





Separation of organic components from crystalline silicon solar cells by supercritical fluid technology

Master's thesis in Applied Physics

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Separation of organic components from crystalline silicon solar cells by supercritical fluid technology

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Department of Chemistry and Chemical Engineering Energy and Materials Industrial Materials Recycling CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden 2020 Separation of organic components from crystalline silicon solar cells by supercritical fluid technology

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Cover: SEM images of the topography of the surface of sample of type 2 treated in $scCO_2$ and 3ml DMSO as a co-solvent with 430x magnification in 15 keV BSE mapping mode.

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Abstract

Photovoltaic solar cells are a safe, efficient, reliable, and non-polluting sustainable alternative to fossil-fuel based energy source. However, decommission of solar modules become gradually an environmental issue themselves. Untreated disposal of the end-of-life modules provokes enormous environmental pollution by the enhancement of leaching of hazardous constituents plus the loss of valuable raw materials. Hence, efficient sustainable and feasible recycling of spent photovoltaic modules becomes crucial to fulfil their sustainability purpose.

The biggest challenge in the recycling of the spent modules is associated with the complete removal of the organic compounds from the solar cell. The current available waste photovoltaic module recycling procedures rely either on high temperature pyrolysis, leaching agents or a combination of both. Although, pyrolysis provides the successful delamination of the encapsulant of the solar cell and the separation of the glass in environmental perspective, it is not the most sustainable solution. First of all the demand in energy during the pyrolysis process is rather high. In addition, greenhouse gases such as carbon dioxide, carbon monoxide and hydrogen fluoride are produced during the process and lead to environmental pollution. Thus, a more sustainable and simultaneous economically feasible technique for the separation of the solar cell from the encapsulation and the glass layer has to be developed. Super-critical fluid technology is proposed to be a sustainable approach as a replacement of incineration or pyrolysis methods.

In this work the effects of supercritical carbon dioxide (scCO₂) with and without a co-solvent on organic separation from crystalline silicon solar cell samples were investigated. Apart from pure scCO₂, the solvent power combination of scCO₂+DMSO and scCO₂+Ethyl lactate at various pressure conditions were tested. The analysis of the FTIR-spectra of the exhaust gas as well as SEM images of the samples are leading to the conclusion that the combination of scCO₂ and DMSO partly dissolves the organic layerr from the cell.

The results were compared with those of the common incineration techniques on the same type. For this, FTIR-spectra from previous as well as new experiments were used to determine the exhaust gas emission of incineration system depending of temperature and high temperature reactor design. Acetic acid, carbon dioxide, carbon monoxide and hydrogen fluoride were detected in the exhaust gas.

Keywords: Photovoltaic, c-Si solar cell, Recycling, Supercritical scCO₂, Incineration, Separation, EVA, Backsheet, FTIR, SEM.

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Acronyms

\mathbf{CO}_2	Carbon Dioxide
$scCO_2$	Supercritical Carbon Dioxide
a-Si	Amorphous Silicon
BSE	Backscattered Electron (mode)
c-Si CdTe CIGS	Crystalline Silicon Cadmium Telluride Copper Indium Gallium Selenide
DMSO	Dimethyl Sulfoxide
EOL ETFE EVA	End-of-life Ethylene Tetrafluoroethylene Ethylene-vinyl Acetate
FTIR	Fourier Transform Infrared Spectroscopy
IR	Infrared Spectroscopy
OPD	Optical Pathlength Difference
PET PV PVDF PVF	Polyethylene Terephthalate Photovoltaic Polyvinylidene Difluoride Polyvinyl Fluoride
SCF SE SEM	Supercritical Fluid Secondary Electron (mode) Scanning Electron Microscope
THV	Terpolymer of Tetrafluoroethylene, Hexafluoropropylene and Vinylidene Fluoride

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1 Introduction

Environmental pollution caused by consumption of fossil-fuels is the driving force behind global warming and climate change. A major share of those environmental harmful emissions can be directly linked to the electricity generation [1]. A shift from fossil-fuel based energy sources towards to more sustainable renewable energy technologies is therefore inevitable. In 2016, 76% of the electricity generation worldwide was based on fossil-fuels [2]. Renewable technologies such as Hydropower (17%), Solarpower (1%), Windpower (4%) and other renewables (2%) contributed only 24%. Although, solar power played in 2016 a minor part in the global share of energy generation, it can be forecasted to be one of the primary globally energy resources within this century [3] contributing to a quarter of the electricity generation by 2050. In fact, the Photovoltaic (PV) market skyrocketed since the early 2000s, which is mainly accompanied by the falling prices of solar cells, in special of silicon. Between year 2010 to 2019 the Compound Annual Growth Rate (CAGR) of cumulative PV installations was 32% reaching 635 GW worldwide [4]. Following this exponential growth rate a rise to $4500 \,\mathrm{GW}$ by 2050 can be forecasted as shown in figure 1.1.



Figure 1.1: Projected cumulative global PV capacity based on the IRENA reports [5].

Although, PV modules can be considered to be a safe, efficient, reliable, and nonpolluting energy source during its life-time of 25-30 years, they become gradually an environmental issue themselves after their end-of-life (EOL) [5–7]. Their complex electronic design contains several different layer of materials (see section 2.1.2), which are considered to be non-hazardous and hazardous waste [6]. Unntreated disposal of the decommissioned modules, therefore, enhances leaching of hazardous constituents which consequently lead to enormous environmental pollution posing a health risk not only for human beings.

Currently, the first batch of decommissioned panels enter the waste streams making up for more than 250 000 metric tonnes of waste in 2016 [5]. This corresponds roughly to 4% of the new installations of the same year. However, the waste stream will be alongside the PV capacity. By 2050 the decommissioned modules are expected to cover up to 60-75 million metric tonnes of waste [5]. But are those end-of-life panels waste in the common sense?

In fact, PV panels contain valuable raw materials such as silver, copper and silicon altogether worth roughly 450 MUSD[5]. Hence, solar solar panel recycling is not only necessary in an environmental perspective, but also economically favourable (see section 2.2).

However, the main research in the PV sector focuses mainly in the improvement of solar cell efficiencies and production capacities. End-of-life management and recycling technologies are seldom considered and face, in technical aspect, still many problems in the achievement of economically feasible and non-toxic recovery of the valuable raw-materials. The biggest challenge is associated with the complete removal of the organic compounds from the solar cell [6]. The current available waste PV recycling processes rely either on high temperature pyrolysis, leaching agents or a combination of both. Although, pyrolysis and incineration provide the successful delamination of the encapsulant of the solar cell and the separation of the glass [8], it is not the most sustainable solution in environmental perspective. First of all the demand in energy during the pyrolysis process is rather high. In addition, greenhouse gases such as carbon dioxide, carbon monoxide and hydrogen fluoride are produced during the process and lead to environmental pollution [6, 9, 10]. Hence, a more sustainable and at the same time economically feasible process for the separation of the encapsulation and the glass layer from the solar cell has to be developed. Supercritical fluid technology was proposed to be a more sustainable alternative to incineration.

In this work the proposed new approach was investigated. More precisely, the impact of supercritical carbon dioxide ($scCO_2$) with and without a combination of a cosolvent on commercial EOL crystalline silicon solar cell samples was studied and compared to the results of incineration experiments on the samples of the same PV panel.

2

Theory

2.1 Photovoltaic module materials

2.1.1 Structure of solar panels and materials

The components of solar panels (PV module) and material requirements are reviewed in this section. Solar panels are complex electronic devices containing several layer of different materials as illustrated in figure 2.1.



Figure 2.1: Structure of an average solar panel belonging to the first or second generation.

The conversion of of photon energy into an electric current is based on the photovoltaic effect, first demonstrated by Edmond Becquerel in 1839. When light is exposed to the semiconducting material, the core of the solar panel, the electrons or other charge carriers in the valence band absorb energy and get excited into a higher energy-state, the conduction band. In there they become free electrons with an effective mass, allowing the to become free charge carriers for an electric current [11].

Nowadays, several types of PV modules composed of various technologies for solar cells, backsheets and encapsulant materials are available on the solar market and

their variety will spread in the future [12, 13]. In general, solar modules are called depending on the absorbing material type, such as crystalline silicon (c-Si), amorphous silicon (a-Si) or copper indium gallium selenide (CIGS). Moreover, they can be classified into three different types often referred as first, second and third generation.

2.1.1.1 Solar panel types

The first generation are wafer-based solar cells including crystalline silicon (c-Si) which can be mono- or multi-crystalline [11, 14]. Still, this generation holds the largest share of the solar market with 95% [4], due to the price drop of silicon and their high efficiencies. [14].

