Chemical delamination of ethylene vinyl acetate for solar module material and cell recovery

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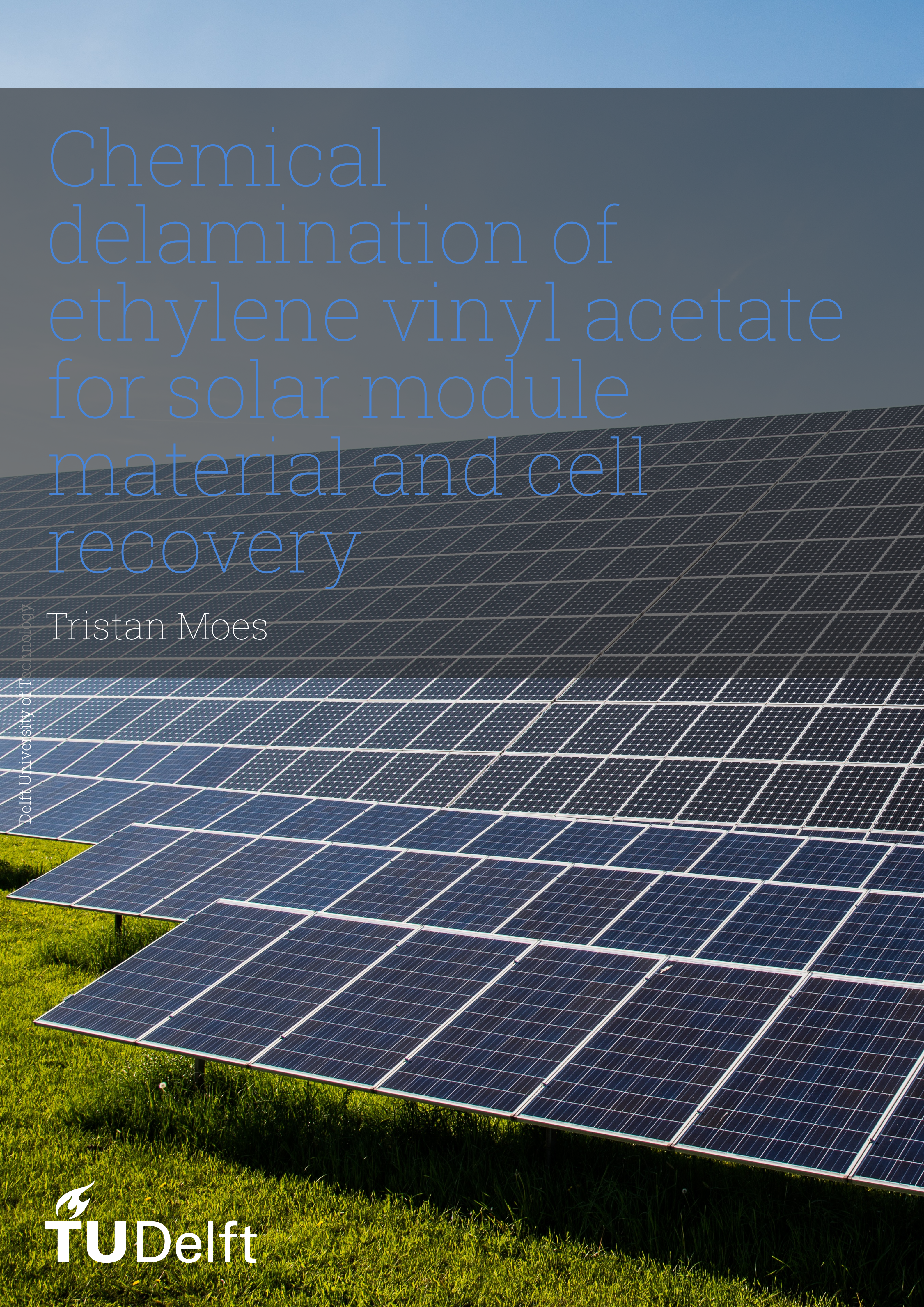

TU Delft

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by

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Preface

This thesis was conducted for the completion of a M.Sc. in Sustainable Energy Technology at TU Delft. This project was a collaboration between the Photovoltaic Materials and Devices and Process and Energy research groups. This thesis investigates the possibility of chemical delamination as a solution to the challenges of photovoltaic recycling.

The energy transition has been the key point of discussion throughout my masters program. Although a large portion of this discussion focused on the need for rapid growth of renewables, included in the discussion was also the need to change how the externalities of technologies are viewed. A circular economy where materials at the end-of-life of a technology are recycled and reused was a particular interest of mine. This thesis topic allowed me to explore one pathway that could lead to a sustainable future. The research I have completed for this thesis has included a review of the existing literature, a screening of potential solvents for chemical delamination and an in depth analysis on the most promising solvent. I hope that this project will contribute to the discussion about solar circularity and motivate others to advance this important topic.

I would like to thank my supervisors Malte Vogt and Luis Cutz for their guidance, support, and feedback throughout my thesis project. Additionally, I would like to thank the lab technicians of both the PVMD and Process and Energy groups for their assistance in both procuring materials and equipment training without which my thesis would not have been possible.

Tristan Moes
Delft, July 2024

Summary

Photovoltaic energy has become a key technology in the energy transition and has achieved a cumulative installed capacity of 1.6 TW by 2023. As policies and technological advancements accelerate the energy transition, more resources are required to develop sustainable pathways for end-of-life solar modules. Developing a process for solar recycling improves the environment, conserves resources and reduces the energy payback period of solar modules but recycling processes face challenges in economic and technological feasibility. The most challenging aspect of solar recycling is separating the different layers and extracting the different components in it. Chemical delamination is an attractive option for solar recycling as it has the potential to separate the layers of a module and recover the cell intact.

A growing number of studies into chemical delamination of solar modules have been conducted, however it remains a highly specialized subject. Chemical delamination remains in lab scale feasibility studies and typically use petrochemical based solvents. Alternatives to petrochemical-based solvents have begun to be investigated because of their sustainability. Solvents with low cost, high boiling points, and low health and environmental hazards are beneficial for the process. In this work, four primary testing factors were considered to optimize the process: solvent, temperature, residence time and ultrasonic irradiance. The primary goal of the optimization was to reduce the reliance on fossil based solvents, improve the reliability of cell material recovery and to attempt to recover cell materials intact.

Preliminary testing was conducted on eleven solvents based on previous knowledge and or their green solvent characteristics; three of the solvents benzaldehyde, toluene and xylene have previously been tested as solvents for chemical delamination. The remaining eight solvents, benzyl alcohol, castor oil, cyrene, γ-valerolactone (GVL), guaiacol, oleic acid, 2-methyltetrahydrofuran (2-MeTHF) and pinacolone, had not been tested previously. Four of the solvents had little to no effect on the encapsulating ethylene vinyl acetate (EVA) and should not be considered as possible solvents for this process. Toluene and benzaldehyde were the best fossil fuel based solvents tested. Three potential green solvents were found to be suitable for chemical delamination each with different strengths and weaknesses.

An optimization was conducted using a simple testing setup with a green solvent. The success of a test run was primarily evaluated by isolating the weight of EVA removed during the test. The result of the optimization found that the predicted optimum test conditions were at the near boundary conditions of the test at high temperatures and long residence times. The result of the optimization found that the predicted optimum test condition were at the boundary conditions of the test at 160◦C for 3 hours. The highest amount of EVA removed during the testing was 60% of the EVA removed in 3 hours, though this result was not reliably achieved. Additionally, no silicon leeching by the solvent was detected and purposefully dissolving the backsheet significantly sped the delamination and provides the possibility of scaling. Further research into green solvents for chemical delamination would require a pressurized environment with a non reactive gas to avoid oxidation of the solvent and allow for higher temperatures and longer residence times.

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1 Introduction

Photovoltaic (PV) energy has become the leading source of renewable energy growth making it a key technology in the energy transition. PV technologies generate renewable clean power in a safe and reliable method. Manufacturing optimization and the effects of economies of scale have enabled PV to become one of the cheapest energy sources in the world and the fastest growing technology by installed capacity at 407-446 GW in 2023 [1]. PV growth is expected to continue as favourable renewable energy policies and reduced costs drive the energy transition. As PV deployments grow so do the associated waste in the form of decommissioned panels. With a typical operational lifetime of 25-30 years early solar installations are beginning to be decommissioned. Global PV waste is expected to rise rapidly in the coming decades, reaching 5.5-6 million tons annually or 10% of all global electronic waste in 2050 [2]. While PV waste has the potential to develop into an environmental hazard it also provides opportunities for a robust photovoltaic circular economy.

Developing an end-of-life (EOL) process for solar technologies benefits the environment, conserves resources and reduces the energy payback period of PV modules. Thin-film cadmium-telluride (CdTe) modules have successfully developed and benefited from an EOL process due to the high value and toxic materials that create economic incentives for recycling [3, 4]. Crystalline silicon (c-Si) PV technologies, which represented over 95% of manufacturing capacity in 2021 [5, 4], do not have a dedicated recycling industry. Unlike CdTe modules, c-Si modules are primarily made from abundant materials and the low costs associated with manufacturing these modules does not incentivize recycling or reusing materials. The composition of c-Si modules by weight is approximately 70% glass, 18% aluminum, 8% plastics, 4% silicon and less then 1% of copper and silver [6]. Despite being only a small fraction of the weight of a module the silicon solar cells represent approximately half the cost, half of the climate change footprint and 60% of the manufacturing energy [6, 4]. The implementation of a recycling method which recovers intact solar cells has the potential to reduce the manufacturing costs of c-Si PV modules 20% [6], improve the environmental impact of PV technologies and avoid hazardous electronic waste.

The challenge of c-Si PV recycling is separating the solar cells from the other layers of module. To protect the solar cells from the environment and achieve the typical 25-30 years lifetime, solar cells are encapsulated in a polymer, figure 1.1 shows a typical c-Si PV module. The encapsulated solar cells are further bonded to a glass front sheet and a plastic or glass backsheet. The standard polymer adhesive used in c-Si manufacturing is ethylene-vinyl acetate (EVA) [7]. EVA has good optical properties, low costs and enables solar panels to reach or often exceed their expected lifetimes. Solar cell thicknesses have historically ranged from 80 to 500 µm [7] while current manufacturing practices typically produce a cell 130 to 160 µm and are susceptible to breaking. Using current methods delaminating the cells from an EVA are uneconomical, time and energy intensive and often damage the cells in order to recover more abundant materials.

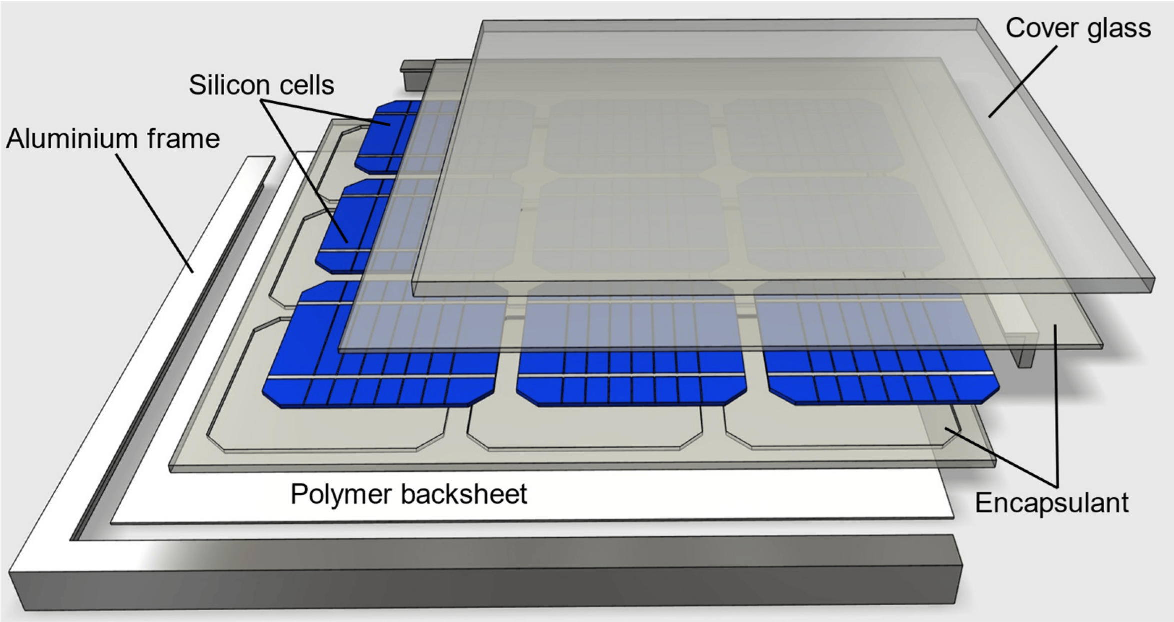


Figure 1.1: Exploded view of a standard crystalline silicon solar module.[8]

1.1. Types of Photovoltaic Recycling

Most decommissioned PV modules have been disposed of in landfills [3]. Policies such as the European Unions addition to its Waste Electrical and Electronic Equipment (WEEE) regulation have created an incentive to develop and optimize PV recycling. The WEEE regulation on PV modules require a 80% weight that needs to be recycled. In c-Si PV modules a 80% weight requirement can easily be achieved with the aluminum frame and glass. As a consequence of this policy, the majority of PV recycling is downcycling of bulky materials. The energy intensive and high value refined materials are often discarded in the recycling process. Studies have shown that recovery of solar cells or the high value materials in the module can be economically viable [3, 4, 9] but require an efficient process to enable upcycling of high value materials in the panels. The types of PV recycling are split into categories based on their delamination method: mechanical, thermal or chemical. In all these processes the junction box, copper cabling and aluminum frame are removed and the remaining module is further processed. After delamination the cells, if intact, can be recovered or materials can be sent for leaching processes to isolate materials for reuse.

1.1.1. Mechanical Delamination

Using mechanical means to break up the PV module is the most mature and widely used PV recycling process. One mechanical method is to shred the module, then sort the fragments to find glass without contamination. Multiple shredding operations can reduce the glass particles and increase the recovered uncontaminated glass [10]. The amount of glass recovered can vary from 80-91% depending on the process used [3]. The remaining shredded PV module can either be disposed of in a landfill or sent on for further treatment and extracted as raw materials. A second method developed in the Full Recovery End of Life Photovoltaic (FRELP) project is called hot knife cutting. Hot knife cutting uses a heated high frequency blade to remove the glass from the module in one piece [3]. While cutting excels at recovering glass, the solar cells remain encased in EVA and would require further processing to recover. Mechanical methods benefit from having low energy requirements and high throughput [3]. Mechanical delamination focuses on weight recycling primarily through the recovery of glass. Solar cells are either destroyed or require another delamination process to recover the cell or its material.

1.1.2. Thermal Delamination

Thermal delamination is the process of burning the off the encapsulant from the module, this process is know as pyrolysis. Pyrolysis of PV modules can occur either in a chamber with inert gases to thermally decompose the EVA or the EVA can be burned off in an oxygen environment [9]. If the c-Si module has a flourine based backsheet specialized scrubbers are needed to extract flourine from the air. Alternatively, a method for removing the backsheet after softening the EVA at 200°C has been proposed [9]. Cells have been successfully extracted intact using pyrolysis at 450 to 500°C [9]. The intact cells were not tested for unwanted contamination during the process. Cracking of solar cells has been seen during thermal delamination, caused by gas build up behind the glass and thermal deformation of the EVA. Compared to mechanical delamination, thermal delamination requires more energy, produces unwanted gases and has a significantly lower throughput [3]. However, this process benefits from being able to separate the high value cell material in the recycling process.

1.1.3. Chemical Delamination

Chemical delamination for PV recycling has been proven with inorganic and organic solvents [3]. The development of this process has focused on finding an organic solvent and conditions which are able to quickly delaminate the module. Solar cells were first successfully recovered in organic solvents in 2001 [11]. However, the process required 2 days to recover a 12.5x12.5cm^2 cell. Chemical delamination was expanded upon by exploring the effect of ultrasonic irradiance on the delamination process [12]. Chemical delamination provides a reliable method for recovery of cell material and the opportunity to recover cells intact. Research in chemical delamination has focused on decreasing the time required for delamination by testing different solvents and optimizing the process. Chemical delamination suffers from lower throughput then both mechanical and thermal methods. Despite several successful test studies, further research is required to make this method viable for industrial use.

Principles of Chemical Delamination

Laminating the layers of a PV module using an encapsulate creates multiple different interfaces: the glass-encapsulant, encapsulant-cell and the encapsulant-backsheet interfaces. EVA is the most commonly used encapsulant and has approximately a 80 % market share [13]. Prior to lamination, the layer interfaces will be doped with a coupling agent that enables bonding between organic (encapsulant) and inorganic (glass and cell) materials. Silanes are the most common coupling agent used to create a bonding layer [13]. Figure 1.2-A explains the chemical bonding process of silanes with glass. In the figure the -X group in the silane is responsible for bonding with the organic (EVA) layer while the -OR group bonds with the inorganic (Glass, Cell) layer. The resulting EVA-glass chemical bond is detailed in figure 1.2-B. Close to the EVA-glass bonded interface formation of cross-linked EVA will occur (white circles in figure 1.2), resulting in an increase in bond strength. The amount of cross-linked EVA gradually decreases moving away from the interface into the bulk of the EVA. The interface detailed in figure 1.2 can be generalized to approximate all three interfaces in the PV module. For chemical delamination to be effective a solvent must disrupt these interfaces. Two possible methods of delamination are available, the first disruption of the interface bonds and second removal of the bulk EVA by dissolution.

