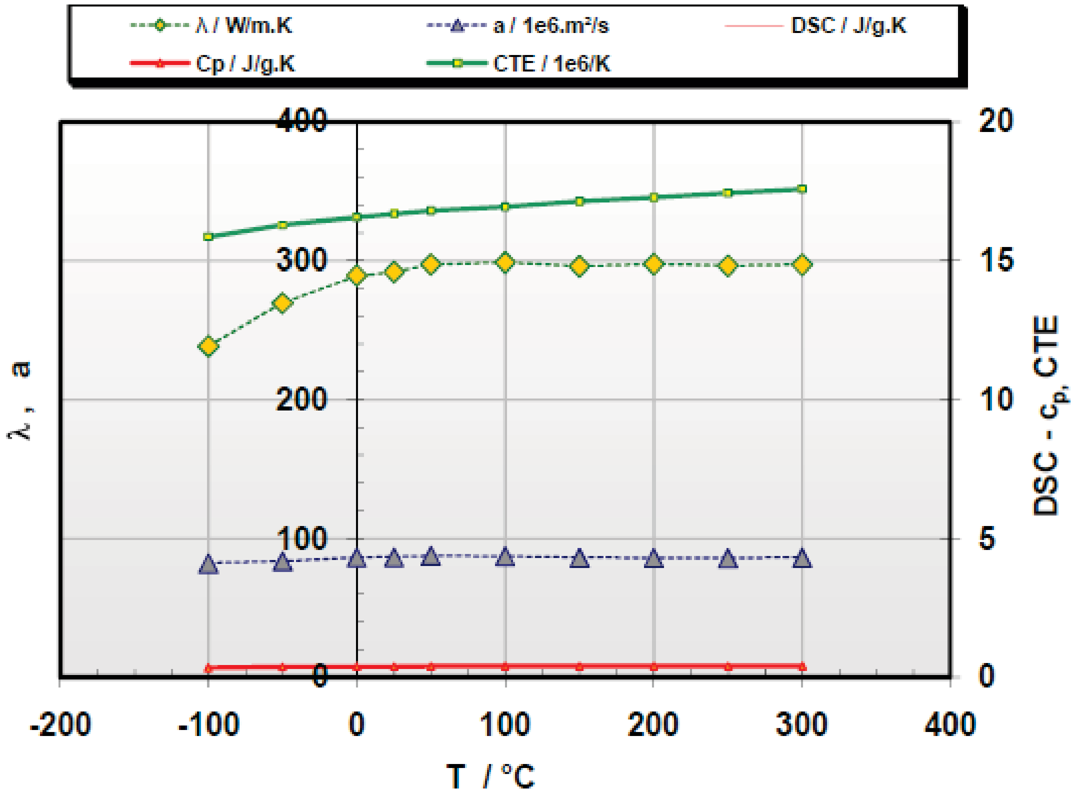

Figure 6: Thermophysical properties of a new copper manifold pipe

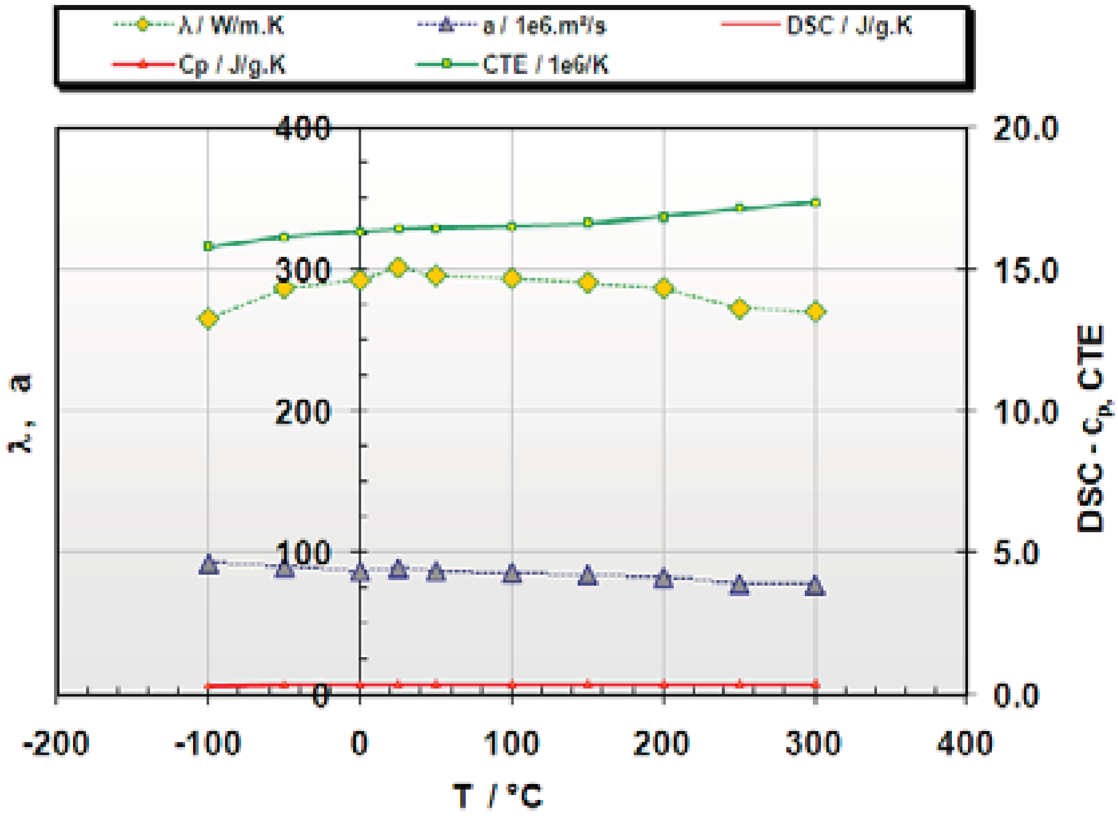

Figure 7: Thermophysical properties of a copper manifold pipe after brazing

4. Insulation

Thermal insulation is a key component of each standard flat plate collector. Heat is prevented from being lost mainly through the back side by material layers with low thermal conductivity. Most widespread are different types of mineral wool with various densities and binder content. Especially the latter one is responsible for outgassing problems in collectors and thus has to be analyzed in great detail.

Building integration of solar thermal collectors can be an architecturally appealing way to include solar energy. Especially in façades it is important to prevent overheating of the inside room, when the collector is in stagnation. One way of ensuring that is to use better insulation (lower thermal conductivity) that can withstand high temperatures.

Besides mineral wool, also other insulation materials are available on the market (e.g. various polymeric foams, bio-based materials like hamp or flax, and anorganic foams, aerogel-based materials, vacuum insulation panels), which however are often not designed for solar thermal applications and thus have to be analyzed separately.

Figure 8 shows a thermogravimetric analysis of a certain type of hard polyurethane foam. The measurements were conducted under synthetic air. The heating rate was 10K/min in the beginning followed by a 30 minute isothermal segment at 230°C and a short cooling phase.

It can be inferred that the maximum operating temperature of this material should be below 120°C. Also, at least three different mass-loss regimes can be identified, which cumulate to a total mass loss of 20% most likely too much for an application in a solar thermal collector, but still acceptable for a hot water storage tank.