As an absorber material, silicon has the advantage to be a stable, non-toxic, abundant raw material and is well known from the IT and microtechnology sector [14]. Moreover, it is favoured as a semiconductor since its band gap of $1.12 \,\text{eV}$ is very close to the optimum theoretical value given by the Shockley-Queisser limit of about $1.2 \,\text{eV}$ [11, 12]. The state-of-art power conversion efficiency of solar modules on the market are 17% and 18% for mono- or multi-crystalline [3] and are expected to improve substantially until 2039 [4]. However, apart from the required impurities in the n-and p-doped parts, the c-Si wafer require high-level chemical purity [11]. Thus, the elaborate production process is high energy demanding and rather expensive. However, the production costs of c-Si dropped rapidly in the last decade, which is one of the main reasons of the PV price decrease of almost 76% between 2010 to 2018 to 1.18 USD/W [15].

Tremendous cost savings can be achieved with thin-film cells generally categorised as second generation. Due to the higher absorptivity of the non-single crystal structured absorbing material, the semiconductor can be made with a thickness of few micrometers [14]. The thin layer can be deposited on a low-cost supporting material such as glass, metal or plastic, making mass production much more feasible due to fast and cheap decomposition techniques. However, the lower optimum efficiency in the Queisser-Stockley limit of 21.5% to 26% [12], originated from its non-single crystalline structure, is the main drawback of second generation cells and balances the lower manufacturing cost. The thin-film market is dominated by cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) cells. Also available are amorphous silicon (a-Si) cells.

Third generation technologies, also referred as emerging technologies, do not play a major role in the current PV market, yet [6]. In the near future there is, however, expected to be a shift towards organic-, dye-sensitized-, quantum dot-, and perovskite solar cells since they promise to be economic highly efficient cells.

The upcoming listed specification of structure and materials relates primary on the first and second generation cells due to their major contribution of the PV market.

Regardless the type of solar cells, electron collectors have to be attached to the face and rear of the cell. They have the requirement to be highly electric conductive with matching energy bands to the semiconducting material. Screen-printed silver contact lines and aluminium pastes are the most common choices of material. Roughly, 6-8% of the face cell area are typically covered by silver. However, replacements with copper or copper-/nickel and other varieties are still in progress [3].

To ensure stability, reliability and durability, the solar cell needs to be protected from environmental influences of all sorts. Therefore, the cell is embedded in different layer (encapsulant, backsheet, glass and frame). The function of those and their most important properties are reviewed in the following.

2.1.1.2 Encapsulant

The encapsulant holds the solar cells and interconnects in place and protects them from weather-related corrosion among residues of moisture penetration and protects them against environmental stress. Additionally, the layer provides electrical isolation of the PV circuit and minimises the mechanical stress. Moreover, the encapsulant couples the superstrate materials (e.g backsheet, glass) optically to the cell [11, 16].

Hence, a long-term reliable encapsulant needs to fulfil several requirements over the whole life-span (25-30 years) of the module. During this period the module is exposed to the most severe climate including prolonged periods of extreme temperatures, humidity, mechanical loads and strong UV-radiation. The most important requirements for the encapsulant material are mechanically strong, moisture resistant adhesion properties, high transmittance over the entire solar spectrum, low thermal expansion coefficient close to the one of the cell, UV- stability, low electrical resistivity, low permeability to atmosphere pollutants such as oxygen, water vapour and dust [11, 16–18].

The most widely used encapsulant material is ethylene-vinyl acetate (EVA) [16, 19]. Although EVA has not the best combination of properties, the polymer provides strong adhesion and high transparency while being economical feasible with an established history of long durability. The establishment of new encapsulant products is challenging because of the limited room of improvement in terms of price reduction and transmittance.

2.1.1.3 Backsheet

The rear of the encapsulated solar cell is fixed to the, so called, backsheet. The white polymeric film typically reflects the unabsorbed beams diffusively with the aim to recycle and redirect the photons to the active layer of the solar cell by total internal reflection. The backsheet is the last layer of the solar module and hence the last electrical protection against the environment. Consequently, the electrical insulation and dielectric properties are one of the most important properties of the material of choice. [20] As well as an encapsulant, backsheets play a significant part in the protection of the cell from outside forces and environmental damages outlined in the previous section. Thus, backsheets are an essential material for providing long-term durability, safety and reliability of solar cells [11, 21, 22].

Often backsheets are a compound of multi-layer films. Each layer of those has a different function to fulfil the versatile requirements stated above. The polymeric compound composition can be broadly divided into fluoropolymers- and nonfluoropolymers [21]. Fluoropolymers have the advantage to not degrade in elevated temperatures. Additionally, they are chemical inert and stable to moisture and UV-radiation. For a long period a three layer combination of bi-axially stretched polyvinyl fluoride (PVF) and polyethylene terephthalate (PET) commercialised by the company DuPont under the name Tedlar was the unique selling point on the backsheet market [22]. Nowadays, however, the backsheet market is filled with many different solutions. Besides PVF, multi-layer films based on polyvinylidene difluoride (PVDF) supplied by Arkema marketed as Kynnar and other suppliers entered the market. In 2016 backsheets including PVF and PVDF made up the main backsheet technology share. Other common used fluorine based materials are ethylene tetrafluoroethylene (ETFE) and a terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride (THV) [21, 22].

PET is the most used polymer among the non-fluoropolymer segment, but also as a core layer in the multi-layer compounds listed. This is due to its high dielectric properties and material stiffness [21, 22].

As mentioned, solar panel producers have the opportunity to select among a wide range of variation of backsheets such as the classical Tedlar and PVDF compositions but also to pure polyester based solutions and many different other coating variations.

2.1.1.4 Glass

The top of the encapsulated solar cells is typically protected by tempered glass. The most important requirement, besides its function in the protection of external stress and damages from moisture, dust and dirt, is a high transmittance of the glass over the entire solar spectrum. Most commonly, tempered soda-lime glass is used. Some more expensive modules come with an anti-reflection coating [5].

2.1.1.5 Frame

The very last protection of the internal compounds from thermal and mechanical tension is the frame. The frame provides mounting attachments points and protects the module during its transportation. Anodised aluminium is the most common used material [5].

2.1.2 Material composition of a solar panel

The solar cell market is currently dominated by c-Si solar panels. CIGS and CdTe panels play a minor role [3, 4]. In c-Si panels the main processed materials are glass, polymers (encapsulant and backsheet), silicon, aluminium, silver, lead and others [5, 6]. For CIGS solar panels glass, polymers (encapsulant and backsheet), aluminium, cadmium, gallium, indium, selenium, silver and others and for CdTe glass, polymer, cadmium telluride, silver, nickel and others [5].

Figure 2.2 shows the estimated development of the material share of the most common solar panels in weight percent from 2014 to 2030. Independently of its type, glass and aluminium contribute the majority of the weight of the panel. Next are the polymer layer manufactured in the encapsulant and backsheet. A minor role play silicon, silver, copper, compound semiconductor and other metals with in total less than 10% of the total solar panel mass [5].



Figure 2.2: Estimated evolution of materials used for different PV panel technologies as a percentage of total panel mass from 2014 to 2030 [5].

However, the reverse picture emerges when analysing the relative material value in mass percent. In the specific example of a crystalline silicon solar panel ,as seen as in figure 2.3, the by far most expensive compound per unit mass is silver with 45%, followed by copper, silicon, aluminium, glass and polymers [5].



Figure 2.3: Relative material value share of a c-Si PV panel [5].

This emphasis that each solar panels adds to a large stock of raw materials of significant value. The prognosis for 2030 states that technically recoverable raw materials from PV panels could cumulatively yield a value of up to US-\$450m. In 2050 the recyclable value could even exceed US-\$15B. Hence, recycling is not only essential in environmental aspect, but also undoubtedly in an economic point of view [5].

2.2 Solar panel recycling

Research in solar technology has focused mainly in the improvement of power conversion efficiencies, production efficiencies, savings in materials and costs. Dismantling and recycling of end-of-life solar panels are seldom considered. However, sustainable and economically viable treatment of decommissioned solar panels will be undoubtedly necessary in the world's transition towards a renewable based energy future [6, 7].

The durability of a solar panel lasts for 25 to 30 years. The large-scale installation of solar modules begun in most countries in the mid 2000s. Hence, the ratio of EOL to new installed panels is currently rather low [5]. However, as seen in figure 2.4, this ratio is estimated to increase steadily over time. By 2030 significant amounts of waste will be generated since most of the panels will have reached their end-of-life time [5]. According to previous studies a ratio of 6-14% of waste per new installed panels will be approached. By 2050 this ratio can be expected to exceed 80% contributing to approximately 60-78 million tonnes of PV panel waste, globally.



Figure 2.4: Annually installed and EOL PV panels 2020-2050 mass including the ratio of waste versus installed mass [5].

As mentioned in the previous section, the highest share of solar panels by weight are glass, aluminium and plastics. Those types of materials can be classified as non-hazardous waste. However, the panels also consist of materials classified as hazardous waste including silver, tin, traces of lead and semiconductor compounds of thin-film technologies. Hence, untreated disposal of the waste enhances leaching of hazardous constituents which consequently lead to enormous pollution of the environment posing a health risk not only for humans [23–26]. Additionally, an enormous loss of natural raw materials will be generated which, in the long run, will lead to problems in the security of future supply.