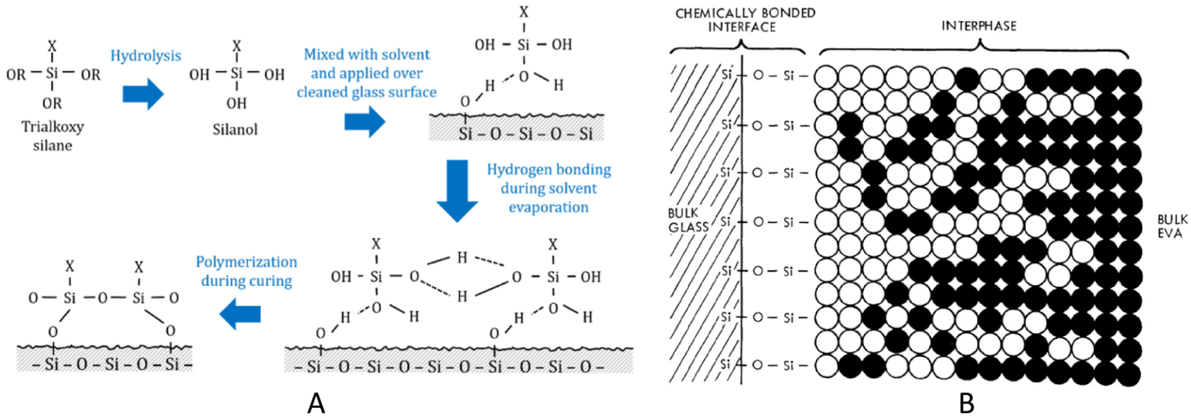


Figure 1.2: Process of adhesion bond formation at various interfaces of PV module (A). Schematic of interfacial bonding at glass-EVA interface involving silane-based adhesive, white and black circles indicate cross-linked and uncross-linked EVA respectfully (B). [8]

Disruption of the interface bonds involves targeting the bonds created by the coupling agent or the cross-linked EVA and separating the organic and inorganic materials. Under normal operating conditions the presence of moisture and high temperature, can affect the chemical, mechanical, structural, and thermal attributes of the encapsulant material [13]. In PV recycling a solvent is used to reproduce this effect in a faster and controlled manner. The solvent could provide thermal and mechanical stresses or electrochemical mechanisms to break the interfaces.

Dissolution of the encapsulant occurs when the encapsulant molecules interact with the solvent and begin to separate from the surrounding material. A general rule for dissolution is like dissolves like, specifically molecules of similar polarity form solutions. Polarity describes the distribution of elections or electronegativity in a molecule, while the terms are binary the polarity of a molecule exists on a spectrum. Polar molecules are molecules that have an uneven distribution of electrons causing a dipole moment, water is an example of a polar molecule. Non-polar molecules are molecules that share electrons evenly, hydrogen molecules are an example of a polar molecule. EVA is composed of both of non-polar and polar elements with majority of the material being non-polar. For dissolution of EVA to be effective it is likely that a non-polar solvent would be required to dissolve the bulk EVA.

1.2. Research Objective

There exists a great opportunity to develop a complementary c-Si PV recycling process for both economic and sustainability reasons. The largest challenge facing PV recycling is separating and extracting the different layers of materials. Chemical delamination of PV modules is an attractive option for PV recycling due to its ability to fully separate the module layers in a single step. Additionally, recovered materials can be recovered intact and the process does not release unwanted gases. The objective of this report is to address knowledge gaps in the chemical dissolution process and recommend possible changes in the process to make chemical delamination a viable solution to industrial photovoltaic recycling. This objective can be split into two sub-objectives:

First, to investigate alternative green solvents as a replacement for petroleum produced chemicals. Green solvent is a broad term which typically refers to a liquid with low toxicity with minimal risks to the environment and to human health [14]. Providing a green solvent alternative for chemical delamination would bring the process in line with sustainable chemistry recommendations.

Second, to optimize the process to maximize cell recovery and speed of delamination. The experimental factors, temperature, residence time, pressure and ultrasonic irradiance will be considered as options to test for an optimal delamination process. By speeding up the reaction, chemical delamination becomes more viable as an alternative to mechanical delamination.

1.3. Document Structure

This report details the steps taken to achieve the research objective and is divided into several chapters to easily navigate. The report has the following structure:

Chapter 1: Introduction

This chapter provides the research objective of the report as well as the context surrounding the topic. An overview of photovoltaic recycling and the challenge of delaminating the PV module is provided. The different types of delamination are expanded upon, including benefits and drawbacks.

Chapter 2: Literature Review

Previous studies of chemical dissolution are analyzed and discussed. Key recommendations and observations from the studies are noted. Using the information from the literature review notable test factors and results are determined.

Chapter 3: Methodology

The experiment setup and testing procedure for both preliminary, extreme conditions, and optimization testing are recorded. Information on the testing equipment, solvents used and test samples are also provided.

Chapter 4: Results and Analysis

In this chapter, results from preliminary tests are provided. An analysis of the results of the preliminary tests is conducted to choose the ideal solvent to proceed with in-depth tests. The results of a subsequent extreme condition study of selected solvents are recorded and analyzed. Finally, the results of an optimization of a chosen solvent are recorded and an analysis of the results carried out.

Chapter 5: Conclusion and Recommendations

This section provides a summary of the ideal chemical recycling process for PV modules and recommendations for further research in this field.

2
Literature Review

The purpose of this literature review is to investigate the existing research on chemical dissolution of EVA using organic solvents. Section 2.1 details the solvents recommended for chemical dissolution and the ideal properties to look for when selecting new solvents. Additionally, this section reviews the different test factors of each study and the findings of the various test conducted. Section 2.2 provides a summary of the research findings relevant for this report.

2.1. Previous Chemical Dissolution of EVA Research

A search of academic papers for chemical dissolution of ethylene vinyl acetate for the purposes of PV recycling resulted a wide variety of research papers found. These studies focus on organic solvents as a solution for dissolution of the EVA; older studies have been written on using inorganic solvents but have not been reviewed for this thesis. The research of chemical dissolution of EVA for PV recycling is a highly specialized topic, and as such, they build off of and replicate earlier studies. However, the focus of these studies can vary widely in the desired material recovered and the status of recovered material. The review of these research papers will focus on the conclusions relevant to cell recovery in PV recycling.

2.1.1. Recommended Solvents

An important recommendation from the research papers is the selection of a solvent for the process. In studies on this topic, it is common to conduct a solvent comparison test either as the sole objective of the report or as a preliminary test prior to conducting experiments [11, 15, 16, 17, 18, 19, 20, 21]. Alternatively, studies have used the type of solvent as a factor in optimization [12, 22] or conducting a case study on a solvent [23]. In total, 30 unique solvents have been tested in the 11 research papers reviewed. Only five of these solvents have been recommended for use in this process, table 2.1 provides the recommended solvents and the associated research paper. The table clearly shows that toluene is the heavily favored solvent for this process. Toluene is generally favored due to its favorable reaction to EVA, a relatively high boiling point of 110°C, low health and environmental hazards [24] and low price when compared to other traditional solvents. Despite toluene's relatively low toxicity it has recently been restricted by REACH (Registration, Authorisation of Chemicals, EC Regulation) in Europe. Additionally, the primary method for manufacturing toluene is through the use of petrochemicals. Green solvent alternatives have been proposed as replacements for solvents like toluene because of their biodegradability and synthesis through renewable sources.

From historical solvent testing various ideal solvent parameters can be discovered. The temperature that dissolution is carried out at greatly effects the speed of delamination [11]. Higher temperatures provide more energy into the system and allow for EVA to be dissolved quickly. A high boiling point is beneficial for a solvent in order to allow higher temperatures to be reached in the process before pyrolysis of the solvent begins to slow the reaction [12]. EVA is considered to have weak polarity [23] but has both polar (10-50%) and non-polar (50-90%) elements. Non-polar solvents are considered

Table 2.1: Summary of recommended solvents from research papers.

Solvent	Reference
Trichloroethylene	[11, 17]
O-dichlorobenzene	[12]
Butanone	[22]
Toluene	[15, 16, 18, 19, 20, 21]
D-Limonene	[23]

more preferable for this process as all of the recommended solvent in table 2.1 are non-polar apart from butanone which is a polar aprotic solvent. Additionally, a layer in the backsheet is soluble in polar solvents over 100 °C, using a non-polar solvent reduces the chance of unwanted use of a solvent. High concentrations of solvent have been found to have a positive impact on the speed of delamination [12]. Therefore, a low cost and readily available solvent is a benefit to this process. Chemical delamination, if adopted on the industrial scale, it would require millions of tons of solvent in order to process projected PV waste. Finally, it is important to to consider the hazards to the environment and humans, as well as the sustainability of the chemicals production when selecting a solvent. A solvent that can be sustainably sourced is critical for this process to be considered. In addition, a solvent with minimal hazards would would provide a safer conditions for both workers and the environment.

2.1.2. Process Optimizations

An important goal for chemical delamination research is to determine the fastest possible dissolution of EVA. A fast dissolution would make chemical delamination more viable for industrial adoption. Various testing factors have been proposed and experimented on to determine the optimal delamination conditions. Table 2.2 details a selection of recommended processes from the reviewed papers. The selected processes were chosen due to their unique factors and parameters; studies that recreated or had only a tangential focus on cell recovery are omitted from Table 2.2 for clarity. Although each research paper uses similar methods, differences in testing conditions make comparisons difficult. Each test factor will be discussed individually to evaluate their effect on the chemical delamination process. The challenges in the evaluating the results of the chemical delamination process and the different approaches are discussed in section 2.2.

Table 2.2: Summary of selected chemical delamination processes after optimization. If factor is missing from a test the factor was not used in the test (Temp = Temperature, Ultr = Ultrasound, Mech = Mechanical Pressure, Samp = Sample Conditions, Pret = Preteatment, Solv = Solvent to Module Ratio). Sample conditions are abbreviated as (m) for unbroken module, (s) for cut strips of module.

Factor	Value	Material Recovered	Time	Ref
Temp Samp Mech	80 °C 2.5x12.5cm^2-(m) Yes	Cell - Intact Glass - Intact Backsheet - Intact	10 days	[11]
Temp Samp Ultr	70 °C 5.5x2.5cm^2-(m) 900W	Cell - Intact Glass - Intact Backsheet - Intact	30 min	[12]
Temp Samp Ultr Pret	60 °C 7.0x1.7cm^2-(s) 200W None	Cell - Fragments Glass - Fragments Backsheet - Intact	60 min	[25]
Temp Samp Solv	70 °C 30g-(s) 1:7.44	Cell - Fragments Glass - Fragments Backsheet - Intact	8 hours	[17]
Temp Samp Ultr Pret	60 °C 5.0x3.0cm^2-(s) 450W None	Cell - Fragments Glass - Fragments Backsheet - Intact	120 min	[23]
Temp Samp Ultr Pret	35 °C 5.0x5.0cm^2-(s) 450W Removed Glass	Cell - Fragments Backsheet - Intact	35 min	[21]

Sample Conditions

The condition of PV samples prior to conduction chemical delamination is an important test factor that influences the results. A review of the research papers on this topic shows that sample conditions vary significantly between papers, from purpose built modules [11, 12, 22, 16], strips of hand cut EOL modules [25, 17, 23, 19, 21] and crushed or shredded PV material [15, 18]. The choice of sample condition often depends on the desired outcome of the chemical delamination process or the available materials. From the table 2.2 the differences in sample size varies from 12.5x12.5cm^2 modules [11] to 5.0x3.0cm^2 strips.

A fractured PV sample will expose more EVA to the solvent increasing the speed of EVA dissolution at the cost of recovered material being broken. In an extreme case, Królikowski et al. [21] demonstrated that fully removing the glass allows EVA to dissolve in toluene in 35 minutes at 35°C. This is much faster then other processes using toluene and requires less energy if the energy required for the removal of glass is not considered. Alternatively, the sample could be crushed in order to increase the surface area [15]. While both of these modifications to the sample decrease the time needed for EVA delamination they would require mechanical recycling equipment adding additional costs to the system. In the case of crushing the PV module a large portion of the potential value would be lost due to damaging the cell. The ultimate goal of the chemical delamination process is to provide a single step delamination process that can recover the cell material intact and compete with mechanical recycling.

In many experiments, the PV sample is created by cutting down a EOL solar module [25, 17, 23, 19, 21]. The EOL solar modules are cut using common tools and cause the glass layer to shatter. A shattered glass layer could allow for a greater amount of EVA exposed to the solvent. By shattering the glass the swelling characteristics will also change and consequently the forces applied to the cell layer will differ from a unmodified sample. No direct comparison of the different sample conditions has been made.

Temperature

Temperature is the most common factor used to speed delamination in the chemical process. Doi et al. [11] observed the effects of temperature on a variety of solvents. At room temperature only three of the 12 solvents tested had a noticeable effect on the EVA. However, when the temperature was increased to 80°C, 10 of 12 solvents affected the EVA. Doi et al. [11] research also found that the temperature effect was muted in EVA which has been cross-linked, which occurs in the lamination process.

Kim and Lee [12] conducted experiments which observed the effect temperature had on the speed of dissolution. They showed that increasing temperatures can drastically increase the dissolution speed of a solvent. The relation between dissolution rate and temperature was observed to vary depending on the solvent. In some cases the relation was observed to be approximately linear in the temperature range observed (25-70°C). However, some non-linear behavior was shown, O-dichlorobenzene showed a dramatic increase in EVA dissolution at 70°C after relatively poor dissolution ratios at lower temperatures. Kim and Lee [12] observed that when using trichloroethylene the ratio of dissolution at the higher temperatures began to decrease. Kim posited that ”solvents with lower boiling points may undergo decomposition due to the occurrence of pyrolytic reactions” [12].

Xu et al. [22] also investigated the effect of temperature on the chemical delamination process, comparing backsheet removal at 50 and 70°C. All four solvents tested showed an increase in backsheet removal when temperature was raised. Azeumo et al. [25] findings found that temperature had a positive effect on the dissolution rate of EVA using toluene. Azeumo conducted their experiment at the boiling point of toluene and observed this condition to have the fastest dissolution rate. However, this process required capture and reintroduction of evaporated toluene. Prasad et al. [17] conducted a temperature study of trichloroethylene in the range of 25-70°C and found an approximate linear relationship of increasing EVA dissolution. Notably, Prasad did not observe the same negative effects as Kim and Lee [12] due to no ultrasonic irradiation being present. Brenes et al. [18] compared the effect of three different solvents at varying temperatures and observed faster and stronger reactions at elevated temperatures. Additionally, they observed that EVA will separate from toluene when cooled. Królikowski et al. [21], temperature study was performed at relatively lower temperatures (25, 35, 45°C) with the glass removed from the PV sample beforehand. Królikowski noted that temperature had a significant effect on delamination time, by removing the glass prior to delamination the experiment also required significantly less energy to delaminate the sample.

Kang et al. [15], Chitra et al. [16], Vaněk et al. [19], and Trivedi, Meshram, and Gupta [20] did not conduct temperature studies but did use elevated temperatures during their chemical delamination studies.

Ultrasonic Irradiation

Ultrasonic irradiation was first proposed as an addition to the chemical delamination process by Kim and Lee [12]. Kim chose ultrasound due to its use in a ”variety of processes such as cleaning, sterilization, plastic welding, dissolution, biological cell disruption, and extraction” [12]. In chemical reactions ultrasound induces cavitation which cause the formation and collapse of microbubbles [12]. Near the microbubbles local environments can reach both temperature and pressure extremes. Figure 2.1 illustrates the cavitation phenomenon, temperatures in the cavitation can reach approximately 5000 kelvin and 500 atmospheres of pressure while at the interface of the cavitation temperatures of approximately 2000 kelvin are seen. The induced local environment caused by ultrasonic irradiation is attractive for speed the delamination process. Some detriments to using ultrasound is an increase in temperature in the experiment and possible degradation of the solvent caused by the extreme conditions.

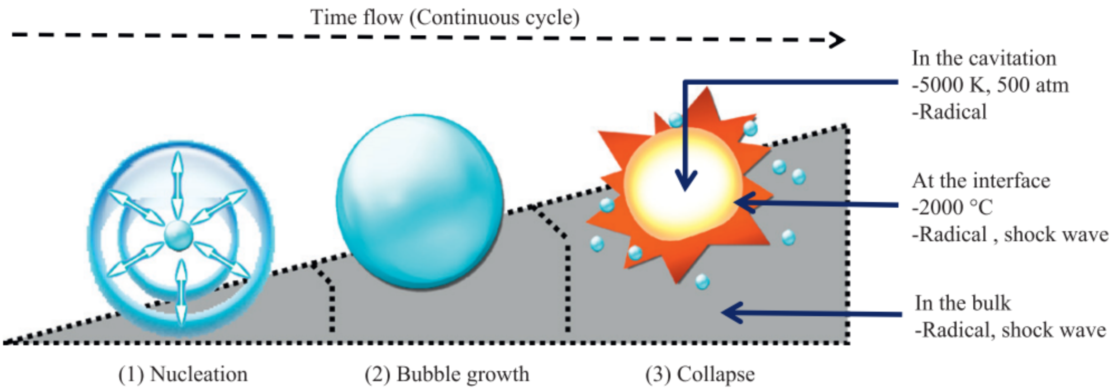


Figure 2.1: Microbubbles and cavitation phenomenon induced by ultrasonic radiation.[12]

Kim and Lee [12] used a 900W ultrasonic probe in their experiments. Two ultrasonic powers, 450W and 900W, were tested and compared to each other. The two ultrasonic powers were tested on four different solvents for various temperatures, at 25, 50 and 70°C. At lower temperatures ultrasound had varying effects dependent on the solvent. In o-dichlorobenzene, higher ultrasonic power reduced the dissolution of EVA at 25°C but increased the dissolution at both 50 and 70 °C. In toluene ultrasound had a negligible difference between the two ultrasonic powers at all temperatures. Finally, trichloroethylene had increased EVA dissolution at 25 and 50°C with higher ultrasonic power but had a drop in performance in the 70°C 900W experimental condition due to pyrolytic degradation of the solvent. The experiments observed in Kim and Lee [12] show that the effects of ultrasonic irradiation will vary depending on the experimental conditions. Notably, higher ultrasonic power may not improve the EVA dissolution speed and in some cases may reduce the effectiveness of the solvent.