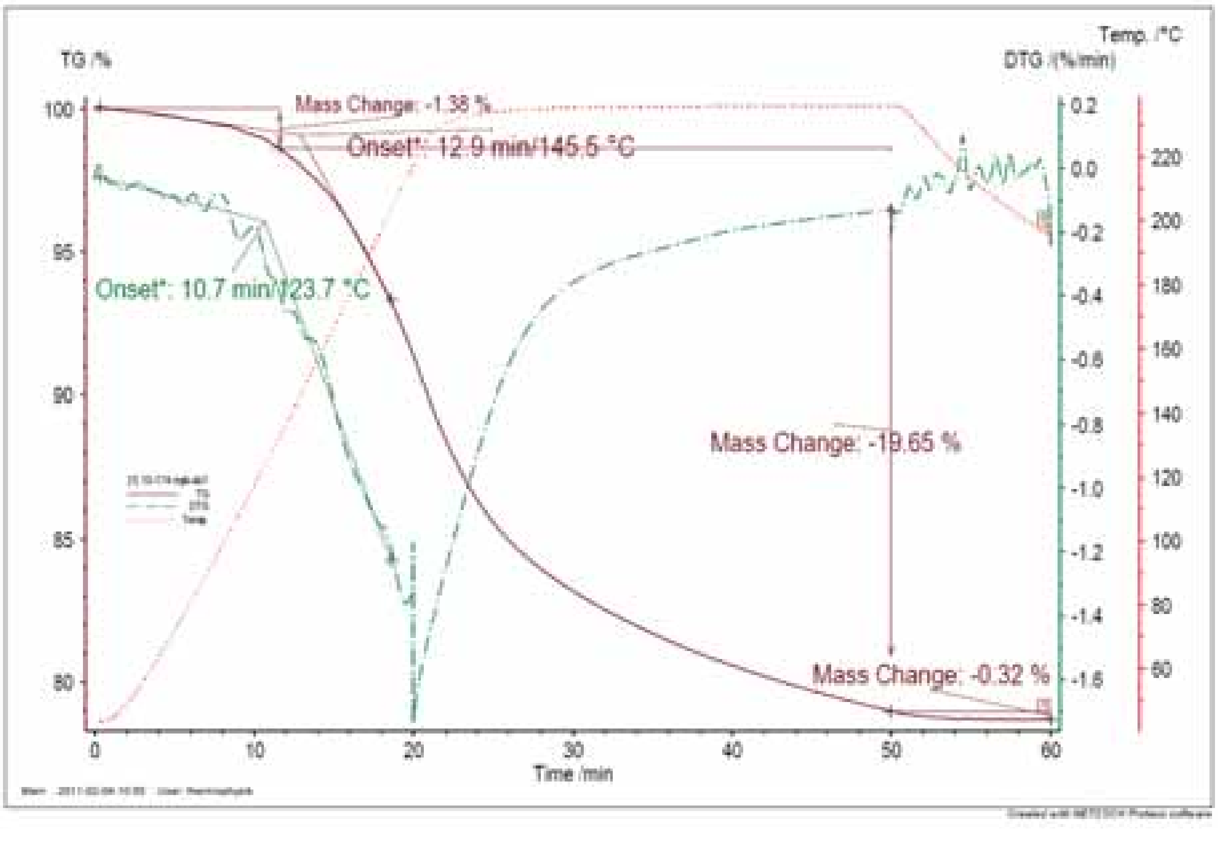

Figure 8: Thermogravimetric analysis of a certain type of hard polyurethane foam (left axis: relative mass change, right axis: derivative of the relative mass change (green), sample temperature (red))

The thermobalance can be combined with a mass spectrometer (Aeolos 403C) and a FTIR-spectrometer (Bruker Tensor 27) to perform a simultaneous evolved gas analysis. Possible outgassing products can be analyzed in more detail, which is shown for a mineral wool sample in Figure 9.

The sample was heated in synthetic air atmosphere up to some 230°C followed by an isothermal segment. Weight reduction of the mineral wool starts around 200°C and is accompanied by peaks in the total mass spectrometer as well as FTIR Gram Schmid signal, which confirm the outgassing process.