The growth of PV panel waste raises the opportunity for an enormous environmental and economical value. Recovered raw materials can be either provided to the solar technology sector itself to reduce production costs by economising energy-use and emission of virgin-material production. Alternatively, the material can enter the global market for secondary materials [5, 7]. In 2030 technically recoverable raw materials may generate a value of up to US-\$450m [5]. When reprocessed this is equivalent of the production of 60 million new panels or 18 GW of power generation capacity. By 2050, 60-78 million tonnes of PV panel waste being worth over US-\$15B could be recirculated into 2 billion new panels which is the equivalent to 650 GW of power generation [5].

The environmental impact of the PV waste as well as its economical benefits attracts increasing interest from research groups worldwide. The common goal is to recover as much valuable (e.g silver, copper, glass, aluminium), scarce (e.g indium, tellurium) and hazardous (e.g lead, cadmium, selenium) materials as possible. In the near future end-of-life management will play a significant part of the PV value chain [25]. However, the recycling system chain with its long and challenging process, is still incomplete and researchers are steadily faced with ongoing cell and panel innovations. The following of this sections summarises the achievement in research made so far and stresses the challenges of sustainable and feasible recycling [3, 5, 6]. High material recovery rates of the major compounds such as glass and aluminium yielding 85% of the solar panel weight can be currently achieved trough mechanical separation in existing recycling plants [6]. That includes the dismantling of the metal frame and wires from the remaining panel. The aluminium or steel frames and the copper wires become part of the well established metal recycling loop resulting in the material with the best potential for efficient recovery. The leftovers of the solar panel including glass as the heaviest part will be crushed and the glass fraction treated as thermal insulation material in the glass-foam and glass-fiber industry. The most valuable, scarce and most hazardous materials such as silver, silicon, lead, can be predominately found in this fractions and a recovery process of this materials is not included [6].

Recovery of those materials requires additional more advanced methods and can not be recycled without a combination of thermal, chemical or metallurgical steps. The critical step in the recovery of those materials is the delamination or removal of the encapsulant materials (see section 2.1.1.2) such that the solar cell is completely detached from the glass and the backsheet [27, 28]. This enables efficient extraction of silver and semiconductor compounds via various metallurgical processes, chemical etching and electrostatic separation or in best case scenario the reveal of an intact solar cell with the possibility of reutilisation [25].

Successful techniques for the removal of the encapsulant including mechanical crushing, grinding, chemical treatment with multiple types of organic solvents, acid, alkali solvent, organic solvent-assisted ultrasonic radiation, cygoenic breaking, laser-blade cutting, micro-emulsions pyrolysis and incineration [6] are published. However, those methods come along with some considerable disadvantages. Crushing, grinding or cygenic breaking the solar panels produces a huge amount of dust containing glass fiber and resin and creates high noise levels. The dissolution of the EVA layer using chemical treatment of various solvents such as trichloroethylene [29] and toluene [30] is time consuming. Even though the dissolution time can be shortened by using ultrasonic assistance, the sample had to stay 10 hours inside the organic solvents bath. Additionally, a large amount of volatile liquid waste is generated, which, itself, is in most cases difficult to treat. Although it is a high energy demanding process and generates toxic waste gases (e.g. hydrogen fluoride), the most promising and commercialised method is high temperature pyrolysis at roughly 500 °C [8].

In conclusion, none of the listed methods for the encapsulant delamination fulfils the aim to be environmental friendly and simultaneously economically feasible.

2.3 Supercritical carbon dioxide

Sustainable development is necessary and commonplace among a variety of fields. In the chemical industry volatile, toxic, flammable, hazardous organic environmental damaging solvents are often used in processes [31]. In order to overcome those shortenings a tremendous effort has been devoted towards Green Chemistry. Paul Anastas and John Warner developed "Twelve Principles" of Green Chemistry to define its main goals and realisations in practise [31, 32]. Following those principles green solvents such as water, ionic liquids, organic carbonates, bio-solvents and supercritical fluids have been employed in industry scale in the pharmaceutical, cosmetic industry and food industry. Much attention has been focused on supercritical fluids (SCFs) [33].

A substance reaches its supercritical state and is therefore called a supercritical fluid once pressure and temperature exceed its critical values [34] as illustrated in figure 2.5.



Figure 2.5: Schematic pressure - temperature phase diagram for a pure component showing the supercritical fluid (SCF) region. T and C marks the triple point and critical point, respectively. The variation in density of the substance in the different regions of the phase diagram is represented by the blue circles [34].

In this state, the substance obtains unique properties. They exhibit liquid-like densities, gas-like viscosity diffusion coefficient and negligible surface tension allowing them to penetrate into solid matrices inaccessible for liquids. Furthermore, those physical properties can be tuned by varying the temperature and pressure within the supercritical region which makes them a powerful solvent for many substances [33–36].

Supercritical carbon dioxide (scCO₂) outstands other potential SCFs by its easily accessible critical parameters. The critical temperature and pressure of carbon dioxide (CO₂) are 31.1 °C and 73.8 bar, respectively [31, 33, 34, 36]. In addition to its common benefits in the supercritical state mentioned above, CO₂ is unrestricted by the US Environmental protection agency, chemical stable, non-flammable, recyclable. cheap and as being a by-product of various industrial technologies abundant [31, 35]. Hence, the use of scCO₂ technologies has already been employed in the food and nutrition industry. Here it successfully replaces former used chlorinated organic solvents as an extraction medium for decaffeinating of coffee beans and tea, soy bean processing, and the extraction of essential oil and flavour compounds. Other employment areas are in the beverage, cosmetic, painting and dyeing industry, cleaning solvent in the fields of microelectronics, plastizisers in the polymer processes to name just a few [35, 36].

However, the carbon dioxide molecule is linear and centrosymmetric and therefore has no electrical dipole. Thus, $scCO_2$ can be classified as a non-polar solvent being a good solvent for many non-polar low molecular weight compounds. Due to its large molecular quadrupole it has also shown solvent characteristics to polar molecules. But under readily achievable conditions, $scCO_2$ is an ineffective solvent for high molecular weight polymers and ionic compounds of high polarity. Nevertheless, the solubility properties of $scCO_2$ can be significantly improved by adding a co-solvent or a modifier [33, 36, 37].

Recently, the implementation of $scCO_2$ in the recycling process of Lithium-Ion batteries [38] and liquid crystal displays [39] has been studied. This study is the first attempt to separate the organic components from the solar cells by $scCO_2$.

2.4 Analysing methods and techniques

2.4.1 Fourier transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical methodology to obtain an infrared (IR) spectrum of any liquid, gaseous or solid sample. While exposed to radiation within the infrared region, particularly between $4000 \,\mathrm{cm^{-1}}$ and $400 \,\mathrm{cm^{-1}}$, the molecules in the sample absorb selectively photons of specific wavelength, whose matching its vibrational energy level gaps. Consequently, transmission of those photons will not occur, resulting in an unique molecular vibrational spectrum, the IR spectrum. The vibrational energy level configuration, affected by the interaction of and within the functional groups, are very unique for every molecule. By analysing the quantities, positions and intensities of the peaks in the transmission or absorption spectrum, the composition and chemical structure of the sample can be determined.



Figure 2.6: Illustration of the procedure of a classical FTIR spectrometer

The set-up of a classical FTIR device is illustrated in figure 2.6. Its essential elements are the Michelson Interferometer and the software relevant for the Fourier Transform. A Michelson Interferometer consists of a light source, beam splitter, one fixed and one movable mirror, a sample compartment and a thermal or photonic detector. The beam splitter divides the broad band infrared beam generated by the light source into two different paths. The transmitted and reflected rays strike the stationary and the movable and recombine in the beam splitter. Originated from the optical path difference of the fixed and moving mirrors, the recombination of the beams causes a interferogram which is passed trough the sample. While some of the radiation gets absorbed, the detector collects the transmitted photons. The obtained amplified and converted signal is a function of signal intensity versus time (or OPD). However, the typical IR spectrum is a plot of absorption/transmission intensity versus frequency (or wavenumber). A computer software executes a transformation using a Fourier Transform algorithm. Fourier Transformation is a mathematical method to convert a functions between the time and frequency domain.

The biggest advantage of the FTIR spectroscopy is that the IR spectrum is obtained while detecting the broad range source at once. Hence, the desired result can be obtained within seconds. Whereas, the alternative dispersive spectrometers are much slower, since the signal is detected by sequentially scanning the wavelength of the source. Other also related advantages of the FTIR tool are higher signal-to-noise ratios, resolutions and wavenumber accuracy to name just a few.