Xu et al. [22] used ultrasonic irradiation at three powers, 180, 360 and 720W, for four different solvents at 50°C. The aim of this study was to measure the time it takes different solvents to remove the backsheet of the sample. Xu observed an increase in the effect of separation at increasing power for all solvents. The amount of increase in separation was extremely depended on the solvent used. For example, Benzyl alcohol saw an extreme jump from 5% separation at 360W to full separation at 720W. Xu posited that ”as the power increases, the cavitation rate increases, the molecular collision speed increases, and a large impact force is applied to the interface, which may cause molecular chain breakage” [22]. Low separation of the backsheet in spite of increasing power is due to the week diffusion of the solvent and poor solubility of EVA at the temperature tested.

Azeumo et al. [25] conducted optimization testing using toluene as the solvent to increase the speed of delamination. Sonification at 200W was one variable that was tested for optimization. Results from the optimization found that for ”any value of residence time and at a fixed temperature, the detachment is always greater when ultrasound is used” [25].

Abdo et al. [23] tested d-limonene in combination with ultrasound. The experiment tested the speed of backsheet detachment at different temperatures and ultrasonic powers (200, 450 and 700W). Abdo observed that ”the medium power of 450 W facilitated better detachment than the low power of 200W at temperature ranging from 25°C to 60°C” [23]. However, it was also observed that in the same temperature range the 700W power ”negatively affects the detachment process” [23]. At higher temperatures the negative effect of higher powers was not observed. Abdo posited that this was due to the collision of microbubbles which require more time for the bubbles to break down. Abdo et al. [23] also observed that at higher temperatures the difference in effect of sonification power is greatly reduced.

Królikowski et al. [21] used an ultrasonic bath at 60W with toluene. Królikowski's experiments used glass removed solar samples. They observed that at the temperature range used (25-35°C) ultrasound had a positive effect when paired with mechanical stirring but a negative effect when used in isolation.

Residence Time

An important factor in chemical delamination is the residence time in the solvent. Table 2.3 summarizes the residence times of previous studies. Residence times of previous research can be split into two categories: short-term tests with a duration under 4 hours or long-term tests which are greater than 8 hours. short-term tests are generally used to optimize the experimental factors with the goal of reducing the required time to observe some result in chemical delamination. In order to observe the effect of residence time it is used as design factor in the study and various residence times are observed. For long-term tests the residence time is typically set and no other time intervals are considered. Long-term tests are used when optimizing the chemical delamination process is not the main goal of the study [15, 16] or when a researcher wishes to see the full effect of a solvent on a test sample.

Table 2.3: Residence times of chemical delamination process in different studies.

Maximum Residence Time Observed	Intervals Observed	Ref
10 days	none	[11]
60 minutes	5, 15, 30 minutes	[12]
2 days	none	[15]
120 minutes	10, 30, 50, 90 minutes	[25]
240 minutes	30 minute intervals	[22]
8 hours	none	[17]
3 days	none	[16]
12 days	none	[19]
120 minutes	10, 50 minutes	[23]
60 minutes	5 minute intervals	[21]

Other Experimental Factors

This section covers experimental factors that have been used in previous papers but have not been repeated regularly.

Doi et al. [11] observed that the use of mechanical pressure on the test sample reduced the effect of swelling on the cell material. Using mechanical pressure in the form of binder clips, cells were able to be recovered intact in a process that otherwise crushed the cell during delamination.

Both Azeumo et al. [25] and Abdo et al. [23] tested thermal pretreatment of the sample as an experimental factor. The sample is heated to 200°C [25, 23] to heat the EVA and make it more susceptible to dissolution or delamination in the solvent. Toluene [25] and d-limonene [23] were the solvents tested with thermal pretreatment. Both studies concluded that thermal pretreatment had negligible effects on the speed delamination of the sample.

A common addition to the testing process is to include stirring of the solvent. Doi et al. [11] observed that including stirring increased the speed at which delamination occurs. Kang et al. [15] and Chitra et al. [16] also used stirring to increase the speed of delamination. Królikowski et al. [21] observed that stirring also had a positive effect on delamination when combined with ultrasonic irradiation.

Prasad et al. [17] tested both the solvent saturation and the position of the sample as test factors using trichloroethylene. The testing compared the solvent performance when the PV sample was submerged horizontally to when it was placed vertically. The results showed that a horizontal positioning was the better of the two options. Hydrostatic pressure was proposed as a reason for this improvement in EVA dissolution. Prasad et al. [17] found that for trichloroethylene a ratio of 1 to 7.44 module weight to solvent is the minimum ratio required before saturation of the solvent occurs.

Abdo et al. [23] studied the recyclability of d-limonene, specifically how many tests were able to be performed before with the same solvent before the detachment decreased. They found that d-limonene was able to detach the backsheet of PV modules three times before the grade of detachment started to decrease.

2.2. Discussion of Response Measurements

It is important when comparing the different research studies to be aware of the response measurements that are used to evaluate the delamination.

Doi et al. [11] used a simple result system for their solvent comparison, the result of the test was visually inspected and recorded as either dissolved, separated, swelled or no change. When optimizing the experiment Doi et al. [11] used a visual and physical inspection to determine whether the module was delaminated and if the cell material was recovered intact. Kang et al. [15] and Chitra et al. [16] also used this approach when comparing solvents and evaluating if EVA was fully dissolved.

Kim and Lee [12] used a quantitative analysis to determine the percent of EVA dissolved in the module. A picture of the module after testing was taken and a dissolution ratio calculated. The dissolution ratio was a ratio between the observable area of EVA dissolution and the total area of the module. This approach provides a value for chemical dissolution that can easily be compared. However, this method only observes the side of the module with glass and is subject to human error in evaluating the area where EVA has been dissolved. It is also unclear what visual indicators are being used to determine the area that is dissolved, specifically does the evaluation mean that all EVA is dissolved in that area or is any indication of solvent penetration into the EVA sufficient.

Azeumo et al. [25] used a weight calculation to determine the effectiveness of different solvents and as a result to optimize their method. The a ratio between the difference in weight before and after the test and the initial weight was used to create a grade of detachment percentage. The weight of the backsheet was mathematically subtracted from the calculation using the area of the test sample and an average backsheet weight per unit area. The grade of detachment percentage provides a value that is easily comparable and gives a good indication of a solvent and the methods effectiveness. Not included in this methodology is how the sample is processed after the test. In all test cases the grade of detachment value indicated that weight was lost. It is unknown if any work was done to separate the portion of the material manually or if a drying method was used. The evaluation method assumes that the only weight transfer in the system is EVA dissolving when this may not be the case. For example, a solvent could cause swelling and therefore increase the weight in the sample. In this study all solvents tested (other then water) were highly flammable thus drying would likely be effective in isolating the dissolution of EVA as a result. However, for more stable solvents this may not be the case. This test method also favors solvents that dissolve the EVA rather then breaking the bonds at the material interfaces. Prasad et al. [17] also used this method to evaluate their testing, though they had significantly longer test times so the likelihood of swelling rather then dissolving is reduced.

Xu et al. [22] used separation of the backsheet as a result to evaluate the effectiveness their processes. The value of separation was calculated as a simple percentage of the backsheet is free of EVA after the test process. This evaluation method provides details on a solvents ability to penetrate the EVA and effectiveness in separating the backsheet and EVA layers. This result also does not need to account for effects of swelling of the EVA. A detriment to this evaluation method is it provides no detail on what happens to the EVA during this process (swelling or dissolving) or the cell material.

To evaluate the effectiveness of the process Brenes et al. [18] used a gravimetric approach. The weight of the sample material was recorded, after which the sample was placed into a furnace to burn off any remaining EVA. A calculation is performed to quantify the percentage of EVA that was separated during the process, the amount of recovered cell material, and the amount of EVA that remained contaminating the cell material. Additionally, Brenes used scanning electron microscope morphology and energy dispersive spectroscopy to evaluate if the EVA was present in the sample after the furnace. This method can accurately account for the amount of EVA dissolved in the chemical process and gives an indication of the potential remaining contamination of EVA. This method was used with flammable solvents and could be easily dried for a useful weight calculation.

Vaněk et al. [19] recorded the weight of a PV module before and after separation as using a visual approach similar to Doi. Notably, the module observed did not have its EVA completely dissolve and the weight of the sample increased. This indicates that the solvent used (toluene) swelled the EVA but was not completely removed before the sample was weighted after the chemical process. The amount of weight increase indicated a reaction occurring but does not provide any information on what was occurring in the sample.

Abdo et al. [23] used a weight method combined with separation of the backsheet. The backsheet and any material attached to the backsheet is deemed as the PV sample. The difference between the initial and final material weights provide a percentage of detachment. Like similar methods this requires all solvent to be removed from the sample for the final weight measurement. The solvent used in this case (d-limonene) was also flammable and could easily be dried.

Królikowski et al. [21] developed a method of evaluating the percentage of EVA dissolved by measuring both the density and viscosity of the solvent after the delamination process is conducted. Functions that relate percentage of delamination to the viscosity and the density of the resulting solvent and EVA solution were created. Comparing the test results to the function provides a value for delamination. This method requires careful control of all materials during the test, sample sizes and volumes of solvent must be similar to ensure the measure values accurately reflect the relationship between delamination and the density and viscosity. This test was conducted using toluene as the solvent, toluene evaporates easily at high temperatures which may also effect the results. However, this experiment focused on low temperature applications and evaporation may not have been a significant factor to consider.

2.3. Conclusion of Literature Review

This section will summarize the key discoveries and observations relevant for the experimental setup and procedure of this report.

Since 2001, 30 unique solvents have been tested for their suitability in chemical dissolution of EVA for PV recycling. Despite the number of solvents tested, only five different solvents have been recommended for use in eleven studies. Toluene is the most recommended solvent for chemical delamination, used in six studies. Alternatives to petrochemical based solvents, such as toluene, have started to be investigated due to their sustainability. When choosing a solvent the polarity of the solvent should be considered, EVA contains both polar and non polar compounds but is typically considered non-polar. Consequently, non-polar solvents are preferred but polar solvents can still be utilized. When considering the industrial use of this process, high concentrations, higher temperatures and low toxicity are also factors to consider. As a result, solvents with low cost, high boiling points and low health and environmental hazards are beneficial for the process. When testing new solvents, crossed-Linked EVA should be used as a baseline as previous research has indicated that cross-linked EVA is much more resilient to dissolution. Typically, solvents are tested and compared in simple experiments with a set temperature and residence time. Alternatively the solvents can be compared in combination with optimizing the experimental factors.

Many options are available when optimizing the chemical delamination process. The most common factor to include is the temperature of the system. Higher temperatures increase the ability of EVA to dissolve in the solvent and the speed of delaminiation. Temperature can have a negative effect as the system heated near the boiling point of the solvent; evaporation and degradation of the solvent can occur close to this point. Ultrasonic irradiance is another popular test factor to include in optimization. Ultrasound creates local areas of extreme pressure and temperature as bubbles form and collapse. In most cases, ultrasound has increased the speed of delamination. However, the increase in delamination rate depends on other factors, including the type of solvent, the temperature of the test, and the power of the ultrasonic irradiance. In some test conditions higher ultrasonic power has led to a decrease in delamination efficacy. Additionally, ultrasound exacerbates the pyrolic effects on the solvent when the experimental conditions are near the boiling point of the solvent. Residence time of the sample in the solvent is another main factor that is investigated. Often the aim of the optimization is to reduce the residence time of the sample to a minimum. This can be done by observing the effect of the different experimental factors at differing time intervals. If the speed of delamination is not an important factor to investigate, a longer residence time can be set in order to guarantee the effect of the solvent on the PV sample can be observed. Other testing factors that have been investigated are mechanical pressure, which can stop the swelling of EVA from crushing the cell and pretreatment of the PV sample which has negligible effect on delamination.

The review of the literature of chemical delamination of PV modules provides a clear overview of important testing factors, including temperature, residence time and ultrasonic irradiation. Stirring and a horizontal placement of the sample in the solvent also has a positive effect on delamination. Past studies also provide a good framework on which to investigate this process further. A preliminary solvent testing experiment can be run using a simple experiment. This method allows for a large amount of solvents to be tested and compared. Once a limited number of solvents are selected, an optimization of the process can be run using the solvents. Temperature, residence time and ultrasound should be considered for major experimental testing factors. The evaluation of a solvents effectiveness should be carefully considered. Multiple responses should be used in order to more fully evaluate a solvents effectiveness.

3 Materials and Methods

This section details the materials and the methods used in this analysis of chemical dissolution of EVA. Section 3.1 describes the method used to compare solvent effectiveness. Section 3.1 describes the method used to for extreme conditions testing of solvents of interest from the preliminary screening. Section 3.3 details the experimental procedure used to optimize the process once a solvent has been selected for further investigation.

3.1. Preliminary Solvent Testing

Prior to optimising the chemical delamination process, one or more solvents must be chosen. Therefore, a set of preliminary tests were conducted to qualitatively screen a variety of selected solvents for their effects on EVA and the cell material. The following sections detail the testing method for solvent selection including details on the solvents chosen for comparison, the samples used and the experimental method.

3.1.1. Solvents

A large number of solvents with a variety of properties were selected for testing. Table 3.1, lists the selected solvents, the relevant properties, and the safety hazard pictograms for each solvent. More detailed hazard information is presented in table A.2 in Appendix A. The costs shown in table 3.1 represent the lowest costs per liter in euros from Sigma Aldrich [26] with a ordered quantity under ten liters. The price of solvents can vary greatly depending on the quantity and purity ordered. Thus, values presented should only be considered as a rough comparison. The selected solvents can be divided into two groups; the first toluene and solvents produced largely with toluene or fossil fuels as a reagent. This group includes toluene, benzaldehyde, benzyl alcohol and xylene. The second group are novel solvents which haven't been observed in chemical delamination before. The solvents in this group where chosen for their favorable properties, know reactivity to EVA [27] and or their green solvent characteristics. This group of solvents include castor oil, cyrene, γ-valerolactone, guaiacol, 2-methyltetrahydrofuran (2-MeTHF), oleic acid and pinocolone.

Table 3.1: Properties of selected solvents[24, 26] and EVA resistance (Poor = Poor Resistance, Unk = Unknown Resistance)[27].

Solvent	Boiling Point (°C)	Purity (%)	Cost (€/L)	EVA Resistance	Pictogram
Benzaldehyde	179	99.0	35.68	Poor	
Benzyl Alcohol	206	99.0	86.25	Poor	
Castor Oil	313	Various	99.20	Poor	
Cyrene	227	98.5	133.75	Unk	
γ-Valerolactone	205	99.0	108.25	Unk	
Guaiacol	205	98.0	206.61	Unk	
2-MeTHF	80	99.0	50.00	Unk	
Oleic Acid	360	99.0	47.25	Poor	None
Pinocolone	104	97.0	458.00	Unk	
Toluene	110	99.5	36.00	Poor	
Xylene	141	75.0	22.00	Poor	

Fossil Based Solvents

Benzalydehyde is an organic compound that is produced primarily with the use of toluene; however, other methods of synthesis are available. Compared to toluene, benzaldehyde has a higher boiling point and a comparable cost. A major benefit over toluene is the reduced health hazards, including being less flammable and not carcinogenic (Table A.2). While not present in the ChemWatch gold safety data sheet, benzaldehyde is occasionally labeled as an environmental hazard. Benzaldehyde has been tested as a solvent for chemical delamination and has shown positive results [22] but was not selected as the recommended solvent over toluene. Benzaldehyde's high boiling point of 179°C (Table 3.1) was not utilized in previous testing.

Benzyl alcohol is also produced from toluene, though it also occurs naturally in nature. It has a higher boiling point than both toluene and benzaldehyde but is more expensive [26]. Benzyl alcohol has minimal hazards to both health and environment (Table A.2). EVA's resistance has been tested and shown to have poor resistance to benzyl alcohol [27]. However, as far as the author is concerned, benzyl alcohol has not been test as a solvent for chemical delamination of PV modules before. Among the fossil fuel based solvents considered in this work, benzyl alcohol has the highest boiling point at 206°C (Table 3.1).

Toluene was chosen as a solvent due to previous studies [15, 16, 18, 19, 20, 21]. It is a common solvent for chemical delamination of EVA and it provides a good benchmark for evaluating solvent effectiveness on EVA. Toluene is a non-polar solvent which is the preferred option for polarity for EVA dissolution. Toluene poses significant hazards that negatively impact the viability of chemical delamination, including serious health hazards if inhaled or ingested. Additionally, toluene's high flammability (Table A.2) is not ideal for chemical delamination as large volumes are required to be heated for chemical delamination.

Xylene has been used in previous chemical delamination testing [20, 25, 19]. Despite showing similar results to toluene, xylene has not been recommended in studies or used past an initial screening. Xylene is mainly produced in conjuncture with toluene and benzene from petroleum. Xylene's higher boiling point of 141°C (Table 3.1) has not been investigated for benefits over toluene. Compared to toluene, xylene has fewer health and environmental concerns (Table A.2).

Green Solvents

Castor oil is a vegetable oil made from the castor bean [28], and it is known that EVA has a poor resistance to castor oil [27]. Castor oil is a mixture of primarily ricinoleic acid with smaller amounts of oleic acid, linoleic acid and others. Castor oil can be considered a green solvent because of its sustainable feedstock [28] and has minimal hazards to both health and the environment (Table A.2). A high boiling point of 313°C (Table 3.1) allows this solvent to be tested at higher temperatures.

Cyrene is a promising green solvent which can be produced from various biomass materials [29]. Cyrene has been proposed as a replacement for solvents such as dimethylformamide ,N-methyl-2-pyrrolidone, di-methyl sulfoxide, and dimethylacetamide [29]. Evidence has shown that cyrene has low toxicity to both health and the environment with only warnings for eye irritation (Table A.2). A high boiling point of 227°C (Table 3.1) and the fact that cyrene is miscible in water make it appealing for use in chemical delamination, although the reaction of cyrene to EVA remains unknown in literature.

γ-valerolactone (GVL) is a potential green solvent with suitable properties for sustainable chemical delamination. GVL can be generated from biomass feedstocks; however, the supply of precursors limits the amount of GVL that can be produced and maintains the solvent price high [30]. It has a high boiling temperature of 205°C (Table 3.1) and is soluble in water. GVL's low toxicity (Table A.2) would be beneficial when working large quantities needed for PV recycling.