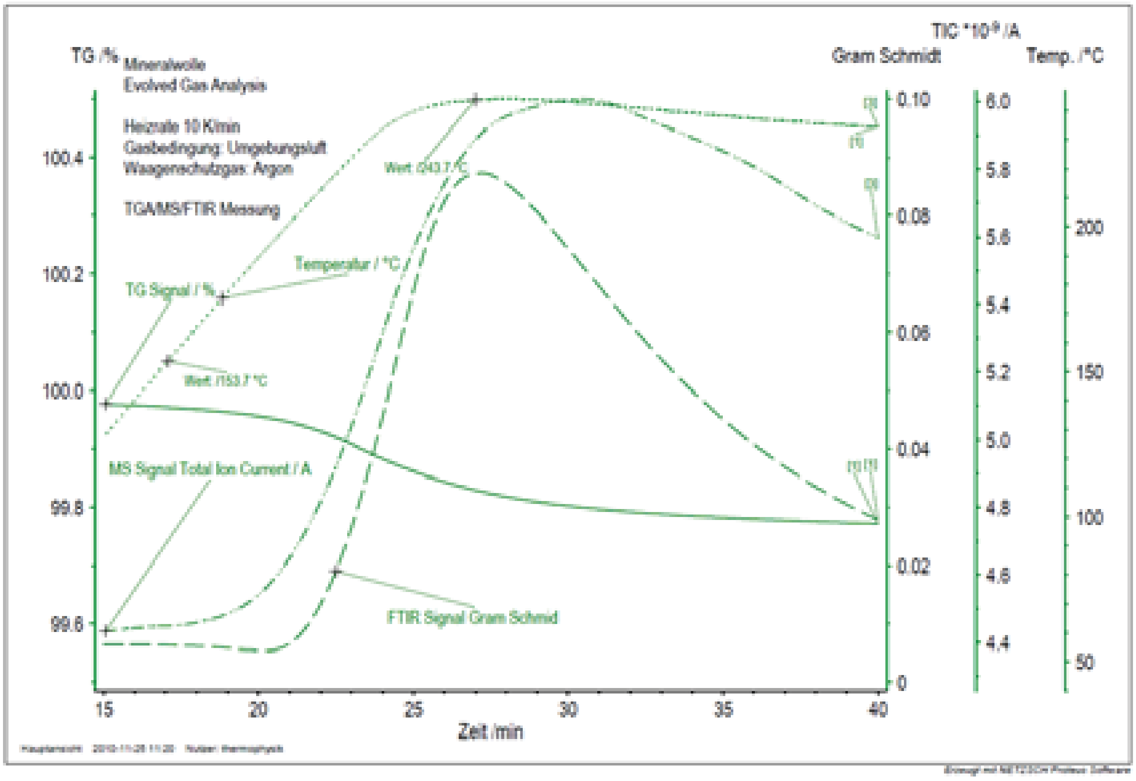

Figure 9: Evolved gas analysis of mineral wool via simultaneous thermogravimetric analysis, mass spectrometry and FTIR spectroscopy

The wavelength dependent FTIR signal also bears information on which compounds of the material are responsible for the outgassing and is useful for investigating aging effects of various materials.

In order to demonstrate the capability of this method, we investigated the behavior of a new type of polyurethane foam, which is stable up to temperatures that permit the use in solar thermal collectors.

A miniature collector provides temperature, humidity and solar irradiation loads close to realistic conditions (in contrast to certain climate chamber or oven experiments). This is a cheap way (less material, easier to manufacture, less exposure area) to expose materials for longer durations and to analyze the aged samples regularly (Figure 10).

SEM pictures (Figure 11, measured by Österreichisches Forschungsinstitut (OFI)) of the as-produced and the degraded, yellowed foam surface reveal that increased temperatures deteriorate the cell structure. In addition by employing ATR-FTIR spectroscopy (Figure 12, measured by Österreichisches Forschungsinstitut (OFI)), more details about the aging mechanisms can be inferred. Increasing or decreasing peaks upon collector exposure provide early-stage hints to certain chemical reactions that are responsible for later component failure.

Thus this set of methods is immensely useful to ensure and improve the long-term quality of the solar thermal collectors and components of various types.

Figure 10: Miniature Collector (70x40 cm²) employing a special type of soft polyurethane foam insulation. Left: Collector was exposed more than one year in Vienna. Right: yellowing of the foam below the absorber and sample for SEM and ATR-FTIR.