2.4.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a powerful technique to study the surface topography, composition, or crystallography of an electric conductive sample. The core of the instrument is a convergent electron beam. Interactions between the impinged electrons and the sample atoms induce a signal, which is detected by a detector and then transformed into the intensity of a pixel of an image. The electron beam, then, scans across the surface generating pixel by pixel of the image. Dependent on the energy of the electron beam, the SEM can be operated in different modes. The most common modes are energy dispersive X-ray (EDX), secondary electron (SE) and backscattered electron (BSE) mode. Their induced signals originate in inelastic, elastic scattering and ionisation, respectively. EDX is typically used for the determination of the chemical composition of the samples, whereas SE and BSE modes are used to study the surface topography of a sample. This work uses the BE mode to study the surface of the solar cell samples. The electron energies in the BE mode are typically ranged between 15 to 30 keV. In this range the backscattering coefficient is independent of the acceleration voltage of the electron beam, but increases with increasing atomic number. Therefore, compositional (or elemental) contrast can be observed in the images, when the specimen has features with different compositions.

Methods

In the following, the experimental set up and procedure of the experiments of the supercritical fluid technology system and incineration process in this work are described. The c-Si solar panel sample preparation and gas collection process for the FTIR analysis were similar for both types of experiments and therefore explained in one paragraph.

3.1 Sample preparation

The samples in this work stem from a commercial end-of-life photovoltaic module with the series number D6M285E3A of the brand Neo Solar Power. The incineration and SCF systems demand different sizes of the samples. Therefore, the module was first cut into $50 \times 20 \,\mathrm{mm}$ pieces. Those type of sample dimension was used in the incineration process. To fit in the reactor of the SCF system, the dimensions of the samples used in SCF experiments were chosen to be $20 \times 5 \,\mathrm{mm}$. Two types of those samples were used in the SCF system. The pre-cut pieces were cut into their final size by a Precision Disc saw (Struers Minitom) using the Diamond Cut-off Wheel M0D10. To avoid further cracks and splitting of the front glass of the solar panel, the glass was covered by a stripe duct tape. Those samples were sample type 1. For sample type 2, the pre-cut pieces were manually separated to detach the part below the solar cell (encapsulant, backsheet) from the upper part (solar cell, encapsulant glass layer). Then, the lower part of the cell was cut by a scissor to its selected dimensions of $20 \times 5 \,\mathrm{mm}$. In the following those type of samples are referred to sample type 2. The dimensions of the samples are portrayed in the images in figure 3.1.



Figure 3.1: Image of sample dimensions and types used in this work. a) Pre-cutted sample used in the incineration experiment. b) Sample type 1 used in the scCO2 technology experiment. c) Sample type 2 used in the scCO2 technology experiment.

3.2 Supercritical fluid technology system

3.2.1 Experimental set up

The supercritical fluid technology system, as illustrated in figure 3.2, used in this work was constructed in a fume hood. Liquid carbon dioxide (99.9% purity) provided by a pressure cylinder (1) was pressurised by an ISCO 260D syringe single pump system (2) (Teledyne ISCO, Lincoln, NE) and heated by an external heat system (4) (Model F10 & CM, Julabo). A manual valve (3a) was used to direct the gas flow into the core of system, the reactor (5) manufactured of stainless steel in which the samples and co-solvents were placed. The temperature of the pressurised gas inside the reactor was heated and stabilised by water pipes controlled by an external thermostat (6) (Model F12 & ED, Julabo). The temperature and pressure in the reactor volume were monitored by an inserted thermocouple (7) and connected manometer (8). The flow-rate of the evacuation of the gas was controlled by the second valve (3b). To avoid freezing of the CO₂, the valve was heated by a thermostat (9). For the collection of the exhaust gas for the FTIR analysis, a gas chamber (10) was connected with plastic pipes. Finally, the outlet gas was released after passing trough a water system (11) to capture eventual toxic gases.



Figure 3.2: Illustration of the experimental set up of the supercritical fluid system.

 CO₂ pressure cylinder, (2) Syringe pump system, (3) Manual valve, (4)(6)(9) Thermostat, (5) Reactor, (7) Thermocouple, (8) Pressure gauge, (10) Gas collection chamber, (11) Water system

3.2.2 Experimental procedure

A c-Si solar panel sample, as described in section 3.1, was placed inside the reactor. Optional, DMSO (Sigma-Aldrich, 99%) or Ethyl lactate (Sigma-Aldrich, 98%) as a co-solvent (0.5 - 4 ml) was added with a pipette. Before the pressurisation of the reactor (70 - 110 bar), the water pipes connected to the external heater were extensively whirled along the reactor to stabilise temperature inside the reactor to the preset temperature (40 - 85 °C). By opening valve 3a, the reactor was then

pressurised with CO_2 until the experimental pressure was reached. The experiment time (12 - 40 min) started with closing of value 3a. When the experiment time was over, value 3b was opened to evacuate the reactor and regulate the flow-rate. The exhaust gas was collected by a gas chamber for the FTIR analysis. It has been observed that the way of gas collection in terms of flow-rate, time and pressure influences the intensities of the FTIR spectrum. Therefore, the presented spectra in this work were obtained by collecting the gas in the span from the preset pressure down to 40 bar. The flow-rate was tried to be similar throughout the experiments runs and estimated by the bubble creation inside the water. Then the reactor was entirely depressurised, the water pipes removed and opened manually by wrenches. The sample was collected and in case of the existence of a co-solvent, the latter removed and the inside of the reactor and thermoelement cleaned with acetone to remove eventually residues of dissolved organic compounds. Before and after the treatment the samples were weighted by a high precision scale. In addition, SEM (ProX, Phenom Desktop, Thermo Scientific) images in BSE mode of selected samples were obtained to study their surface topography after the $scCO_2$ measurements.

3.3 Incineration process

3.3.1 Experimental set up

The incineration set up consisted of two connected quartz tubes (7) placed inside two different furnaces (denoted as 4a and 4b). Air-flow (1) trough the quartz tubes was controlled by a valve and measured by a flow-meter (2). The outlet of the gas tube was connected with a gas chamber (5) for the exhaust gas collection for FTIR analysis and a water system (6) to hinder the release of risen toxic gases during the burning time. The solar panel sample (3) was placed in the middle of furnace 4a inside the quartz tube as illustrated in figure 3.3.



Figure 3.3: Illustration of the experimental set up of the incineration experiments.

(1) Air-inflow, (2) Flow-meter, (3) Sample, (4a,b) Furnace, (5) Gas collection chamber (6) Water system (7) Quartz-tubes.

3.3.2 Experimental procedure

The temperature of furnace 4a and 4b was heated to $550 \,^{\circ}\text{C}$ and $800 \,^{\circ}\text{C}$, respectively, and the gas flow-rate was set to $1.5 \,\text{L/min}$. Two pieces of the incineration sample (see section 3.1) were placed inside the quartz tubes and the experiment time of 32 minutes started. The exhaust gas was collected during this time by the gas chamber for FTIR analysis in sequences of two minutes covering 1-3 min, 4-6 min, 10-13, 15-17min, 20-22 min, 25-27 min, 30-32 min.

3.4 FTIR analysis

The infrared spectrum of the collected exhaust gas was recorded by a FTIR spectrometer (Spectrum Two, Perkin Elmer) in the range of 4000 cm^{-1} to 900 cm^{-1} and a resolution of 4 cm^{-1} . As a background served the empty gas chamber and was subtracted automatically by the software. Before the next experiment, the gas chamber was entirely cleaned with acetone to remove all eventual residues brought up by the collected gas. Python 3.7.3 was used to visualise and analyse the data.
4

Results

The results of the conducted experiments in the extent of this work are presented in the following. At first, the findings of the experiments in connection with the supercritical fluid technology, including FTIR-spectra and SEM images, are shown. Then, the FTIR results of the incineration process are presented.

4.1 Supercritical fluid technology results

The impact of supercritical carbon dioxide first without and then in combination with a co-solvent on crystalline silicon solar cell samples was analysed with the use of FTIR-spectra of the exhaust gas of the system and SEM images of the sample after the treatment. In order to investigate the optimal system conditions and supportive co-solvent for the dissolution of the organic components, experiment runs of different preset pressures were conducted. During those trials, first pure $scCO_2$ was used. Then, dimethyl sulfoxide (DMSO) or ethyl lactate were added as a co-solvent. The obtained results of the FTIR-spectra and SEM images are presented in the following.

The FTIR-spectra were used to draw conclusions about the impact of the different pressure conditions and co-solvent combinations in the separation of the organic compounds from the solar cell. Therefore, the characteristic peaks of the used solvents and carbon dioxide has to be known.

A typical infrared spectrum of carbon dioxide at experiment conditions in this work is plotted in figure 4.1. It shows peaks at 3728 cm^{-1} , 3704 cm^{-1} , 3624 cm^{-1} and 3599 cm^{-1} , which can be assigned to the combination band of in- phase and out-ofphase CO₂ stretches, as well as the broad characteristic infrared CO₂ peak at around 2349 cm^{-1} [40, 41]. C-O stretching bands of carbon monoxide can be observed at around 2075 cm^{-1} . Furthermore, the spectrum reveals peaks at 3515 cm^{-1} and 1933 cm^{-1} , which could not be classified with absolute security.