Guaiacol is produced from guaiacum or wood creosote and has potential as a green solvent. Typically, guaiacol acts as a precursor to different favoring agents like, vanillin and roasted coffee [26]. With sources of guaiacol naturally occurring in a variety of plants, guaiacol has many sources of sustainable production. Guaiacol is also a byproduct of the thermochemical conversion of lignin [31]. A boiling point of 205°C (Table 3.1) allows for higher temperatures to be reached without pressurizing the system. Guaiacol is considered substantially safer (Table A.2) than solvents investigated in this work for chemical delamination due to its limited warnings of skin and eye irritation, as well as the warning that it is dangerous if consumed. The effect of guaiacol on EVA has not been previously studied.

2-methyltetrahydrofuran is a promising green solvent which can be derived from renewable sources [32]. 2-MeTHF can naturally degrade in the environment by sunlight and air [32]. Its low boiling point of 80°C (Table 3.1) is not ideal in chemical delamination but does allow for rapid drying of recovered materials. 2-MeTHF has some major hazards that must be highlighted when considering it for application in chemical delamination (Table A.2). In addition to common irritant warnings, 2-MeTHF is a highly flammable fluid and is corrosive. When selecting a solvent for chemical delamination high flammability is substandard for a process that uses elevated temperatures. Corrosive properties are also detrimental as chemical delamination would require addition safety and material measures. Despite some health and safety hazards, 2-MeTHF would be an improvement over fossil based solvents currently favored in chemical delamination.

Oleic acid is a colourless fatty acid that has numerous natural sources, including olive oil [26]. Oleic acid has many promising properties for use in chemical delamination and is known to degrade EVA [27]. Oleic acid has a high boiling point of 360°C and a relatively low cost when compared to other selected green solvents (Table 3.1). In addition, oleic acid has no health or safety precautions [24]. These characteristics make studying oleic acid particularly advantageous.

Pinacolone has been suggested as a replacement for non-polar solvents, including toluene [33]. Pinacolone can be synthesised through sustainable biomass sources and can therefor be considered a green solvent. In table 3.1, Pinacolone shows a similar boiling point of 80°C and the same hazard pictograms. The details of the specific hazard assigned to pinacolone are less severe the toluene with health warning limited to swallowing or breathing in the solvent (Table A.2). Pinacolone is also highly flammable which is a detriment for high temperature operations. If pinacolone shows similar dissolution rates of EVA as toluene it could be considered as a one-for-one green solvent replacement for toluene.

3.1.2. Preliminary and Extreme Testing Sample Production

The samples used in the preliminary solvent comparison and extreme conditions testing were mini modules created by the PVMD group at TU Delft for previous studies. These mini modules, see figure 3.1, were hand cut into smaller pieces for the test. As a result, the mini module samples after cutting were not homogeneous, with differences in size and material composition. The approximate size of the resulting samples used were $2.0x2.5cm^2$. Due to the heterogeneity of the samples, the preliminary testing results will be qualitative. Laminated module material was chosen due to the crosslinking effect that occurs in EVA after lamination.

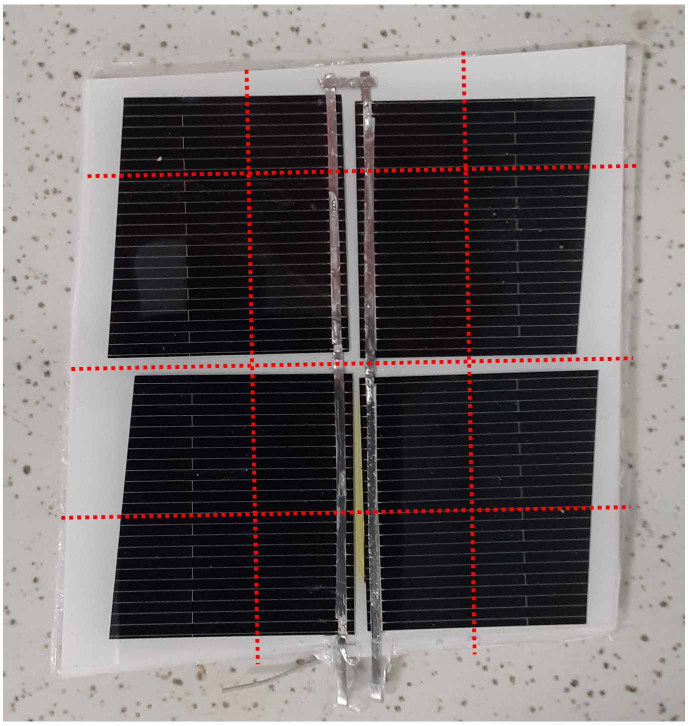


Figure 3.1: Example of mini module used in preliminary testing, dotted red line indicates cuts made for smaller sample sizes.

3.1.3. Preliminary Testing Experimental Setup

The samples were placed in a 50 ml beaker with 30ml of solvent. A hotplate (Cole-Parmer® SHP-200) was used to heat the solvent to the desired temperature. Figure 4.1 shows the preliminary testing setup where the PV sample is placed in a 50ml beaker with the glass side faced down for consistency. Both low and high temperature tests were conducted on the solvents. The initial test, which involved a lower temperature, was carried out at 80°C for all solvents. The 2-MeTHF test was performed at 75°C to reduce evaporation due to the low boiling point of the solvent. A higher temperature test was conducted at 160°C using solvents with higher boiling temperature. The high temperature test was performed for benzaldehyde, benzyl alcohol, castor oil, cyrene, γ-valerolactone, guaiacol and oleic acid. The residence time for each test was 105 minutes. The samples were weighed both before and after the test to get a quantitative result for comparison.

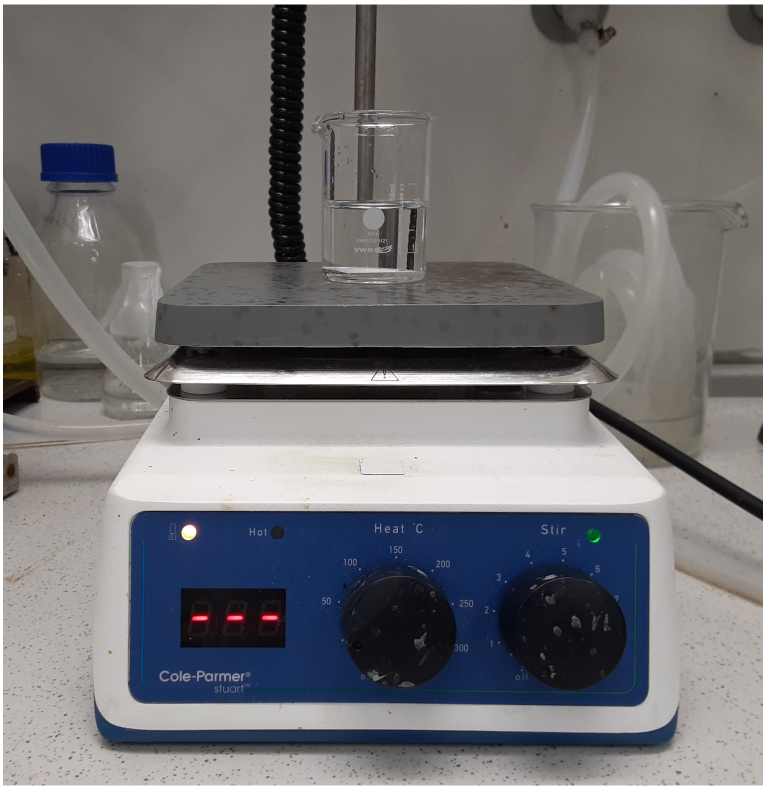


Figure 3.2: Testing setup for preliminary tests.

3.2. Extreme Conditions Testing

Once the solvents of interest were identified from the preliminary testing, an extreme condition test was conducted. A detailed explanation for the choice of solvents can be found in section 4.1.1. The test was performed for a maximum period of 24 hours with observation points at 1, 2, 4, 6 and 24 hours. Moreover, the experiment would be terminated if the quantity of solvent at a observation point reduced to half of its initial volume. The temperature of the test was conducted at approximately 80% of the solvents' boiling point to avoid thermal degradation of the solvent. To increase the delamination of EVA during the test, mechanical stirring was incorporated. The sample was also suspended in the solvent using a holder rather than sitting at the bottom to maximize the exposed EVA to the solvent. At each observation point, the sample weight would be measured in order to calculate the percent weight change (PWC) using equation 3.1.

$$PWC_{Solv,Time} = \frac{W_{Observation} - W_{Initial}}{W_{Initial}} \cdot 100 \tag{3.1}$$

Equation 3.1 observes the weight of the sample at different times. It is expected that the weight (W$_{Observation}$) will initially increase due to the solvent swelling the EVA until either the sample pieces start to separate or the EVA dissolves into the solvent. The PWC calculation was coupled with observations to give context to what effect changes the weight of the sample.

3.2.1. Extreme Conditions Experimental Setup

The samples were placed in a 150ml beaker with 100ml of solvent. A hotplate (Cole-Parmer® SHP-200) was used to heat the solvent to the desired temperature. Figure 4.1 shows the extreme conditions testing setup, the PV sample is placed in a 150ml beaker and is held by a sample holder at the mid-point of the solvent. The larger beaker and volume of solvent was used to allow for longer residence times, to avoid the amount of solvent limiting the delamination process and to allow for clearance of the sample holder. A stirring rod at the bottom of the beaker stirs the solvent throughout the test. The temperature was regulated with a Cole-Parmer TC-200D temperature controller for temperatures below 200°C. Above 200°C a thermometer was used observe and set the hotplate temperature. This test was conducted for guaiacol, oleic acid and a 50/50 guaiacol oleic acid mix.

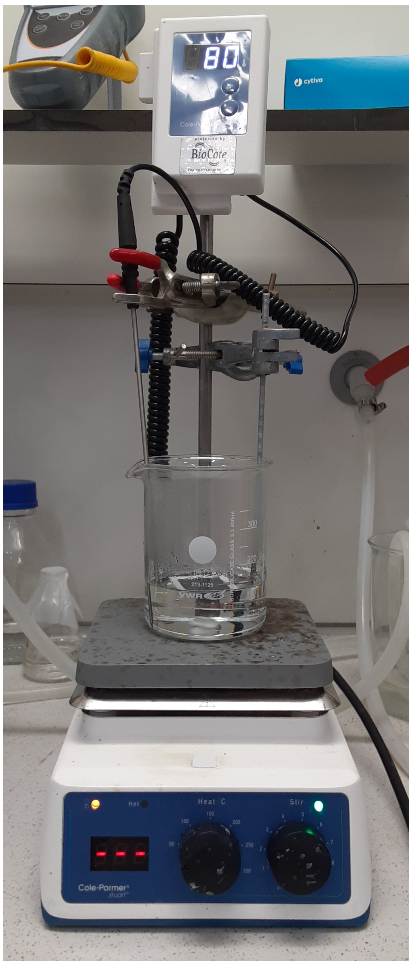



Figure 3.3: Testing setup for extreme and optimization testing. Left: total setup shown. Right: closeup of sample in solvent. The beaker size shown is for optimization tests.

3.3. Optimization Testing

Based on the data collected during extreme conditions testing, it is possible to estimate the upper and lower limits of time and temperature variables for optimization purposes. Ultrasonic irradiance was intended to be an additional factor used in the optimization but suitable equipment was not available. An ultrasonic bath or probe that could handle temperatures greater than 100°C could not be obtained for a sustained residence time.

The optimization was carried out with guaiacol as the solvent. An explanation of the solvent choice is detailed in section 4.2.1. The Stat-Ease® 360 software [34] was used to create a design of experiment (DOE) method. DOE is a powerful tool which can generate more information on a process in a more efficient manner than traditional approaches [35]. Using the DOE methodology can result in half as many test required than traditional approaches [35]. DOE works well both early in process development when optimal conditions are unknown and for optimizing conditions [35]. For this chemical delamination process, DOE can optimize the test factors found in the literature and observe which factor is statistically significant. To create a matrix of experiments that will be performed an experimental design must be chosen for the DOE. A central composite design (CCD) is a common experimental design used to create surface responses [36]. A CCD has three sets of experimental test points: center points, factorial points and axial points. Figure 3.4 shows a representation of these points for a three factor design, the volume defined by these design points is called the design space. Once completed the DOE will be able to create response surfaces which predicts the result anywhere in the design space. To increase the accuracy of the surface response multiple replicates of each type of design point can be performed.

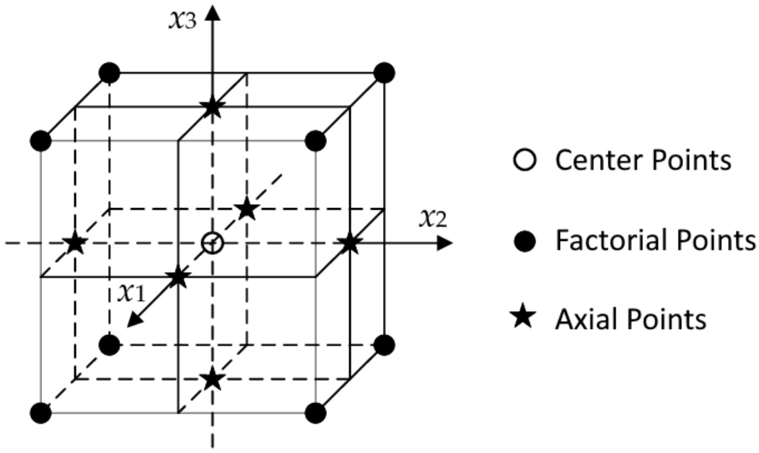


Figure 3.4: Three-factor layout for face-centered central composite design.

To build the experimental matrix a CCD was used with temperature and time as the two testing factors. Two replicates of factorial points, one replicate of axial points and three center points were used for a total of fifteen runs for the optimization. The temperature range was set at 80-160°C and the residence time range at 0.5-3 hours based on the results of the extreme conditions testing.

3.3.1. Optimization Testing Sample Production

Mini modules were created specifically for this optimization to have homogeneous samples for testing. Figure 3.5 shows an example of one of the modules used. The samples created were a 4x5cm^2 module with a 3x4cm^2 silicon wafer added to simulate a solar cell. As seen in figure 3.5, the location of the silicon wafer is slightly different between each sample. The weights of the glass backsheet and silicon wafer were measured and recorded prior to lamination in order to have a detailed understanding of the module composition.

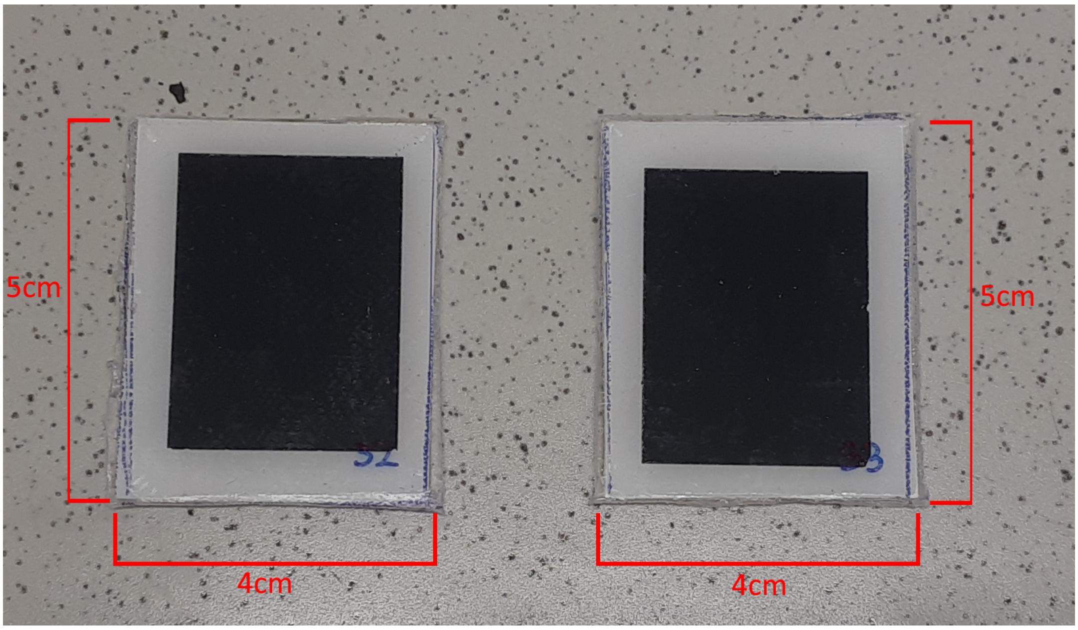


Figure 3.5: Example of mini modules used in optimization testing.

3.3.2. Optimization Testing Responses Measured

In order to have a deeper understanding of the impact of chemical delamination on the EVA during the optimization testing, several responses were monitored and measured.

EVA Removal

By understanding the material composition of the PV modules, we can more effectively isolate the change in EVA weight using equation 3.2, where the final weight of EVA is calculated with equation 3.3 and the initial weight by equation 3.4. If the backsheet dissolves during the test, its weight is excluded from the final weight computation. The weights of the glass and backsheet were individually measured and recorded prior to lamination. The wafer weight was calculated as an average weight of the silicon wafers. Once measured, the different materials were given a sample number to build up a sample and ensure the recorded values were tracked through the lamination process (Table A.1). Figure 3.5 shows the sample number on two different samples, on the left is sample 32 and the right sample 33. The final weight of the module is measured after the test sample has been dried in an oven for four hours at 120°C. The drying procedure evaporated the remaining guaiacol without effecting the remaining EVA.

$$\%EVA = \frac{W_{FinalEVA} - W_{IntialEVA}}{W_{InitialEVA}} \cdot 100 \tag{3.2}$$

$$W_{FinalEVA} = W_{FinalMeasured} - W_{Glass} - W_{Wafer} - W_{Backsheet} \tag{3.3}$$

$$W_{InitialEVA} = W_{InitialMeasured} - W_{Glass} - W_{Wafer} - W_{Backsheet} \tag{3.4}$$

Backsheet Removal

To try and quantify the speed in which enough solvent diffuses into the EVA to disrupt the lamination, the percent of backsheet removal was observed. Observation of the backsheet removal was conducted prior to drying, to isolate the effect of the solvent. The approximate area where the backsheet is delaminated is highlighted and a picture taken. An example of the procedure to quantify backsheet removal can be seen in figure 3.6. After the test, the sample was removed from the solvent, and tweezers were used to examine the amount of backsheet delamination. During examination, minimal mechanical force is used to observe and outline the portion of the backsheet that has been removed with the testing setup. Once photographed, the approximate area of backsheet remove is compared with the total backsheet area by counting pixels. This testing method is subject to observational errors that should be considered when analyzing the results of the optimization.