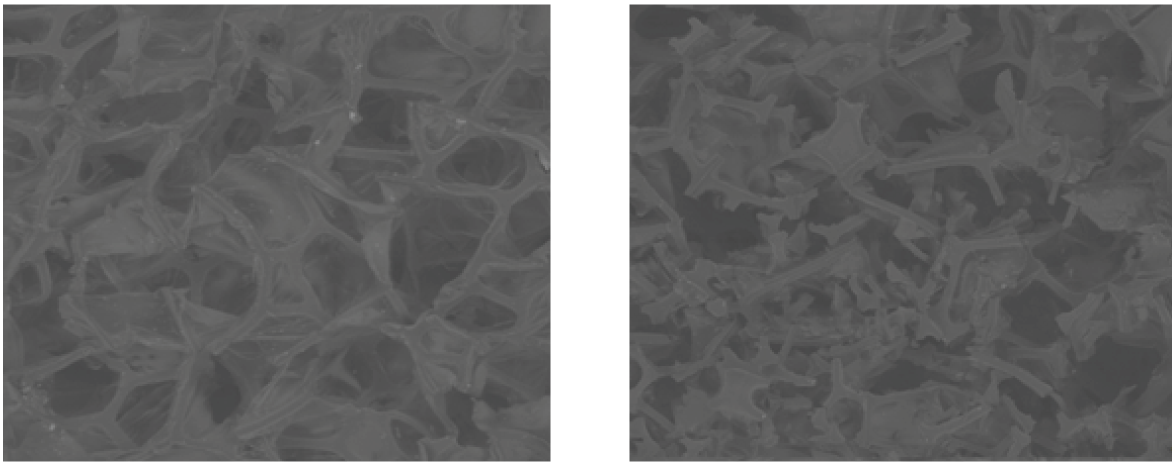

Figure 11: SEM pictures (measured by Öesterreichisches Forschungsinstitut (OFI)) of the new (left) and aged (right) soft polyurethane foam revealing deteriorated cell structure

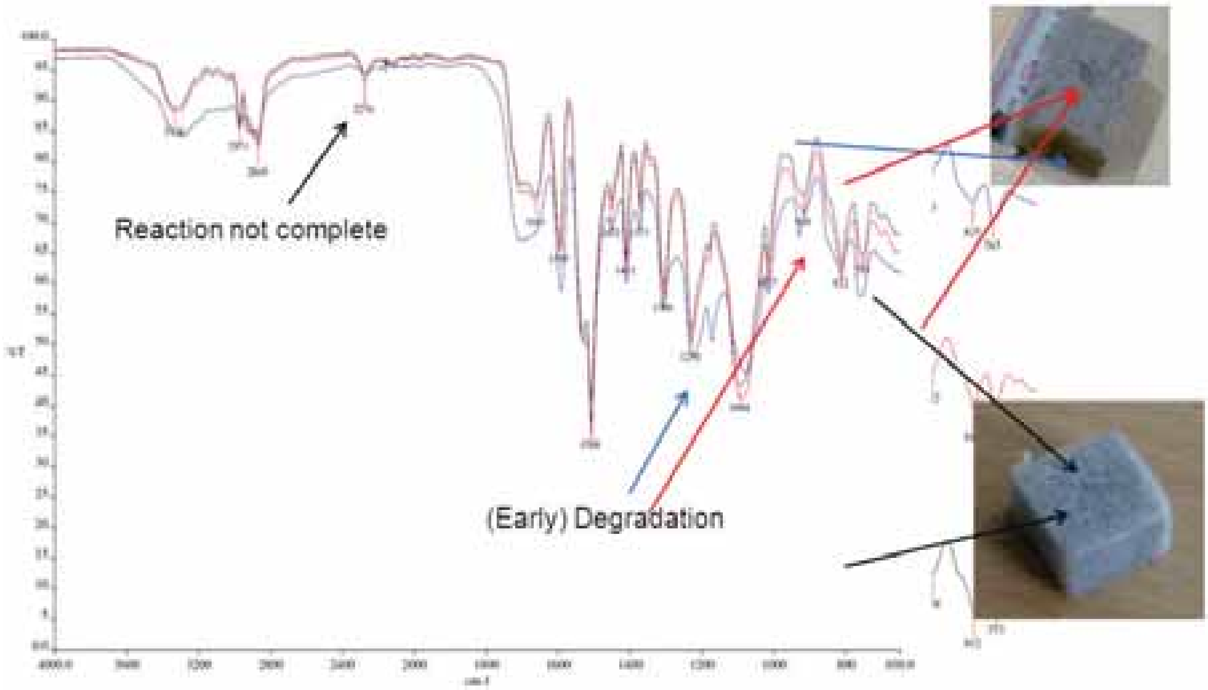

Figure 12: ATR-FTIR spectroscopy (measured by Öesterreichisches Forschungsinstitut (OFI)) of new and aged samples revealing also early-stage sub-surface degradation

5. Acknowledgement

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6. References

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