Figure 4.1: FTIR-spectrum of pure carbon dioxide at experiment conditions.

The spectrum plotted in figure 4.2 presents the characteristic peaks for the DMSO solution used in the experiments.



Figure 4.2: FTIR-spectrum of the DMSO solution used as a co-solvent in the SCF-experiments.

Another important factor in the analysis of the FTIR-spectra is the direct influence of the exhaust gas collection process on the intensity outcome as discussed further in section 5. The plots in figure 4.3 visualise the differences of the peak intensities of the CO_2 peaks and other peaks, which are in the following assigned as leaving groups of the organic compounds, when the exhaust gas is collected at different pressure ranges within and outside the supercritical region (85-78 bar, 78-65 bar, 65-10 bar). During the gas evacuation from 65 to 10 bar the intensities of the peaks were the strongest. Between 85 to 78 bar, within the supercritical region, a bit weaker. The peaks almost vanished between 78-65 bar , whereas the carbon dioxide peaks were similar in all collection ranges. Based on this, it was decided to collect the exhaust gas sample within the pressure range of set-pressure to 40 bar. However, it has to be mentioned that there were also time differences between the sample collection during which separation could have occurred. 40 bar was chosen to keep the density inside the gas collector high and at the same time the collection time short.



(b)

Figure 4.3: FTIR-spectra cut-outs of the same sample using different collection pressure ranges from 85 to 78 bar, 78 to 65 and 65 to 10 bar, respectively. a) Carbon dioxide peaks. b) Peaks of leaving groups between $1950 \,\mathrm{cm}^{-1}$ and $900 \,\mathrm{cm}^{-1}$.

4.1.1 SCF treatment with pure supercritical carbon dioxide

At first, the effect of $scCO_2$ without the addition of a co-solvent was investigated. For this purpose samples of type 1, see section 3.1, of the EOL solar module were treated for 12 and 20 minutes, respectively, at different pressure and temperature conditions. Swelling of the organic compounds, especially the EVA layer, in the samples could be observed at every set of experiment conditions. Images of the change of the samples provoked by the $scCO_2$ procedure are shown in figure 4.4.



Figure 4.4: Image of sample type 1 a) before and b) after the exposure to supercritical CO_2

In order to clarify whether decomposition occurred during the treatment, FTIR spectra were obtained from the exhaust gas of the system. Table 4.1 displays the temperature, pressure conditions and experiment times selected for the samples.

Table 4.	.1:	Temperature	and pre	ssure co	onditions	and	experime	ental	time	set i	in t	the
	ex	periment sessi	ion with	scCO_2	treatmen	nt for	samples	of ty	vpe 1.			

Sample	T [°C]	P [bar]	t [min]
1	78	70	12
2	82	70	20
3	82	80	20
4	80	74	20

The results of the FTIR analysis are shown in figure 4.5. Absorption peaks linked to the presence of CO₂ and CO are present in the exhaust gas of all samples. Whereas in sample 4 no additional peaks raised, sample 1, 2 and 3 show additionally characteristic peaks at 2970 cm⁻¹ (ν_a CH₃), 1739 cm⁻¹ (ν C=O), 1725 cm⁻¹ (ν C=O), 1375 cm⁻¹(δ CH₃), 1364 cm⁻¹ (CH₃C = O), 1352 cm⁻¹ (δ CH), 1228 cm⁻¹, 1216 cm⁻¹ and 1204 cm⁻¹ (all ν C-O). Besides those, characteristic peaks at 3000 cm⁻¹ (C-H), 2920 cm⁻¹ (ν_a CH₂), 1440 cm⁻¹ (δ CH₃), 1115 cm⁻¹ (δ C-H), 1100 cm⁻¹ (C-F) and 1090 cm⁻¹ (ν C-F) could be observed in the spectrum of sample 2 [40–44]. Here, ν , δ , a and s represent stretching, bending, asymmetric and symmetric defor-

Here, ν , δ , a and s represent stretching, bending, asymmetric and symmetric deformations.



Figure 4.5: FTIR-spectrum of the exhaust gas from the samples at experiment conditions presented in table 4.1 using pure $scCO_2$. The corresponding wavenumbers and assignments of the annotations for the peaks can be found in table 4.2.

Table 4.2: The table presents the wavenumbers and assignments of the annotations for the peaks used in this work [40–44]. ν , δ , a and s represent stretching, bending, asymmetric and symmetric deformations.

Plot annotation	Wavenumber $[cm^{-1}]$	Assignment
a	3000	C-H
b	2970	$\nu_a CH_3$
С	2920	$\nu_a CH_2$
d	1739	C=O
е	1724	C=O
f	1440	$\delta_a CH_3$
g	1372	$\delta_s CH_3$
h	1365	$CH_3C=O$
i	1352	C-H
j	1228	C-O-C
k	1216	C-O
1	1205	C-O
m	1115	δ_s C-H
n	1105	C-F
О	1090	C-F

The peaks observed in the spectrum are a first indicator that a separation process occurred during the experimental time. On the basis of the presence of two carbonyl peaks at 1739 cm^{-1} and 1725 cm^{-1} it can be concluded that under the exposure of CO₂ two types of leaving groups exist from the detachment of the vinyl acetate part of the EVA polymer. In accordance to literature those peaks can be assigned to ethylaldehydes and unsaturated ester, respectively [40, 41]. This assumption can be supported by the presence of the CH₃, CH₃C = O, CH and C-O bands. The bands assigned to CH₃, CH₂ and C-F can be linked to the separation of the fluoropolymer (PVF or PVDF) in the backsheet of the solar module [42]. Although, the C-F bonds in a fluoroplymer are known to be strong and nonreactive, it has been shown in previous studies that CO₂ is able to dissolve fluoropolymers due to its low electro negativity and large quadrupole [45], [46].

However, the present peaks linked to separation are rather weak and the the assignment of absorbance bands has to be taken carefully. As stated above and seen in figure 4.4 swelling of the organic layer occurred in all samples and is to believed the main mechanism under the exposure of CO_2 [47]. Besides by observation, swelling of the sample can be also confirmed by comparing the CO_2 peaks in the spectra presented in figure 4.1 and 4.5 which are plotted in figure 4.6. In there, a clear difference in the intensity of the carbon dioxide peaks of the exhaust gas and the pure CO_2 can be seen.



Figure 4.6: Enlarged part of the spectra presented in figure 4.5 for the comparison of the carbon dioxide peaks between 4000 cm^{-1} and 3400 cm^{-1} .

Separation products might be, however, also trapped in the bubbles or between the layer observed in sample [19]. In order to be able to verify the separation of the organic components during the scCO₂ treatment, the second type of samples with dimensions of $20 \times 5 \text{ mm}$ (see section 3.1) were used in the following. This type of samples enables to study the surface of the inner part of the organic components using SEM images, which give, in addition to the FTIR-spectra, further information of possible degradation and separation processes. Mass-change of the samples after the treatment is another type verification of possible separation of the organic components. It could be ascertained that during the treatment glass fragments of the already broken glass layer detached from the sample. Consequently, the precise determination of the mass-change was not possible with the samples of type 1, which is another advantage of the usage of sample type 2. Hence, the results of the supercritical fluid technology measurements, shown in the following, were obtained by using this type of sample.

The properties of supercritical fluids can be tuned by the change of pressure and temperature [33]. However, in the experiments conducted above, a conclusion about the optimal temperature and pressure conditions were hard to draw because of the arbitrary selection of conditions. Hence, to improve the solubility of $scCO_2$, at first the optimum pressure was investigated. Therefore, different pressure conditions at a constant temperature of 80 °C and experiment time of 20 minutes were tested (see table 4.3). The FTIR-results are plotted in figure 4.7.

Table 4.3: Temperature, pressure conditions and exposure time in the experiment session with pure $scCO_2$ treatment for samples of type 2.

Sample	T [$^{\circ}$ C]	P [bar]	t $[min]$
5	80	82	20
6	80	90	20
7	80	95	20
8	80	100	20
9	80	110	20

In addition to the peaks assigned to the CO_2 , again, as in the spectrum of sample 2, peaks assigned to (C-F) bonds can be observed for all samples, except in the exhaust gas of sample 5, with similar intensities. However, the CH_3 , CH_2 bands for sample 7, 8 and 9 are almost invisible. Only sample 6 shows weak peaks. In addition, once again the characteristic C=O peaks of ethylaldehydes and esters, respectively, can be observed, as assigned above.



Figure 4.7: FTIR-spectrum of the exhaust gas of samples of type 2 at experiment conditions presented in table 4.3 using pure $scCO_2$. The corresponding wavenumbers and assignments of the annotations for the peaks can be found in table 4.2.