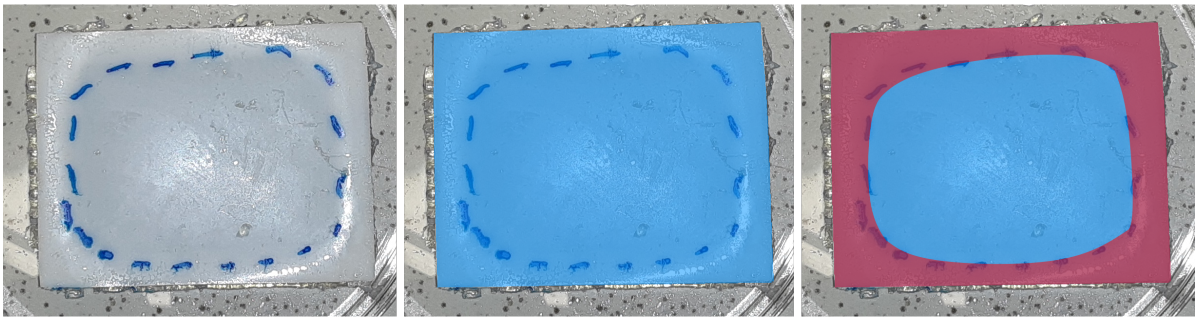


Figure 3.6: Example backsheet delamination analysis. Left: original picture. Middle: backsheet area. Right: delaminated area overlaid on total area.

Silicon Content

The final result observed was the silicon content in the solvent after the test. During the extreme condition testing evidence of silicon leeching was observed. An inductively coupled plasma optical emission spectroscopy (ICP-OES) test was used to observe if silicon was being leeched by the solvent. ICP-OES uses plasma to excite atoms and ions of a sample; the excited atoms emit light with characteristic wavelengths. The wavelengths measured by the ICP-OES can be compared to calibrated data to give the relative amount of an atom in the sample. A sample of 1 milliliter solvent and 9 milliliters of diluent (HNO_3^+) was used to prepare the samples. The weights of the solvent and diluent were recorded and a ratio was calculated to provide the amount of silicon present in the solvent. Control tests of both the solvent and the diluent were conducted to observe if silicon is present in either prior to the optimization tests.

3.3.3. Optimization Experimental Setup

The optimization test has the same basic test setup as the extreme testing setup, section 3.2.1 describes the setup. A 400ml beaker was used with 125ml of solvent to accommodate a larger sample size.

4 Results and Discussion

This section details and discusses the results of experiments conducted during this thesis project. The results of the preliminary screening of selected solvents are recorded and discussed in section 4.1. Section 4.2 covers the extreme condition testing results and describes the reasoning for choosing a final solvent for optimization testing. Section 4.3 includes details of the test results of the optimization, the predicted optimized test conditions and the validation results of the prediction.

4.1. Preliminary Solvent Testing

A total of 18 preliminary solvent tests were completed to screen the selected solvents for their effects on EVA. Eleven low temperature tests and seven high temperature test were conducted on eleven unique solvents. Table 4.1 details the results of the preliminary testing. The nature of the test makes quantitative comparison challenging thus four broad categories of results were defined: no change, minor swelling, major swelling and partial delamination.

Table 4.1: Testing results of preliminary testing. The effect of the solvent on EVA is given for the low temperature test and when applicable the high temperature test. The greatest effect is labeled as "Partial Delamination" while the least effect is "No Change". If the solvent had a high temperature test performed then the effect on the backsheet is also recorded.

Solvent	Low Temperature Test	High Temperature Test	Backsheet Status After High Temp Test
Benzaldehyde	Major Swelling	Partial Delamination	Dissolved
Benzyl Alcohol	Minor Swelling	Major Swelling	Partially Dissolved
Castor Oil	No Change	Minor Swelling	Not Dissolved
Cyrene	No Change	No Change	Partially Dissolved
γ-Valerolactone	No Change	Minor Swelling	Dissolved
Guaiacol	Major Swelling	Partial Delamination	Dissolved
2-MeTHF	Major Swelling	-	-
Oleic Acid	Major Swelling	Major Swelling	Not Dissolved
pinacolone	Minor Swelling	-	-
Toluene	Partial Delamination	-	-
Xylene	Major Swelling	-	-

Figure 4.1 gives an overview of what these result categories describe, row one shows results from the lower temperature testing while row 2 shows results from the high temperature tests. Columns A, B,

C and D show results described as no change, minor swelling, major swelling and partial delamination respectfully.

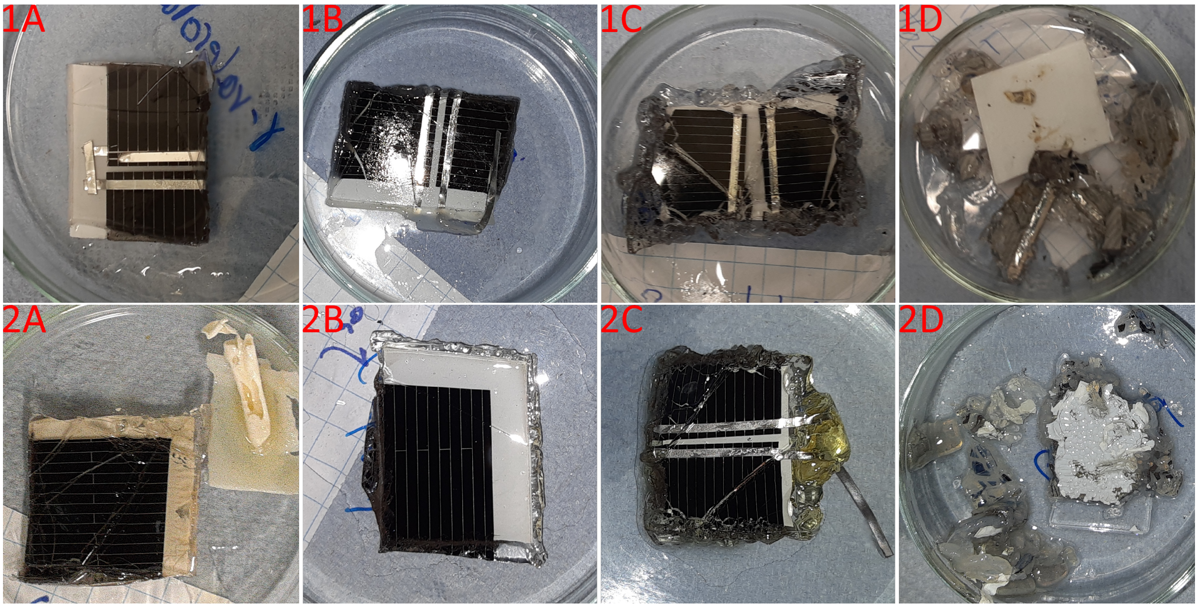


Figure 4.1: Selection of preliminary testing results. Row 1: 80°C Temperature Test (Note: 2-MeTHF test was conducted at 75°C), Row 2: 160°C Temperature Test. Column A: No Change, Column B = Minor Swelling, Column C = Major Swelling, Column D = Partial Delamination. Solvents used: 1A = γ-Valerolactone, 1B = Benzyl Alcohol, 1C = Benzaldehyde, 1D = Toluene, 2A = Cyrene, 2B = Caster oil, 2C = Oleic Acid, 2D = Guaiacol.

The test result designation explains how the solvents affected the EVA; the outcome is unrelated to the backsheet's condition following the test. A no change designation indicates that no visible change to the EVA was detected. Figure 4.1-1A and 2A show these results, notably 2A shows that the backsheet has been severely effected by the solvent but upon inspection no effect on the EVA of the sample could be seen. Minor swelling indicates that the solvent is visibly effecting the EVA at the edges of the sample. However, despite the visible effect to the EVA the sample retains its form and strength, and no effect is visible in the center of the sample. Major swelling describes when the sample undergoes a large volume expansion due to EVA swelling. Furthermore, this classification reveals observable impacts on the cell's inside. Under this designation the cell material in the interior of the sample shows visible changes. The effects on the cell material can be movement of the cell pieces as in figure 4.1-1C or fracturing of the cell as swelling moves inward as in figure 4.1-2C. Despite the visible changes, major swelling results indicate that the glass-EVA and the cell-EVA interfaces remain intact and continue to hold the sample layers together. The final designation, partial delamination, indicates a test result that shows the same properties as major swelling coupled with the breakdown of either the glass-EVA and the cell-EVA interfaces. In figure 4.1, 1D shows the partial delamination of the sample due to toluene, this is likely caused by EVA dissolving into the solvent until the strength of any remaining EVA can't hold the interfaces together. Conversely, in figure 4.1-2D shows that guaiacol swelled the EVA and delaminated the glass-EVA interface but the majority of the EVA remained undissolved.

The status of the backsheet was recorded for high temperature tests due to its solubility in non-polar solvents above 100°C. The results are split into three designations: Not dissolved, partially dissolved and dissolved. Not dissolved indicates that no dissolution of the backsheet was detected. Partially dissolved indicates at least one of the composite layers of the backsheet is being dissolved by the solvent. A designation of dissolved indicates that the backsheet has been dissolved by the solvent such that it provides no resistance to the solvent contacting the EVA, some portions of the backsheet may still be visible under this result.

Difficulty arose when evaluating the weight data measured. The initial samples used were not uniform, and therefore had different amounts of EVA present in the sample as well as different amount of EVA exposed to the solvent. With the distribution of weight in each sample unknown, an overall weight change was observed. This overall weight change could have many factors contributing to either an increase or decrease in the sample. As the EVA swells the weight will increase, and once the EVA begins to detach or dissolve the weight will decrease. The hand cut samples had pieces of glass and cell material that would detach also effecting the resulting weight change. In high temperature tests the backsheet can be dissolved, but as seen in figure 4.1 the back sheet may not fully dissolve. When drying, it was found that some of the solvents dried as a resin on the sample and could not be removed. If wetted weights were measured the amount of solvent present on and in the sample would skew the results. It was determined that too many unknowns were present in the test to effectively use the measured values as a comparison.

The preliminary testing results have some limitations that must be considered. The results of these tests are subjective and rely heavily on visual results. The results also favor solvents that cause the most extreme swelling in the sample. However, it is possible that a solvent could break the bonds between interfaces without swelling the EVA. The strength of the interfaces were tested with tweezers. The residence time of the test, 105 minutes, must also be considered when evaluating the results. The residence time is relatively short and it is possible that some solvents test if given more time would show a reaction. Notably, castor oil, which has a known effect of EVA, showed no change in the sample at 80°C. It is likely that if the test residence time was longer, the castor oil would begin to show a visible effect. In each test, 30ml of solvent was used, the volume of solvent was not corrected for the purity of the solvent. This favors solvents that where able to be obtained with high purity. While the preliminary test experiment may have missed some nuanced reactions, it provides an overview of each solvents reaction to EVA and the other layers of a PV cell.

4.1.1. Discussion of Solvents

Of the eleven solvents tested ten solvents show some effect on EVA. Higher temperatures resulted in more pronounced results in the same solvent. Additionally, at higher temperatures the backsheet was partially or fully dissolved by four solvents. Two distinct types of swelling can be seen in the results. The first is swelling that expands the volume of the EVA but in general keeps the same shape of the original material, see figure 4.1-1C. These results are typical of polar solvents and their effect on EVA. EVA swelled by polar solvents retains limited strength depending on the degree of swelling that has occurred. The probable cause of this effect is the solvent effecting the minority polar elements of the EVA while the polar elements are enough to keep the original shape of the EVA. The second type of swelling is caused by more non-polar solvents, see figures 4.1-1D and 2C. Non-polar solvents cause extreme volume expansion in the EVA and the original shape of the EVA is not retained. The EVA swelled by polar solvents is a gel that has no strength and is in the process of being dissolved fully into the solvent.

Based on the results of the preliminary test screening and their properties, oleic acid and guaiacol were chosen for additional experiments. Guaiacol and oleic acid displayed strong reactions to EVA, especially at higher temperatures. Additionally, both solvents have high boiling points, 205°C and 360°C for guaiacol and oleic acid respectfully, and have minimal health and safety hazards (Table A.2). Guaiacol is harmful if swallowed and causes skin and eye irritation. Oleic acid has no health or safety warnings. Finally, both solvents have the potential to be green solvents with sustainable sources of production.

The following subsections detail the results of the preliminary testing in depth. The result of each solvent is given and discussed.

Fossil Based Solvents Results

Benzaldehyde was tested both at 80°C and 160°C, the results of the tests can be seen in figure 4.2. In figure 4.2-A, the lower temperature test, benzaldehyde caused major swelling in the EVA. The cell material was shifted by the swelling of the EVA. Swelling caused fragmenting of some cell material at the edges of the sample while the majority of the cell moved relatively intact. The backsheet of the sample could be removed using tweezers and light mechanical force. The glass EVA interface retained some strength after the test but could be delaminated with mechanical force. The higher temperature test, shown in figure 4.2-B had a more pronounced result. The backsheet was effectively dissolved, exposing more of the EVA to the solvent. Portions of the EVA swelled to the point that no strength remained and it broke off the main sample when removed from the solvent. Notably, the EVA did not appear to dissolve in the EVA, this is likely due to benzaldehyde mainly effecting the minority polar elements of EVA. Portions of the glass were delaminated during the process. It is possible that dissolving of the backsheet exhausted some of the ability of the solvent to achieve delamination of cell materials. Overall, benzaldehyde demonstrated good reactivity to EVA, its higher boiling point and fewer hazards then toluene make further experimentation of benzaldehyde of interest. However, because benzaldehyde is primarily produced through fossil fuels and toluene itself, it was not chosen for further study in this report.

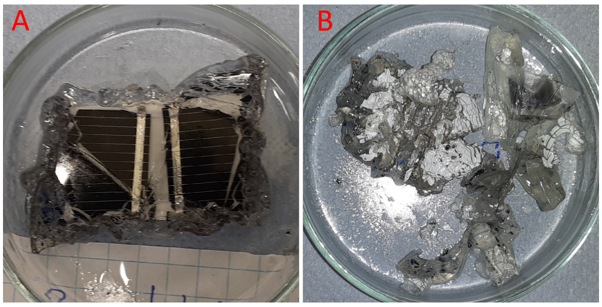


Figure 4.2: Results of benzadehyde tests. A = 80°C test, result shows major swelling of the sample. B = 160°C test, result shows partial delamination of the sample and the backsheet dissolved.

Benzyl alcohol was tested both at 80°C and 160°C, the results of the tests can be seen in figure 4.3. The lower temperature tests show minor swelling of the EVA at the edges of the sample. The swelling in this test is characterized by the EVA retaining its strength and adhesive properties. In the high temperature test, shown in figure 4.3-B, the increase in reactivity due to temperature can be observed. The backsheet is dissolved in these test conditions, opening more area for the solvent to contact EVA. The EVA swelled significantly more then at lower temperature. The swelling can be seen to primarily be located at the edges of the sample and around the glass fracture lines. During this test, cell material is moved by the swelling of EVA. However, the bond between the EVA and the glass remained intact after the test. While the benzyl alcohol showed some positive results its primary production through fossil fuels is a detriment and was outperformed by other fossil based solvents.

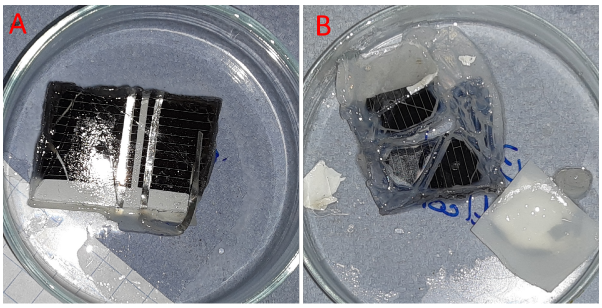


Figure 4.3: Results of benzyl alcohol tests. A = 80°C test, result shows minor swelling of the sample. B = 160°C test, result shows major swelling of the sample and the backsheet partially dissolved.

Toluene was tested at 80°C, the result of the test can be seen in figure 4.4. As the literature review suggested, toluene had one of the most significant effects on EVA throughout all the tests. Despite only being tested at 80°C, toluene completely disrupted the layers of the PV sample. The backsheet was delaminated and the cell material fragmented into major pieces. Portions of the glass was also delaminated in this process. EVA was not completely dissolved into the solvent, possible causes of remaining EVA could be the limited residence time or not enough solvent present in the system. A relatively large amount of toluene evaporated during the test, using toluene in a closed system such as the setup proposed in Azeumo et al. [25] would benefit the process. The results of the toluene test could be considered the best result of the preliminary testing; however, toluene's use in chemical delamination has been extensively studied in other papers, thus alternative solvents were chosen for further experimentation.

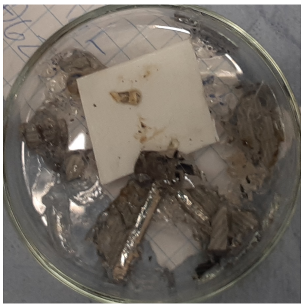


Figure 4.4: Result of toluene test, result shows partial delamination of the sample.

Xylene was tested at 80°C, the result of the test can be seen in figure 4.4. The results show large amount of swelling was caused by the xylene, concentrated towards the edges of the sample. The swelled EVA at the edges of the sample had negligible strength and detached when the sample was removed from the solvent. Some fragmenting of the cell material indicate that the solvent was starting to move inwards from the edges of the sample. Evidence of EVA dissolving in xylene was observed when a gel formed in the remaining solvent after the test when cooled. The higher boiling point of xylene when compared to toluene was not considered in the preliminary testing as the boiling point of xylene (141°C) was less then the cut off point for the high temperature tests. Further investigation of xylene as an alternative to toluene could explore the benefits to the higher boiling point. Xylene was not chosen for further study in this report due to its primarily fossil based production and its weaker performance than alternatives.

Figure 4.5: Result of xylene test, result shows major swelling of the sample.

Green Solvents Results

Castor oil was tested both at 80°C and 160°C, the results of the tests can be seen in figure 4.6. While EVA is known to have a poor resistance to castor oil [27], the results of the preliminary testing indicate that castor oil is not especially effective in the observed residence time. No reaction was visible in the EVA for the lower temperature test, shown in figure 4.6-A. It is possible that the castor oil if given time would begin to effect the exposed EVA. As a viscous oil castor oil may have a more difficultly diffusing into the EVA reducing its effectiveness. At higher temperatures castor oil began to show some swelling of the EVA at the edges. However, there was no indication that the solvent is diffusing into sample and the reaction is limited to the exposed EVA. In both tests the layer bonds remained unchanged and no separation was detected. Castor oil was not chosen for additional study due to the poor results in the given residence time.

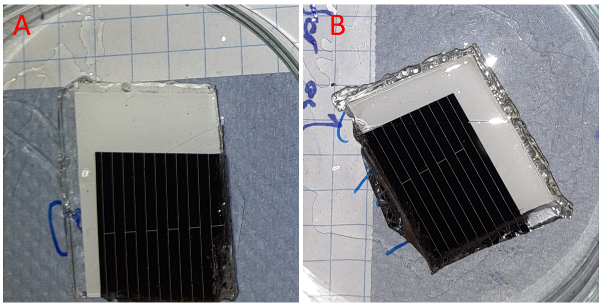


Figure 4.6: Results of castor oil tests. A = 80°C test, result shows no change on the sample. B = 160°C test, result shows minor swelling of the sample and the backsheet unchanged.

Cyrene was tested both at 80°C and 160°C, the results of the tests can be seen in figure 4.7. In both tests cyrene had no reaction with the EVA. In the lower temperature test the sample had no visible changes and no separation of layers could be detected. In the high temperature test the backsheet partially dissolved effectively exposing more of the EVA to the cyrene. Despite more EVA area exposed no change to the EVA or the interface layers could be detected. Consequently, cyrene appears to not be suitable for chemical delamination of PV modules with EVA lamination.

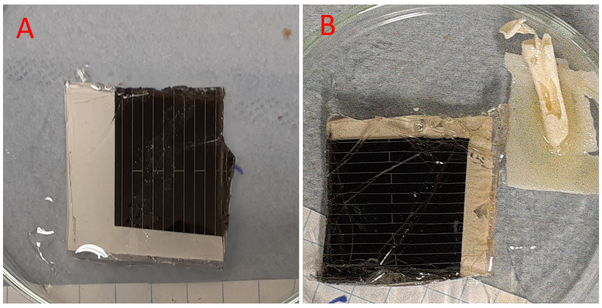


Figure 4.7: Results of cyrene tests. A = 80°C test, result shows no change on the sample. B = 160°C test, result show no change on the sample and the backsheet partially dissolved

γ-Valerolactone was tested both at 80°C and 160°C, the results of the tests can be seen in figure 4.8. At the lower temperature the EVA showed no effect due to the γ-valerolactone. No separation of the backsheet was observed. At the higher temperature test the backsheet was dissolved. At 160°C the EVA showed some swelling at the edges of the sample and at fracture points in the glass. No separation of the glass from the EVA was detected. Despite the better reaction at higher temperatures γ-valerolactone was out preformed by other solvents with similar properties.

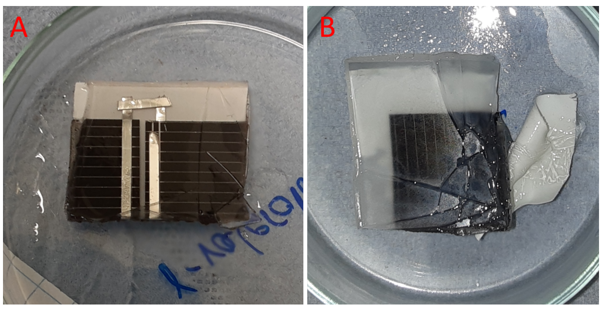


Figure 4.8: Results of γ-valerolactone tests. A = 80°C test, result shows no change on the sample. B = 160°C test, result shows minor swelling of the sample and the backsheet dissolved.

Guaiacol was tested both at 80°C and 160°C, the results of the tests can be seen in figure 4.9. In figure 4.9-A, the lower temperature test, guaiacol caused swelling in the EVA. While the swelling was not as visibly impressive as benzaldehyde, the fractures of the cell material show that the solvent was diffusing into the EVA and causing movement. The backsheet of the sample showed separation from the EVA at the edges of the sample. The glass-EVA interface also separated at the edges. The results of the higher temperature guaiacol tests showed major swelling of the EVA and partial delamination of the glass. The backsheet was dissolved at 160°C and posed no barrier for the solvent to diffuse into the EVA. The swelling of the EVA caused fragmentation of some cell material that remained in the swelled EVA. The observations of the guaiacol test coupled with its minimal hazards and green solvent potential make it a clear choice for further experiments.

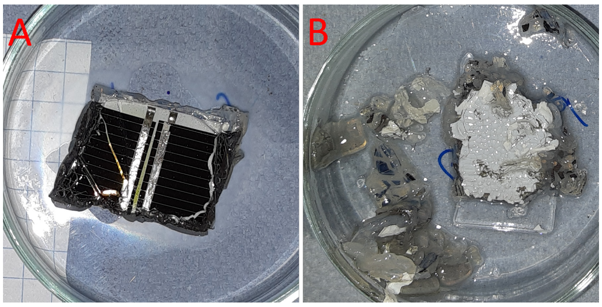


Figure 4.9: Results of guaiacol tests. A = 80°C test, result show major swelling on the sample. B = 160°C test, result shows partial delamination of the sample and the backsheet dissolved.

2-methyltetrahydrofuran was tested 75°C, the result of the test can be seen in figure 4.10. 2-MeTHF was tested at a lower temperature due to its boiling point. Despite the lower temperature of the test, the experiment showed positive test results. 2-MeTHF swelled the EVA significantly and showed some ability to effect the interior of the sample. Some separation of the backsheet was observed. 2-MeTHF should be considered for further investigation if chemical delamination using low temperature processes or pressurized systems are considered. For this report, the low boiling point of 2-MeTHF was significant enough that other solvents were chosen for further study.

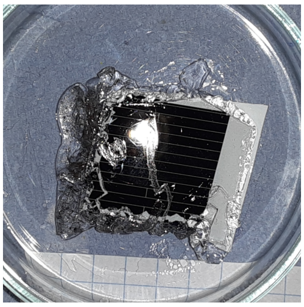


Figure 4.10: Result of 2-methyltetrahydrofuran test, result shows major swelling of the sample.

Oleic acid was tested both at 80°C and 160°C, the results of the tests can be seen in figure 4.11. In both tests the oleic acid swelled the EVA and caused fragmentation and movement in the interior of the sample. The swelled EVA had no strength and could be removed with ease. The backsheet in both cases remained attached and showed no signs of detachment. The higher temperature test showed indications that some EVA was dissolving into the oleic acid. The strong reaction with the EVA, high boiling point, green solvent potential and no hazards made oleic acid an interesting solvent to further investigate.

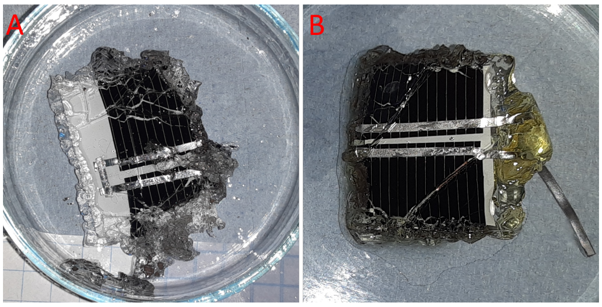


Figure 4.11: Results of oleic acid tests. A = 80°C test, result shows major swelling of the sample. B = 160°C test, result shows major swelling of the sample and the backsheet unchanged.

Pinacolone was tested at 80°C, the result of the test can be seen in figure 4.12. The EVA swelled slightly due to pinacolone at the edges of the sample and along a glass fracture line. The swelled EVA was partially separated from the backsheet. A portion of the glass, cell and EVA material was able to be removed by tweezers. The removal of the section needed notable strength and tearing, for this reason forcefully trying to separate layers was not conducted with other tests. The EVA remained adhered to the glass and showed no signs of separation. The results of the test suggest that pinacolone is not suitable for chemical delamination of PV modules with EVA encapsulant.

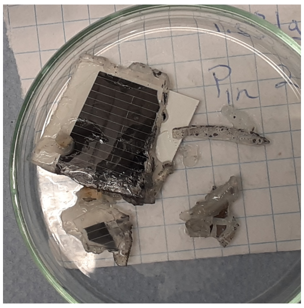


Figure 4.12: Result of pinacolone test. Result shows minor swelling of the sample.

4.2. Extreme Conditions Testing

An extreme condition test was completed to probe the selected solvents for their benefits and limitations in the setup that would be used for optimization testing. Additionally, each test on the solvent would provide information on the appropriate testing ranges to use in the optimization. The extreme condition tests performed include a guaiacol test, an oleic acid test, and a mixture test of 50% guaiacol and 50% oleic acid by volume. The mixture test was used to determine if the combined solvents disrupted the EVA layer better than the solvents individually. The guaiacol targets the polar elements of the EVA and diffuses through the sample relatively quick. The oleic acid targets the majority non-polar elements but seems to have difficulty diffusing into the EVA and disrupting the different material interfaces. At intervals of 1, 2, 4, 6 and 24 hours the sample would be removed, the wetted weight of the sample measured and the weight of the remaining solvent measured. The test would stop after 24 hours or 50% of the weight of the solvent was evaporated.

Two test factors were added into the experimental setup for the extreme conditions testing. Stirring was added and was kept constant throughout the testing procedure. The addition of stirring to the system appeared to have a positive impact on the speed of the procedure, but the effects of stirring were not isolated for the study. The position of the sample was also changed to be suspended in the solvent by a sample holder. The change in sample position had a positive effect in speeding delamination. By suspending the sample in the solvent, the solvent had better access to diffuse throughout the solvent. A suspended sample could also flex around glass fractures which would increase the exposed EVA area. This effect was most pronounced in tests in which the backsheet was also dissolved. In those cases, only the glass and EVA hold the sample together, and in the case of guaiacol leads to a rapid separation of glass fragments. A consequence of this setup is that cell material is more likely to break along the same lines as the glass sections due to swelling and flexing.

The outcome of the extreme condition tests can be seen in figure 4.13. The sample condition prior to the test are provided in figure 4.13-A, -C, and -E for guaiacol, oleic acid, and the mixture respectfully. Additionally, the result after the extreme tests are provided in figure 4.13-B, -D, and -F for guaiacol, oleic acid, and the mixture respectfully.

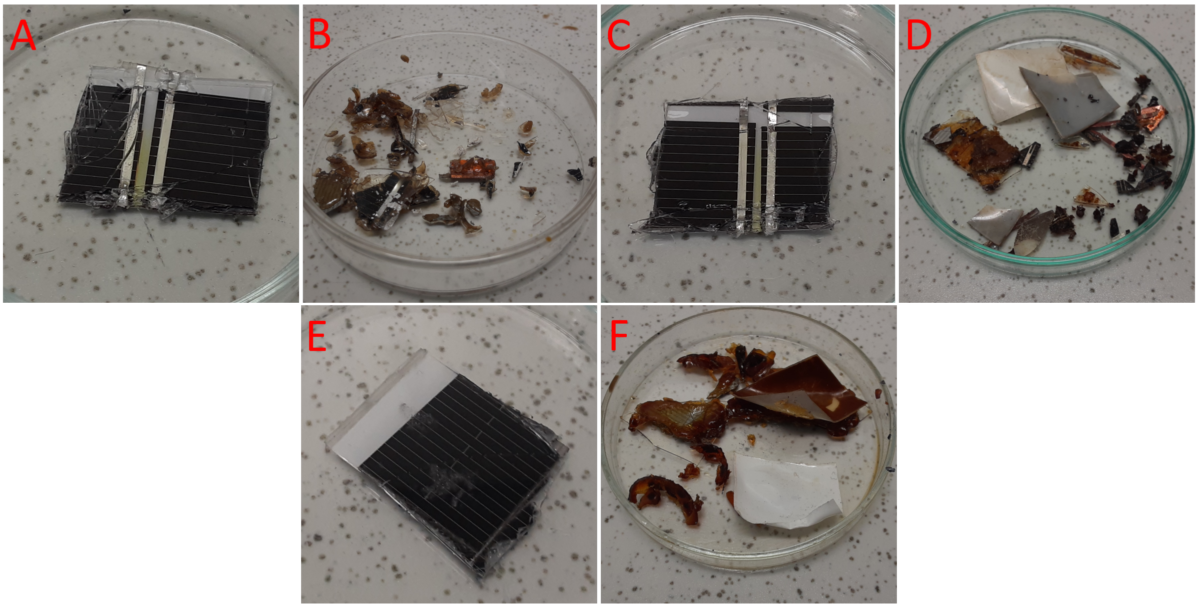


Figure 4.13: Comparison of chemical delamination at extreme conditions. A = Initial guaiacol sample. B = Result of guaiacol test. C = Initial oleic acid sample. D = Result of oleic acid test. E = Initial mixture sample. F = Result of mixture test

Figure 4.14, shows the weight changes measured in the sample for each test and indicate when the test was stopped. The guaiacol test at 160°C was stopped at 4 hours when 53% of the solvent was lost. Oleic acid was able to complete the full test at 280°C, 24% of the solvent was lost during the test. The mixture test was also conducted at 160°C and was stopped after 6 hours, 59% of the solvent mixture was lost during this time, a majority of the loss is likely to be the guaiacol.

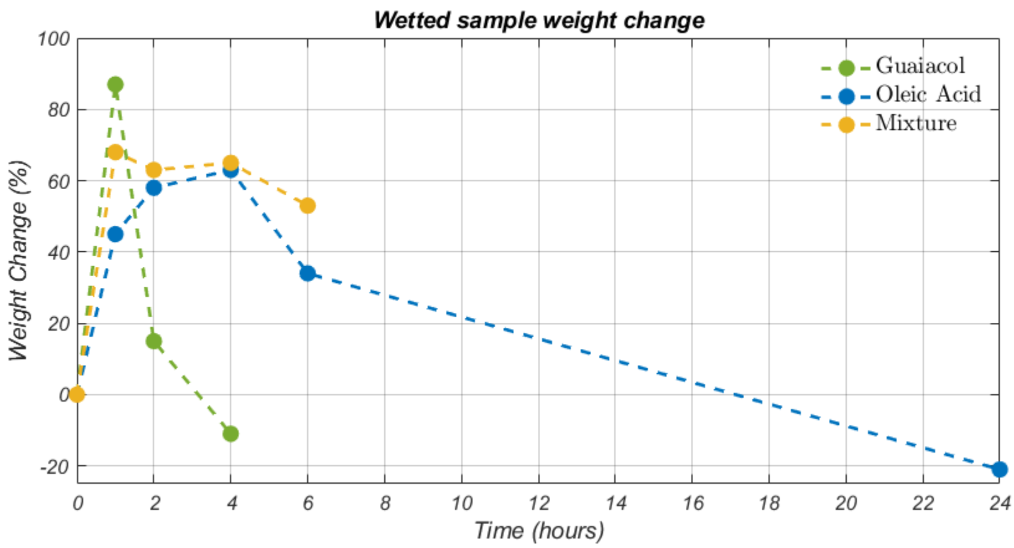


Figure 4.14: Observed weight changes for extreme testing. Dashed lines are added for clarity. The largest weight change occurs during the guiacol test at 1 hour. Oleic acid was the longest test performed, completing the full 24 hour test.

4.2.1. Extreme Conditions Testing Solvent Discussion

Measurements of the wetted weights show that guaiacol has the greatest increase in weight due to swelling with a 87% increase. The guaiacol sample then sees a rapid decrease from the peak weight change as the sample cohesion breaks down and glass fragments and swelled EVA break away from the main sample. At the end of the guaiacol test the sample has a measured weight change of -11%. Once the experiment was stopped, the solvent was filtered, and the detached sample material was recovered. The comparison of the initial and final conditions of the test sample used in the guaiacol experiment can be seen in figure 4.13-A and B respectfully. From figure 4.13-A, the glass in the sample is quite fragmented possibly influencing the speed of swelling and the speed that the sample cohesion broke down. The results shown in figure 4.13-B reinforce the results of the preliminary testing; guaiacol did remarkably well at removing glass, the backsheet dissolved and the EVA did not completely dissolve during the test but remained swelled. The cell material could be separated from the remaining EVA with mechanical force using tweezers, the results in figure 4.13-B show results after trying to manually separate the layers. The measured weight change of the final guaiacol results was 21%, this included recovered swelled EVA.