4.1.2 DMSO as a co-solvent

Supercritical CO_2 is known to be a nonpolar solvent [33, 45, 47]. Therefore, a complete separation of the whole EVA layer was hardly expected. The solvent properties of $scCO_2$ can be significantly improved by the addition of a co-solvent [37]. DMSO was selected as one of the co-solvent investigated in the framework of this work. First, the effects of the dependence of the amount of DMSO on the removal of the organic layer from the solar cell was studied. Therefore, the pressure and temperature was fixed to 85 bar and 95 bar, respectively, and a constant temperature of 80 °C. Thereby, the volume of DMSO was varied from 1 ml to 3 ml as seen in table 4.4 and 4.5.

Table 4.4: Amount of DMSO and corresponding solvent mass ratio used as a co-solvent in $scCO_2$ treatment at 85 bar, 80 °C and 20 minute exposure time. Additional, the ratio between the mass of the sample after and before is given.

Sample	DMSO [ml]	Solvent/mass $[ml/g]$	mass ratio
10	1	10.82	0.9978
11	1.5	13.04	/
12	2	17.73	1.1338
13	3	40.71	1.0678

Table 4.5: Amount of DMSO and corresponding solvent mass ratio used as a co-solvent in $scCO_2$ treatment at 95 bar, 80 °C and 30 minute exposure time. Additional, the ratio between the mass of the sample after and before is given.

Sample	DMSO [ml]	Solvent/mass $[ml/g]$	mass ratio
14	1	10.69	1.0006
15	1.5	19.81	1.0132
16	2	25.41	0.09746
17	3	28.57	1.0028

The FTIR-spectra belonging to 1.5 ml and 2 ml in figure 4.8a) and b) show peaks of high intensity. The CH₃ (2970 cm⁻¹, 1372 cm⁻¹), C=O (1739 cm⁻¹, 1725 cm⁻¹), CH₃C=O (1365 cm⁻¹), CH (1354 cm⁻¹) and O=C-O-C (1228 cm⁻¹, 1216 cm⁻¹, 1204 cm⁻¹) bands are much more pronounced compared to the recent experiments before. In addition, peaks at 2924 cm⁻¹ (ν_a CH₂), 2852 cm⁻¹ (ν_s CH₂), 1458 cm⁻¹ (δ CH₂), 1372 cm⁻¹ (δ CH₃) and 1420 cm⁻¹ (CH₂) arise, which can be assigned to the ethylene group of the EVA polymer [43, 44]. Those peaks and the appearance of the peaks belonging to the vinyl acetate group (C=O,O=C-O-C) are an indicator for the separation of EVA in the selected experiment conditions. Moreover, the spectra of sample 15 and 16 show peaks at 3072 cm⁻¹, 3025 cm⁻¹, 3016 cm⁻¹, 3000 cm⁻¹, 2946 cm⁻¹ and 1440 cm⁻¹, whose assignments can be found in table 4.6.



(a)



(b)

Figure 4.8: FTIR-spectrum of the exhaust gas in the experiment of $scCO_2$ and DMSO as a co-solvent at 80 °C with a set pressure of a) 85 bar and b) 95 bar, respectively. The corresponding wavenumbers and assignments of the annotations for the peaks can be found in table 4.2 and 4.6.

Table 4.6: The table presents the wavenumbers and assignments of the annotations for the new peaks in addition to table 4.2 used in this work [40–44]. ν , δ , a and s represent stretching, bending, asymmetric and symmetric deformations.

Plot annotation	Wavenumber $[cm^{-1}]$	Assignment
р	3072	$\nu_a = CH_2$
q	3025	$\nu_s = CH_2$
r	3016	νCH
\mathbf{S}	2946	$\nu_a C - H$
u	2852	$\nu_s CH_2$
V	1458	δCH_2
W	1420	δCH_2

Based on the FTIR results and the images of the samples before and after the treatment shown in figure 4.9 it can be concluded that the addition of DMSO as co-solvent enhances the separation of EVA and the backsheet. Furthermore, the results indicate that the co-solvent amount is of importance in the separation process. Considering the peak intensities of the FTIR-spectra, 2 ml seems to deliver the best results. However, it has to be stressed that this is only a qualitative analyses. Especially, the intensities of the carbon hydrogen bonds observed in the spectra are very weak.



Figure 4.9: Image of the sample of type 2 a) before and b) after the exposure to supercritical CO_2 and DMSO as a co-solvent.

Further experiments with 2 ml DMSO as a co-solvent at $80 \degree \text{C}$ with 80, 90, 95 and 105 bar for 30 minutes were conducted (see table 4.7). The FTIR results are presented in figure 4.10.

Table 4.7: Solvent mass ratio for the samples of 2ml DMSO used as a co-solvent of the $scCO_2$ treatment at different pressures at 80 °C and 30 minute exposure time. Additional, the ratio between the mass of the sample after and before is given.

Sample	P [bar]	Solvent/mass [ml/g]	mass ratio
18	80	19.76	1.0148
19	90	21.51	1.0065
20	95	25.41	0.09746
21	105	26.64	1.0028



Figure 4.10: FTIR-spectrum of the exhaust gas of $scCO_2$ and 2ml DMSO as a co-solvent at 80 °C and a exposure time of 20 minutes. The pressure was varied from 80, 90, 95, 105 bar, respectively. The corresponding wavenumbers and assignments of the annotations for the peaks can be found in table 4.2 and 4.6.

The FTIR-spectra confirm the assumption that DMSO as a co-solvent enhances the solvent properties of $scCO_2$ and leads to the partly separation of the organic components from the c-Si module. The spectra corresponding to 105 bar and 95 bar show the same absorbance bands (see table 4.2 and 4.6 for peak annotations), as discussed (for the latter) in the context of figure 4.8. Very weak transmission intensities can be observed for 90 bar (see table 4.2), whereas for 80 bar the peaks vanished. According to this, it can be concluded that a threshold pressure of 90 bar has to be exceeded before the separation process begins. However, this is contrary to the results in figure 4.2a). In this plot peaks of high intensities occurred for 85 bar. Those differences can be explained with the nonidentical exhaust gas collection process throughout the measurement series. A discussion about the exhaust gas collection and optimal experimental system improvements can be found in section 5.

4.1.3 Ethyl lactate as a co-solvent

Ethyl lactate is one of the chemicals classified as a green solvent [31]. In recent studies it has been applied as a co-solvent for extraction processes using $scCO_2$ technology [48, 49]. In this studies ethyl lactate showed a similar or even higher extraction yield as conventional solvents such as toluene, ethanol and DMSO [48, 49]. Therefore, the effect of ethyl lactate as a co-solvent has been investigated in the following. Figure 4.11 shows the FTIR results for samples using 1 ml and 3 ml, respectively. It can be observed that, regardless the amount and the pressure and temperature conditions, the spectrum aligns very well with the literature spectrum for ethyl lactate provided by NIST Chemistry Webbook [50] without any shift or appearance of additional peaks. Hence, dependent on the FTIR-results shown in figure 4.11, it can be assumed that the solubility properties of $scCO_2$ were in that case not enhanced by the addition of high concentration ethyl lactate.



Figure 4.11: FTIR-spectra of the collected exhausted gas using ethyl lactate as a co-solvent for the $scCO_2$ treatment. Additional, the literature spectrum for ethyl lactate provided by NIST Chemistry Webbook [50] is plotted.

4.1.4 SEM results

In order to obtain additional information about the separation of the organic components from the sample of type 2, the topography of the surface of the inner part of the organic layer (see figure 3.1) was characterised by SEM. The surface of selected samples before and after the treatment with pure $scCO_2$ and with the addition of DMSO and ethyl lactate as a co-solvent are presented below.

The topography of the surface on an untreated sample is shown in figure 4.12. Beside small cracks, originated in the during the sample preparation process while the inner part of the organic layer was sample was manually separated from the solar cell, the organic layer is dense.



Figure 4.12: SEM images of the topography of the surface of an untreated sample of type 2. a) 39x magnification using the navigation camera. b) 390x magnification in 15 keV BSE mapping mode.

When exposed to supercritical CO_2 more and wider cracks developed at the surface. Tectonic shifts within the organic layer are noticeable in figure 4.13, while being still attached to the sample. This supports the assumption that swelling is the main process in the organic component when exposed to $scCO_2$ and is also in alignment with the FTIR results analysed above.



Figure 4.13: SEM images of the topography of the surface of sample of type 2 treated in $scCO_2$. a) 39x magnification using the navigation camera. b) 390x magnification in 15 keV BSE mapping mode.



Figure 4.14: SEM images of the topography of the surface of sample of type 2 treated in $scCO_2$ and 2ml DMSO as a co-solvent. a) 39x magnification using the navigation camera. b) 390x magnification in 15 keV BSE mapping mode.

When 2 ml DMSO were added as a co-solvent, it can be seen in figure 4.14 that mainly circular spots appear. There, the upper layer separated from the sample. This observation is in alignment with the FTIR results, where absorption bands linked to EVA, ethylaldehydes, ester and other leaving groups could be observed. Furthermore it affirms the assumption that the addition of DMSO as a co-solvent enhances the separation process of the organic layer.