The measured weight change of the oleic acid sample reflects a much more gradual change. The sample experiences a rapid increase in weight in the first hour as exposed EVA is swelled. This increase in weight slows during the interval between 1 and 4 hours and the weight peaks at 4 hours with a 63% increase in wetted weight. There are two probably causes for the slower increase in weight; first oleic acid has shown a poor ability to diffuse into the inner sections of the EVA, limiting its effect to the EVA at the outer edges of the sample. The second cause for the slowing weight increase is that EVA is dissolved by the solvent, reducing the measured weight. The weight change peaked at 63% at 4 hours. The weight change then decreased for the remaining 20 hours of the test. The final wetted test weight was measured at -21%. Figure 4.13-C and D show the initial sample and the results of the oleic acid testing. During this test, the outer layer of the backsheet was delaminated from the other composite layers, the core of the backsheet was cooked by high temperatures and became rigid and discolored but relatively intact. In figure 4.13-D the pitch black pieces of material are discolored fragments of EVA. These fragments of EVA were often found to contain a broken piece of cell material. The remaining EVA had considerable strength and took concerted and careful effort to remove. It is possible that the recovered EVA is primarily cross-linked EVA. Under this theory, the oleic acid would swell and dissolve uncrosslinked EVA while the crosslinked EVA, mainly at the interfaces, would remain intact and keep the PV sample layers laminated. The discoloration of the solvent is likely due to the leaching of silicon in the cell. Although oleic acid naturally becomes discolored over time, the pitch black discoloration is much more severe. The oleic acid also caused discoloration in the metal contacts, which suggests some leaching effects on the metals present in the cell material. The final change in sample weight was measured at -2%.

The mixture test did not result in the desired result, the test was stopped after 6 hours. The weight changes in the sample shown in figure 4.14 indicate the mixture has a result at a mid point between the oleic acid tests and the guaiacol tests. The first observation point shows the influence of the guaiacol in the system, causing a weight change peak at 68%. The weight change at this observation point is less then the guaiacol test. The backing material also did not dissolve during this test, indicating that local guaiacol concentrations were not sufficient to disrupt the backsheet material. The detriments of using a mixture appear in the subsequent observation points, as the test continues the guaiacol is evaporated to the point where it no longer affects the system and only the oleic acid remains. The remaining oleic acid in the mixture is then present at a lower temperature and lower volume then the oleic acid test limiting its effectiveness. Figure 4.13-E and F show the initial sample and the final result. The mixture sample has different makeup then the other samples, coming from a different section of the cut mini module, which may have influence the results. The results in figure 4.13-F show the influences of each solvent, a portion of the glass has been delaminated by the guaiacol; however, the remaining EVA has been discolored by suspected silicon leeching. Due to the mixtures poor performance it was not considered for the optimization. Continued research into using combined solvents would benefit from a two step process with one solvent used before the other. In the case of oleic acid and guaiacol, this process would have an initial guaiacol step followed by an oleic acid step. By splitting the chemical delamination process into two steps the positive aspects of the solvents can be utilized without interference of the other solvent.

4.2.2. Degradation Solvents During Extreme Conditions Testing

The degradation of both solvents was observed during the test under extreme conditions. Figure 4.15 shows the different degradations of both guaiacol (A and B) and oleic acid (C and D) in two time intervals. Both solvents begin as colorless transparent liquids at the beginning of each test but undergo browning during the tests. The probable cause for the browning of guaiacol is the oxidation of the solvent to water and tetraguaiacol. Oxidation of guaiacol is a well known cause of guaiacol discoloration. In figure 4.15-A the guaiacol is discolored by a combination of the dissolved backsheet and the beginnings of guaiacol oxidation. Figure 4.15-B shows that at the end of the guaiacol test the solvent has completely changed to a dark brown and is likely completely degraded. The oleic acid also showed major discoloration throughout its test. The oleic acid changes quickly from a colorless liquid to a deep brown in figure 4.15-C at 1 hour and then a pitch black liquid at 4.15-D. An investigation of possible reasons for this discoloration of oleic acid yielded no results. Coupled with the observations of the sample, it is suspected that the oleic acid is dissolving silicon from the PV sample.

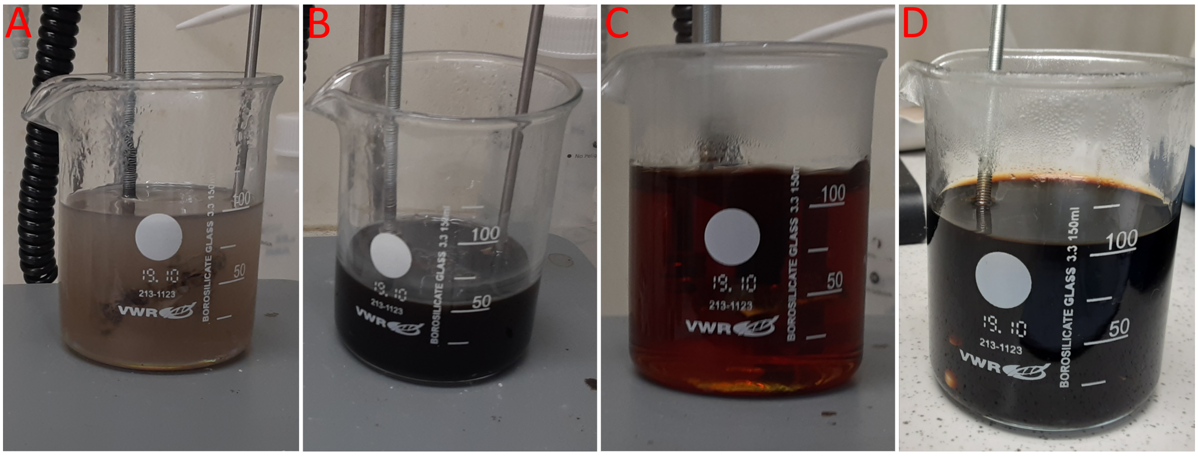


Figure 4.15: Comparison of solvents at different intervals. A = Guaiacol at 1 hour. B = Guaiacol at 4 hours. C = Oleic acid at 1 hours. D = Oleic acid at 4 hours. The figures show that in both cases the initial clear solvent browns during the solvent testing.

4.2.3. Summary of Extreme Conditions Testing

From the results of the extreme conditions testing, guaiacol was chosen as the solvent for optimization. The results of the weight change of the wet sample in Figure 4.14 indicate that guaiacol diffuses into and swells the EVA quickly. The swelled EVA then loose strength and glass fragments break away. Guaiacol showed a particular good ability to delaminate the glass in the PV sample. Dissolving of the backsheet increased the exposed area of EVA and likely led to a faster reaction. The temperature range of interest for the optimization was determined to be 80°C to 160°C due to more solvent degradation at temperatures above 160°C. The residence time range for the optimization was set at 30 minutes to 3 hours. This range will observe the how quickly the guaiacol reaction occurs at lower residence times and avoid complete oxidization of the solvent at higher residence times.

Oleic acid was not selected for optimization but remains a solvent of interest for further research. Oleic acid showed a good ability to dissolve the EVA but possible has trouble with dissolving crosslinked EVA. The weight changes observed in figure 4.14 indicate that after an initial swelling of EVA the sample remains intact and slowly dissolves the EVA. Oleic acid at 280°C showed signs of leeching silicon causing the solvent to go from clear and transparent to an opaque black. Oleic acid also resulted in discoloration of the metal contacts. It is possible that the addition of ultrasound would be beneficial to chemical delamination in this process. Ultrasound has been shown to increase the speed of reaction and increase the ability of a solvent to dissolve cross-linked EVA. Oleic acid's high boiling point and no hazards are also conducive to ultrasound as the most common chemical delamination method using ultrasound uses toluene, a flammable and toxic solvent.

The mixture test displayed results that put it in the middle between the oleic acid and guaiacol tests. The idea behind the testing of the mixture was that both solvents, guaiacol and oleic acid, target different parts of EVA, the polar and non-polar segments respectfully. Additionally, observations of the solvents indicated complementary strengths of each solvent; fast diffusion through the EVA and good separation of the layers for guaiacol, and dissolution of the EVA by the oleic acid. The result indicates that the combined solvents do not have a greater effect than the individual solvents and, in fact, show the weaknesses of both solvents. Notably, the backsheet did not dissolve despite more guaiacol being being present in the system then in preliminary tests. Continued research into combined solvents should focus on multiple step applications. For guaiacol and oleic acid together the first step would be the use of guaiacol to swell the EVA, dissolve the backsheet and disrupt the EVA-glass interface then the use of oleic acid to dissolve the EVA. This general two step chemical delamination process could be used for any polar and non-polar solvent pairing.

4.3. Optimization

Optimization of the chemical delamination process was carried out for guaiacol. The test factors used were temperature and residence time in the ranges of 80-160°C and 0.5 to 3 hours respectfully. The results measured in the optimization were the amount of EVA removed, the amount of backsheet detachment, and the silicon content of the solvent aqueous solution. A detailed explanation of the procedure for measuring results is provided in section 3.3. Fifteen test runs were planned, an extra test run was performed to help clarify the high temperature tests.

The completed experimental matrix is detailed in table 4.2. The order of the experimental runs was determined by the Stat-Ease® 360 software [34]. The test were conducted over two weeks using the same testing equipment and materials. In all tests, the glass in the sample remained intact.

Table 4.2: Optimization testing matrix. The largest amount of EVA removed occurred in tests runs 8 and 16. Backsheet removal was fully achieved when the backsheet was dissolved at 160°C but failed to be removed at lower temperatures. Silicon content remained low in all test runs.

Run Number	Temperature (°C)	Time (hours)	EVA Removed (%)	Backsheet Removal (%)	Silicon Content (ppm)
1	120	0.5	2	0	0.01
2	120	1.75	7	30	-0.01
3	160	1.75	10	100	0.01
4	80	0.5	1	0	0.00
5	80	3.0	0	35	-0.01
6	120	3.0	9	37	-0.01
7	160	3.0	31	100	0.05
8	160	0.5	32	100	0.00
9	80	0.5	0	0	0.01
10	160	3.0	25	100	0.01
11	80	3.0	2	0	0.02
12	120	1.75	6	43	0.03
13	80	1.75	6	10	0.01
14	160	0.5	7	100	0.03
15	120	1.75	9	36	0.02
16	160	3.0	32	100	0.04

4.3.1. Optimization Results and Models

The following subsection details the results of each response and the models created by the Stat-Ease® 360 software [34] to optimize and predict the result of tests within the given range. The each response is detailed and discussed separately.

EVA Removal

The EVA removal response was the primary response observed to quantify the success of a test run. The amount of EVA removed was calculated from the dry weight of the sample after the test and corrected for the weight of the glass, silicon wafer and backsheet with equations 3.2, 3.3 and 3.4. During the tests some general observations on the chemical delamination procedure using guaiacol could be observed.

The primary observation is that of the two test factors used, temperature played a much more significant role in resulting EVA removed then residence time. The different temperatures resulted in EVA removal ranges of 0-6% for 80°C test runs, 2-9% for 120°C test runs and 7-32% for 160°C test runs. At the highest temperature, the largest amounts of EVA removed favored longer residence times especially the 3 hour test runs; however the highest EVA removal occurred in runs 8 and 16 which occurred at 160°C with residence times of 0.5 and 3 hours respectfully. This suggests that the residence time of the process is much less important when compared to temperature.

The increased size of the sample compared to the preliminary and extreme conditions test coupled with an intact glass layer slowed the delamination process considerably, specifically in test runs that had a temperature (80-120°C). This observation indicates that the ability of guaiacol to diffuse into the EVA is more limited with fully intact modules. This observation suggests that at lower temperatures the guaiacol chemical delamination process is not scalable for fully intact modules. Figure 4.16 shows a simplified representation of the exposed EVA in a module, when the backsheet is not dissolved the EVA exposed is limited to the EVA exposed at the edges, denoted as P in the diagram. When the module is scaled the amount of EVA exposed scales slower then the total volume of EVA and would likely increase the time required to achieve a similar result; table 4.3 shows that the volume of EVA scales twice as fast as the exposed EVA on the perimeter. For lower temperature processes other factors should be included into the methodology, such as ultrasound, intentional breaking of the glass or cuts into the backsheet to increase exposed EVA. At the highest temperatures, the backsheet is dissolved in the solvent. When the backsheet dissolves the area of EVA exposed to the solvent substantially increases from a small perimeter of EVA to the entire backside area; in figure 4.16 this equates to the inclusion of the term B when considering the amount of EVA exposed. In table 4.3 the additional benefit to sacrificing the backsheet can be seen, the exposed EVA which is dominated by the newly exposed backsheet area scales with the volume of EVA and indicates that this method could be used on larger modules.

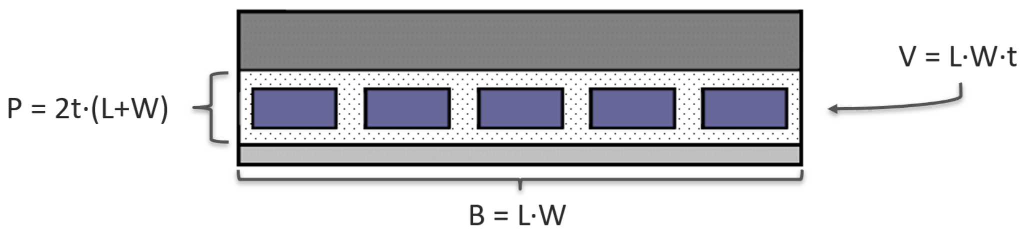


Figure 4.16: Simplified diagram of solar module EVA area and volume. The perimeter exposed EVA (P) is a function of the length (L), width (W) of the sample and the thickness (t) of the EVA. The backside EVA (B) is a function of the length (L), width (W) of the sample. The volume of EVA in a module (V) is a function of the length (L), width (W) of the sample and the thickness (t).

Table 4.3: Effect of scaling on exposed EVA and EVA volume. Volume of EVA increases faster than exposed EVA area when backsheet is not dissolved. The perimeter exposed EVA (P) backside EVA (B) and volume of EVA in a module (V) are detailed in figure 4.16.

Sample Condition	Exposed EVA (m^2)	Module EVA Volume (m^3)	Scaled (2X) Area (m^2)	Scaled (2X) Volume (m^3)
Intact Module	P	V	2P	4V
Backsheet Dissolved	P+B	V	2P+4B	4V

The EVA removal response method has some possible sources of error that must be considered when analyzing the results. The primary possibility of error in this method would be the determination of what EVA is determined to be detached at the end of a test. In every test run EVA was swelled by the guaiacol but the swelling in EVA has a spectrum of effects. The effects on EVA could range from EVA separating fully from the sample, EVA delaminating from from the glass and or silicon but still effectively connected to the sample or EVA only swelling but possible to remove by force. The guideline used for determining EVA removal was to limit as much as possible any forced removal. The EVA removal response tries to isolate EVA that separated from the module during the test run or was separated from the module during retrieval from the solvent as results. It is possible that much more of the EVA could be removed if a different post-test processing method was used.

A linear model was determined to be the best fit for the response. The response surface for EVA Removal is displayed in figure 4.17. The color scale of the surface is set as the maximum and minimum results observed; examining figure 4.17 shows that the response surface does not reach the maximum observed EVA removal in the given ranges of time and temperature. Equation 4.1 is the equation for calculating the EVA removal response surface.

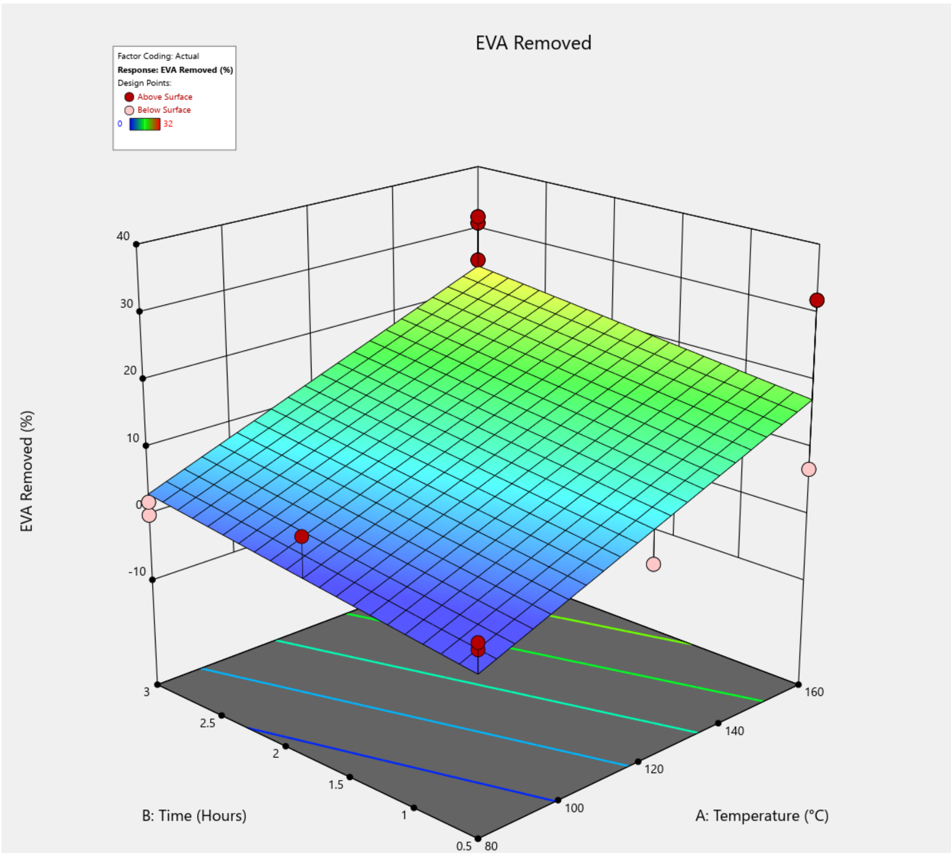


Figure 4.17: Modeled EVA removal response surface. The graph shows that the largest amount of silicon is predicted to occur at the 160°C and 3 hour boundary condition.

$$EVARemoved = 0.260 \cdot Temp + 2.638 \cdot Time - 25.477 \tag{4.1}$$

The analysis of variance values for the linear EVA removal model are detailed in table 4.4. The F-value of the model of 12.56 indicates that the model is significant and that there is a 0.009% chance the responses observed could occur due to noise. The model responses, temperature and time, have a p-value of 0.0005 and 1.644. P-values below 0.05 imply a significant testing factor; this indicates that temperature is significant in the model. Time with a p-value of 0.1644 indicates the factor is not a significant model term.