According to the FTIR results, the addition of 3 ml DMSO did not intensify the solubility of the scCO₂, since no band correlated to possible leaving groups, except C-F, could be observed. However, the SEM results contradict this hypothesis. Indeed, the topography of the surface of the organic layer in figure 4.15 is similar to the one observed in figure 4.14. Based on the SEM image it can be concluded that separation did occur, but the exhaust gas collection was unsuccessful. A discussion about the importance and influencing factor in the gas collection is given in section 5.



Figure 4.15: SEM images of the topography of the surface of sample of type 2 treated in $scCO_2$ and 3ml DMSO as a co-solvent. a) 39x magnification using the navigation camera. b) 430x magnification in 15 keV BSE mapping mode.

In order to verify the importance of the existence of $scCO_2$ in the separation process, a sample of type 2 was drowned into DMSO and was placed in a 80 °C water bath for 30 minutes. The topography of the surface observed in figure 4.16 is similar to the untreated sample.



Figure 4.16: SEM images of the topography of the surface of sample of type 2 drowned into DMSO and was placed in a water bath of 80 °C for 30 minutes. a) 39x magnification using the navigation camera. b) 390x magnification in 15 keV BSE mapping mode.

The SEM images of a sample exposed to $scCO_2$ and ethyl lactate acting as a cosolvent is presented in figure 4.17 below. According to those, the hypothesis drawn based on the FTIR results that ethyl lactate as a co-solvent does not enhance solubility process in the specific experiment conditions could be verified. As well as the untreated sample, the surface topology show only small cracks assigned to the preparation process of the sample.



Figure 4.17: SEM images of the topography of the surface of sample of type 2 treated in $scCO_2$ and ethyl lactate as a co-solvent. a) 39x magnification using the navigation camera. b) 390x magnification in 15 keV BSE mapping mode.

4.2 Incineration results

Recent studies concluded incineration is the most feasible technology for the removal of the organic layer from the solar cell [6]. In addition to the experiment runs based on the supercritical fluid technology, different incineration experiments on two samples with the dimension of 500×20 mm were conducted. Hereby, the effect of the incineration temperature and time was investigated by analysis of the exhaust gas using FTIR.

The first two results presented below came from previous studies conducted in the research group, which have not been analysed, yet. Figure 4.18 shows the temperature dependence of the incineration process. The furnace was heated in this experiment up to 600 °C and the exhaust gas collected, when the furnace reached 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C and 600 °C, respectively.



Figure 4.18: FTIR-spectra of the exhaust gas collected during incineration heating process at different temperatures between 300 °C and 600 °C in steps of 50 °C.

The degradation process of the organic component in the sample begins at 350 °C. Comparing with the gas phase spectrum of acetic acid [51] it can be concluded that acetic acid is the main decomposition product of the sample in the first stage. This is in alignment with previous studies of EVA degradation at high temperatures [19]. It has been found that the EVA polymer degradation process includes two steps. The first step is ester pyrolysis resulting in acetic acid as a leaving group and to a minor amount acetalaldehyde. The second step is the degradation of the remaining polyethylene co-polyacetylene resulting in, inter alia, butene [52]. In addition, acetic acid can degrade further resulting in carbon dioxide, carbon monoxide, ketene and methane [52]. The second step degradation products can be observed in the spectra above 450 °C in the terms of O-H (free alcohol), CO_2 , CO and several carbonyl group absorption bands [40, 41]. At this temperature acetic acid is not present in the exhaust gas anymore. At 450 °C, hydrogen-fluoride (H-F) and C-F peaks appeared in the spectra. Those can be assigned to the degradation of the fluoropolymer present in the backsheet [9, 42, 53, 54]. Fluorocarbons have higher thermal stability than carbon-hydrogen and carbon-carbon bonds due to their stronger bond 490 kJ/mol compared to 420 kJ/mol and 340 kJ/mol, respectively [9]. Hence, the degradation of fluoropolymers requires a higher temperature, which is in alignment with the results obtained. Mainly CO_2 and CO bands are present at 500 °C as well as hydrogen fluoride, carbonyl groups, carbon-fluorine and carbon-hydrogen peaks and their intensities decrease above 500 °C.

It can be concluded that an incineration temperature above 450 °C is required for an entire removal of the organic components from the solar cell. This is in alignment with previous studies on the optimum pyrolysis temperature and time, which are found to be around 500 °C and 30 minutes, respectively [8].

The FTIR-results plotted in the figure 4.19 below map the separation products evolved during time. The exhaust gas was collected for 3 minutes in sequences of 0-3, 4-7, 8-11, 12-15, 17-20, 22-25 and 25-28 minutes, respectively.



(a)



(b)

Figure 4.19: FTIR spectra of the exhaust gas collected during incineration heating process at different time sequences. a) Spectra of the exhaust gas in time sequence of the first 0-3 minutes and the gas spectrum of acetic acid gas provided by NIST chemical webbook [51]. b)The spectra of the exhaust gas collected for 3

minutes in sequences of 4-7, 8-11, 12-15, 17-20, 22-25 and 25-28 minutes,

respectively

The presence of acetic acid absorbance peaks in the spectrum obtained from the exhaust gas during the first 3 minutes reveals once more that ester pyrolysis, as mentioned above, is the first pyrolysis step of the EVA layer. The degradation products of acetic acid in terms of CO_2 , CO, OH and carbonyl groups can be also observed, which is in alignment to the previous results at higher temperatures. Absorbance bands of hydrogen fluoride and carbon-fluorine show that the degradation process of the backsheet also began within the first three minutes, when a certain temperature limit is exceeded. When time passes by the intensities of the H-F and C-F bands increase noticeable as well as the bands assigned to the degradation products of acetic acid as stated above. Acetic acid is not present in the exhaust gas anymore. Furthermore, it can be noticed that hydrogen-carbon (CH2, =CH2, CH3) bands between $3100 \,\mathrm{cm}^{-1}$ and $2700 \,\mathrm{cm}^{-1}$ evolved. This can be linked to the degradation of the polyethylene co-polyacetylene backbone of the EVA polymer. The CO_2 and CO peaks intensities decrease with time and almost vanished after 28 minutes. However, the bands assigned to HF, OH C-F carbonyl group bands are still present in the spectrum. In the analysis, the spectrum related to the measurement at 12-15 minutes had to be ruled out due to a sample gas leak out during the exhaust gas collection.

In the extent of this work, the effect of the composition of the separation products in the exhaust gas has been investigated, when a second furnace with a higher temperature of 800 °C was added to the incineration furnace with a temperature of 550 °C. The motivation behind this experiment was to generate a cleaner exhaust gas under the assumption that the separation products degrade further inside the second furnace.

Figure 4.20 shows the sample after the incineration process. The organic compounds were entirely removed from the module, leaving the glass and broken solar cell as the only residues.



Figure 4.20: Image of the sample after the incineration process.



The resulting FTIR spectrum is plotted in figure 4.21.

Figure 4.21: FTIR spectrum of the collected exhaust gas of an incineration set up consisting of a incineration temperature of 550 °C and second furnace of 800 °C. The reference spectra for ethylene and methane plotted in this figure stem from NIST chemistry webbook [55, 56].

Before the start of the analysis of the data it has to be mentioned that during the first five exhaust gas collection sets (1-3, 4-6, 10-13, 15-17 and 20-22 minutes, respectively) water residues from the cleaning process was present in the gas collector. This gives raise to the noise in the areas between 4000 cm^{-1} to 3600 cm^{-1} , 3200 cm^{-1} to 2800 cm^{-1} and below 1600 cm^{-1} linked to the gas and liquid spectrum of water [57]. However, important conclusions can be drawn from the obtained data. Acetic acid, as being identified as the first pyrolysis step in the degradation of EVA, carbonyl groups as well as H-F are not present in the spectrum. The presence of CO_2 , CO, ethylene and methane suggest that acetic acid and the other pyrolysis products have been entirely degraded inside the second furnace as a result of the high temperature of $800 \,^{\circ}$ C. After four minutes the exhaust consists only of CO_2 , CO residues and weak peak intensities of carbonyl and CH bands can be found.

Based on this data it can be concluded that the connection of a second furnace with a temperature of 800 °C prevents the formation of HF and improves the exhaust gas quality in terms of toxic substances.

Within the first 3 minutes, however, the exhaust gas was entirely black coloured due to a high content of carbon. Figure 4.22 shows the quartz tubes after the incineration process. The parts of the tube, which were not inside the furnace, are covered with carbon residues from the incineration products showing that this process is rather dirty.



(b)

Figure 4.22: Images of the quartz tubes after the incineration experiments. a) Quartz tube placed into furnace 1 at 550 °C in which the sample was placed. b) Quartz tube placed into furnace 2 heated to 800 °C in which the incineration gas leaves the system.

In summary, the incineration experiments show that the separation process of the EVA layer can be divided in two steps. Ester pyrolysis as a first step and the degradation of the remaining polyethylene co-polyacetylene as a second step [19]. Altough the separation of the EVA layer begun at 350 °C, temperatures of 500 °C are required for the removal of the fluoropolymer layer due to its thermally strong fluor-carbon bonds. An incineration time of 30 minutes has been proven to be sufficient. The addition of a second furnace with a temperature of 800 °C improved the quality of the exhaust gas in terms of toxic residues.

Discussion

This study focused only on the qualitative analysis of the separation process of the organic compounds from the c-Si solar cell based on FTIR-spectra obtained from the collected exhaust gas from supercritical fluid technology and incineration experiments. From the obtained data it can be concluded that DMSO as a co-solvent enhances the solubility of $scCO_2$ resulting in a partly separation of the organic layer. Ethyl lactate, however, did not positively intensify the solubility. This assumption was supported by SEM images of the surface topography of the organic layer after the $scCO_2$ treatment. Furthermore, it has been observed that the solubility of pure $scCO_2$ is low and exceeds the solvent/sample mass limit of the experiment setup used in this work. Only ester and ethylaldehydes could be identified as leaving groups of the organic layer. Swelling of the organic polymers was the main mechanism of the treatment in $scCO_2$ as observed in figure 4.4 and concluded from the obtained mass-ratios of the samples after and before the experiment.

Based on the presence of C-F bands in most spectra it can be concluded that the fluoropolymer layer within the backsheet started to separate from the sample. According to previous studies, fluoropolymers indeed can be dissolved in the presence of nonpolar $scCO_2$ due to its low electronegativity and large quadropole [45]. Swelling of EVA, when exposed to $scCO_2$, has been also observed in previous studies and is used in the polymer synthesis [58, 59]. The most common degradation process of EVA, however, results in the production of acetic acid [19, 60], which could be observed in the incineration results and identified as the first incineration step. However, based on the missing OH bands in the FTIR spectra it can be concluded that acetic acid was not produced in the $scCO_2$ process. The absorption bands in the spectrum were mainly assigned to ester and ethylaldehydes, which, were beside the separation products of the fluoropolymer, the only leaving groups of the EVA polymer.

The existing data, however, is not sufficient to make assumptions about eventual reaction processes in the SCF technology experiments. An upgrade of the system including an in situ FTIR spectrometer and a gas chromatograph would allow to measure the exhaust gas content in real time. This gives valuable information about the reaction inside the reactor. As a positive side effect it also helps to determine the optimum exposure time, pressure and temperature.

The aim of this study was to find a more sustainable alternative to incineration for the removal of the organic compounds in the solar module. In this state of research, as stated above, only partly removal of the EVA compounds and fluoropolymer could be observed. Whereas, in the incineration process the organic compounds were entirely removed, leaving glass and solar cells for further recycling steps. Therefore, more research has to be carried out to intensify the separation. However, a comparison of the exhaust gas of each process type can be made based on the obtained FTIR spectra. The incineration gas contains hydrogen fluoride, nitrogen oxide and dioxide toxic pollutant substances harmful not only for the health but also for the environment. Furthermore, the process is dirty and produces dust, black smoke and carbon residues within the system. However, it could be concluded that the installation of a second furnace of higher temperature prevents the emission of hydrogen fluoride during the process. In general and especially with the proposed upgrade, the energy demand of the incineration process is high, which makes the technology unsustainable. Furthermore, it produces also greenhouse gases such as CO_2 , CO and methane, which pollutes the environment and increases drastically the greenhouse balance of non-polluting solar modules during their life time. The advantage of supercritical fluid technologies are their small process scale and portability, which, in turn, is not possible with incineration systems. Moreover, CO_2 and CO do not add up to the greenhouse emissions, since they can be easily recycled and reused in the system. Additionally, it could be observed that whether hydrogen fluoride nor nitrogen oxide and dioxide were produced during the process. This underlines that the proposed alternative is, in general, a cleaner process and more sustainable in terms of pollution than incineration. Additional, absorbance bands assigned EVA suggest that parts of the polymer did not degrade entirely, which opens the possibility of reprocessing and reusing within the solar panel market. Whereas during the incineration process, the EVA polymer was entirely degraded into acetic acid and other leaving groups as observed din the FTIR-spectra.

However, it has to be stressed out that this study is the first attempt to investigate the possibilities of supercritical carbon dioxide as an alternative method for the removal of the organic compounds from the solar solar cell for further processing. Many uncertainties within the experimental procedure and set up arise during the experiments in this work and raised further research question.

As stated in section 4, the FTIR spectrum obtained for 3 ml DMSO did not show any absorbance bands assigned to leaving groups of the EVA layer. However, SEM images proved that partly separation indeed occurred. This shows that the FTIR results obtained in this work have to be handled with care and are effected by the gas collection procedure. As seen as in figure 4.3, different pressure ranges result in different peak intensities. Although the exhaust gas was taken as soon as the pressure in the reactor reached the same pressures, further research has to be done to ascertain the optimum gas collection process for optimal FTIR results. The integration of a flow-meter connected to valve 3b into the system would allow to control the gas evacuation. By taking account of the evacuation time, same collection conditions can be ensured for all measurements. However, the optimum collection time, temperature and pressure must be also investigated. So far it could be only observed, that when the gas is collected in supercritical condition, the intensities of the bands assigned to the leaving groups are weak. This is either because the collection time was not long enough for the leaving groups to reach the collector in time before the valve was closed or most of the separation products result when the scCO₂ evaporates from the system as soon as it leaves the supercritical region when the pressure is decreased and is therefore not measured. Once more it should be stressed that the intensities, especially of the carbon hydrogen bonds, were to weak for a precise assignment and therefore the assignments made in this work should be taken with care.

Another aspect is the optimum placement of the sample inside the system. When the sample is covered by DMSO, the separation products might be trapped in the solution and will therefore not be collected in the exhaust gas. Hence, in future after the experiments the solution has to also be analysed.

DMSO has been proven to improve the solubility parameter of $scCO_2$ in this work which is consistent with the literature [38, 45]. In order to investigate whether the DMSO/sample mass ratio, DMSO/scCO₂ ratio, pressure or temperature is the key factor for the enhancement of the solubility more experiments (including triplicates) with an optimised system and gas collection process has to be carried out. This is proposed to be the next research step. Alternative and in addition to this research the effect of other co-solvents has to be investigated. It has been suggested in previous studies that acetic acid as a degradation product has a catalytic effect for the degradation of EVA. Therefore, acetic acid could be an excellent choice as a co-solvent to enhance the solubility of $scCO_2$.

5. Discussion

Conclusion

In the world's transition towards a renewable based energy future efficient sustainable and feasible treatment of spent solar panels will be, , both in economical and environmental point of view, undoubtedly necessary. By 2050, 60-78 million tonnes of PV panel waste, worth over US-\$15B, are going to be produced. The waste has to be handled with care since parts of its content is classified as hazardous waste. Untreated disposal enhances leaching of those constituents leading to enormous pollution of the environment. The critical step in the recycling process is the separation or removal of the organic components from the solar cell. So far, high temperature incineration at roughly 500 °C and chemical treatment using organic solvents are the state-of-art recycling methods for the latter. In order to find a more sustainable method for the the separation of the organic components from the solar cell, the effects of scCO₂ without and in combination with co-solvents on commercial c-Si solar panel samples were investigated.

The results of the FTIR analysis and the obtained SEM images are evidence for a partly separation of the organic components of the solar module samples. Ethylaldehyde and unsaturated ester was determined as a leaving group during the process. Bands assigned to carbon-fluorine and hydrogen-carbon bonds were also present in the infrared spectra. This is an evidence for a successful (partly) separation of the fluoropolymer within the backsheet of the solar panel sample. The solubility of $scCO_2$ could be improved with DMSO acting as a co-solvent. This resulted in an enhanced separation of the organic components. When DMSO was added into the system, vibrational modes assigned to the EVA polymer were present in the spectrum. Consequential is can be concluded that the examined recycling process has potential to be a portable, sustainable alternative to state-of art recycling methods for the removal of the organic components from the solar cell. However, this study is the first attempt to separate the organic components from solar cells by $scCO_2$ and further research has to be conducted to find optimum temperature, pressure conditions and co-solvent.

The results of incineration experiments, analysed in the extent of this work, show that the separation process of the EVA layer can be divided in to ester pyrolysis as a first and the degradation of the remaining polyethylene co-polyacetylene as a second step. Furthermore, it can be concluded that temperatures of at least 500 °C are required for an entire removal of the organic components from the solar cell. An incineration time of 30 minutes has been proven to be sufficient. Incineration is a dirty and energy demanding process and produces exhaust gases containing hydrogen fluoride, CO_2 and CO. However, the addition of a second furnace with a temperature of 800 °C improved the quality of the exhaust gas in terms of toxic residues.

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