Table 4.4: Analysis of variance values for EVA removal linear model. P-values indicates that the model factors are significant when compared to the noise of the system. Temperature is the most significant of the test factors.

Source	Sum of Squares	df	Mean Square	F-value	P-Value	
Model	1365.60	2	682.80	12.56	0.0009	significant
A-Temperature	1173.71	1	1173.71	21.59	0.0005	
B-Time	118.05	1	118.05	2.17	0.1644	
Residual	706.83	13	54.37			
Lack of Fit	358.50	6	59.75	1.20	0.4034	not significant
Pure Error	348.33	7	49.76			
Cor Total	2072.44	15				

The fit statistics of the linear EVA removal model are provided in table 4.5. The adjusted R-squared value and the predicted R-squared value are reasonably close, indicating that the model will be accurate to future data points. The adeq precision value, a ratio of signal to noise, has a value 8.578 which is higher then the desired threshold signal to noise ratio of 4.

Table 4.5: Fit statistics for EVA removal linear model. Adeq precision indicates that the signal to noise ratio is adequate for the model.

Std. Dev.	7.37	**R^2**	0.6589
Mean	11.19	**Adjusted R^2**	0.6065
C.V. %	65.91	**Predicted R^2**	0.4397
		Adeq Precision	8.5782

Backsheet Removal

The backsheet removal response was a secondary response observed in an attempt to quantify the ability of the solvent to diffuse into the PV module and critically disrupt the EVA-backsheet interface bond. The amount of backsheet removal was calculated by comparing the delaminated area with the total area of the module as seen in figure 3.6.

The method used to quantify backsheet removal has some significant problems in its implementation that must be considered prior to evaluating the results. The area in which the backsheet was removed was defined by marking the boundary that the backsheet had been removed during the process. This method is subject to significant human error which can skew the results recorded. The images captured for the analysis were taken by hand; in the future if this response method is used, a jig should be created to standardize all photos. Due to the criteria defined in the methodology, the area of backsheet removal was only the area delaminated during the process. However, it was observed that once a certain area of the backsheet was delaminated, the remaining backsheet could be peeled off with force. The ability of the solvent to allow the backsheet to be peeled off is not reflected in the results. Finally, distribution of test run factors is not granular enough to accurately define the discontinuity that occurs when the backsheet begins to dissolve. In guaiacol the backsheet dissolves in less than five minutes, which means that in given the time range all observations above a certain temperature will have 100 % backsheet removal as defined in the methodology. The number of test runs used was not sufficient to fully define both the backsheet removal by diffusion and the backsheet removal by dissolving. Future studies should split the tests between backsheet removal due to diffusion or dissolving for more accurate results. Due to the amount of error that may be present in this response it was not used when calculating the desired optimum test conditions.

Despite the possible error in this response, some observations can be made. For test runs that removed the backsheet by diffusion (temperature at 80 or 120°C), no delamination was detected for the 0.5 hour tests. When the time is increased in for these temperatures the amount of backsheet removal increase to a range of 30-43%. The backsheet area can be divided between the wafer area and the glass area, each about 60 and 40% of the total area respectfully. The observations indicate that the guaiacol is able to diffuse into and delaminate the backsheet well up until the silicon wafer when the EVA between the wafer and the backsheet is around half that between the glass and the backsheet. Due to the rate of degradation and evaporation of the solvent a closed system where guaiacol is recovered and reintroduced would be recommended. At a temperature of 160°C the backsheet dissolves. During these tests the backsheet dissolves within 5 minutes of exposure to guaiacol.

A quadratic model was determined to be the best fit for the response. The response surface for backsheet removal is shown in figure 4.18. The color scale of the surface is set as the maximum and minimum results observed; Examining Figure 4.17 shows that the response surface reaches the minimum and maximum values of backsheet removal observed. Equation 4.1 is the equation for calculating the backsheet removal based on the response surface. Due to the limited number of data points, the model assumes a gradual increase of delamination instead of a discontinuity when the backsheet becomes soluble in guaiacol. It is probable that the predicted values are more accurate at lower temperatures.

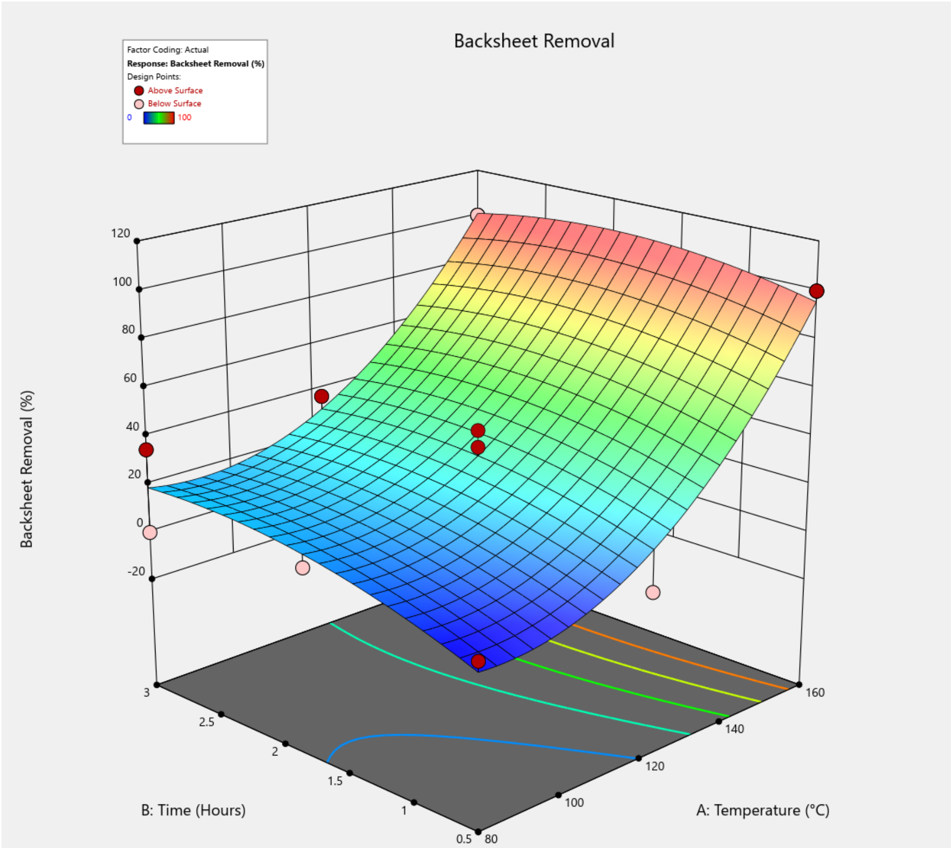


Figure 4.18: Modeled backsheet removal response surface. The surface response indicates that temperature is the primary factor when removing the backsheet.

$$
\begin{aligned}
BacksheetRemoval = 0.018 \cdot Temp^2 - 2.974 \cdot Temp - 0.090 \cdot Temp \cdot Time \\
+4.503 \cdot Time - 5.159 \cdot Time^2 + 107.551
\end{aligned}
\tag{4.2}
$$

The analysis of variance values for the quadratic backsheet removal model are detailed in table 4.6. The F value of the model of 43.26 indicates that the model is significant and that there is a 0. 01% chance that the observed responses could occur due to noise. In the model, the temperature model terms are the most significant while the time terms are insignificant.

Table 4.6: Analysis of variance values for backsheet removal quadratic model. P-values indicates that the model factors are significant when compared to the noise of the system. Temperature is the most significant of the test factors.

Source	Sum of Squares	df	Mean Square	F-value	P-Value	
Model	26412.82	5	282.56	43.26	<0.0001	significant
Temperature	22165.13	1	22165.13	181.52	<0.0001	
Time	544.01	1	544.01	4.46	0.0610	
AB	175.94	1	175.94	1.44	0.2577	
A^2	2287.31	1	2287.31	18.73	0.0015	
B^2	183.76	1	183.76	1.50	0.2480	
Residual	1221.12	10	122.11			
Lack of Fit	523.95	3	174.65	1.75	0.2431	not significant
Pure Error	697.17	7	99.60			
Cor Total	27633.94	15				

The fit statistics of the quadratic backsheet removal model are provided in table 4.7. The adjusted R-squared value and the predicted R-squared value are reasonably close, indicating that the model will be accurate to future data points. The adeq precision value, a ratio of signal to noise, has a value 16.3274 which is higher than the desired threshold signal-to-noise ratio of 4.

Table 4.7: Fit statistics for backsheet removal quadratic model. Adeq precision indicates that the signal to noise ratio is adequate for the model.

Std. Dev.	11.05	**R^2**	0.9558
Mean	49.44	**Adjusted R^2**	0.9337
C.V. %	22.35	**Predicted R^2**	0.8684
		Adeq Precision	16.3274

Silicon Content

The results of the silicon content are divided into separate sets, runs 1 to 10 and runs 11 to 16. Each set of silicon content sets were corrected by a control test conducted at the same time, the results of the control test were 0.01 and 0.08 ppm respectfully. The amount of silicon present for all test runs was considerably small. The quantities of silicon content are extremely close to the resolution of the testing procedure. This indicates that overall no significant silicon leeching was occurring during the delamination process and the discoloration of the guaiacol is due to oxidation. The model suggested by the Stat-Ease® 360 software [34] was a linear model.

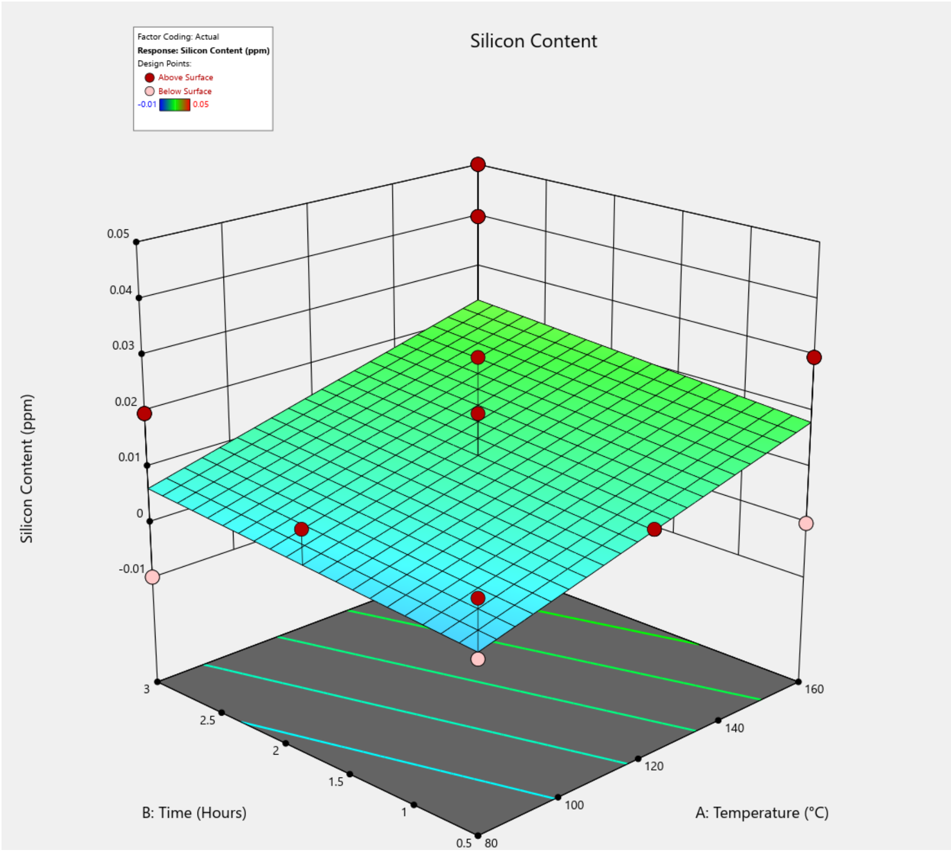


Figure 4.19: Modeled EVA removal response surface. The graph shows that the largest amount of silicon content is predicted to occur at the 160°C and 3 hour boundary condition. The red dots show that many recorded values reside above the response surface.

The analysis of variance values in table 4.8 indicate that the model is not significant with respect to noise. Additionally, both test factors have a p-value greater then 0.05 indicating no significant effect by either factor. The fit statistics in figure 4.9 also indicates that the signal to noise ratio is not adequate for the model. Instead the mean value for silicon content would be a more accurate predictor. The mean value for silicon content is 0.012 ppm.

Table 4.8: Analysis of variance values for silicon content linear model. P-value indicates that the model factors are not significant when compared to the noise of the system.

Source	Sum of Squares	df	Mean Square	F-value	P-Value	
Model	0.0009	2	0.0005	1.59	0.2408	not significant
A-Temperature	0.0008	1	0.0008	2.76	0.1206	
B-Time	0.0001	1	0.0001	0.2565	0.6210	
Residual	0.0038	13	0.0003			
Lack of Fit	0.0011	6	0.0002	0.4901	0.7983	not significant
Pure Error	0.0027	7	0.0004			
Cor Total	0.0047	15				

Table 4.9: Fit statistics for silicon content linear model. Adeq precision indicates that the signal to noise ratio is inadequate for the model.

Std. Dev.	0.0171	$\mathbf{R^2}$	0.1967
Mean	0.0131	**Adjusted** $\mathbf{R^2}$	0.0731
C.V. %	130.44	**Predicted** $\mathbf{R^2}$	-0.2142
		Adeq Precision	3.0386

4.3.2. Optimized Experimental Conditions

Using the response models the optimum experimental conditions can be obtained. The backsheet removal model was not used due to potential errors and the silicon content model indicated that it was not significant relative to the system noise. As such, the system is optimized to maximize the removal of EVA. Optimizing with this criterion provides the boundary condition of 160°C for 3 hours. The predicted EVA removed is calculated at 24%.

Validation of Optimization

Three validation runs were performed to test the created model. The results of the validation runs compared to the predicted value can be seen in table 4.10. The validation runs indicate that the predictive model is not accurate under the optimized conditions. The relative error in the EVA removed observations is 79%. The error in this prediction can be attributable to various factors; first, the model predictive model is hampered by the lower temperature runs in which the backsheet does not dissolve. It is probable that when the backsheet does not dissolve that the amount of EVA removed is linear; however, these results suggest that once the backsheet begins to dissolve due to temperature the behaviour may be non-linear. A second factor in the large error from the predicted EVA removal is the relative success of the validation runs compared to the experimental runs that make up the design matrix. Validation run 1 was the least successful of all the validations, yet had an EVA removal value in the upper range of those observed in the original experiments. Validation runs 2 and 3 had the most successful test runs with 60 and 41% of the weight of EVA removed, much greater then any of the original test runs. Section 4.3.3 examines and discusses these individual test runs in depth. The silicon content of the validation runs is comparable to that of other observation points and does not suggest any silicon leeching by the solvent.

Table 4.10: Predicted values and results of validation runs. Results indicate that the predictive model is inaccurate for the amount of EVA removed, silicon content remains near the prior recorded resolution.

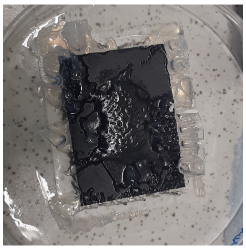
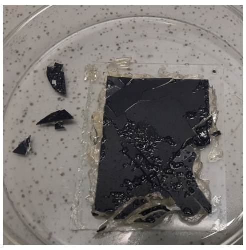
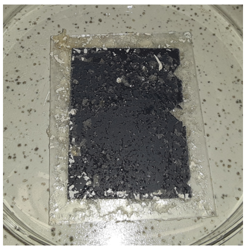
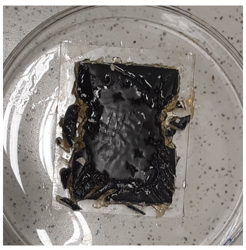
Validation Run	EVA Removed (%)	Silicon Content (ppm)
Predicted	**24**	**0.012**
Val 1	32	0.03
Val 2	60	0.01
Val 3	41	0.02
% Error	**79**	**39**

The results of the validation show that the model is not accurate enough to predict the amount of EVA removed at a given temperature and residence time. The optimized test conditions did provide the largest amount of EVA removed in any test, the optimal test conditions were found to be 160 °C for 3 hours. The experimental matrix should be split between test runs that do and do not dissolve the backsheet. New test runs would be needed in order to provide accurate surface responses. The optimal test conditions are at the boundary of the testing conditions; larger temperatures and residence times should be considered to improve the process. To utilize increased temperatures and residence times, test sets should transition to a pressurized closed system with an environment that prohibits oxidization.

4.3.3. Discussion of Individual Experimental Runs

During the experimental process of optimizing the simple guaiacol delamination process three notable test runs were observed. These test runs were run 8, validation 2 and validation 3. The result of these three tests can be seen in table 4.11, included in this table is the result of run 7 for comparison. Each of the three test runs shows that the silicon wafer is exposed, and in the case of validation run 2 the wafer is almost completely free of EVA on one side. In comparison to these notable testing results run 7 shows the more common result observed, the EVA on the glass only interface is removed, while the EVA on the wafer creates a shell layer that is not removed. It should be noted that the shell layer of EVA is still swelled EVA and could be removed with tweezers. In the three notable tests, instead of creating a shell, the EVA swelled and easily peeled off from the various interfaces exposing the silicon wafer. The run 8 test is particularly notable for occurring in only 30 minutes and keeping the silicon wafer intact. Validation run 2 almost completely freed the wafer on one side, though the wafer fractured pieces of the material could be removed by hand.

Table 4.11: Results of selected test runs: Run 8, Validation 2 and Validation 3. Run 7 results included for comparison. Validation runs 2 and 3 showed an increased amount of removed EVA compared to the more common outcome seen in run 7. Run 8 achieved a similar amount of removed EVA as run 7 in one sixth the time.

Run	Temperature (°C)	Time (Hours)	EVA Removed (%)	Visual Result
Run 8	160	0.5	32	
Val 2	160	3	60	
Val 3	160	3	41	
Run 7	160	3	31	

No definitive reason could be determined for the different results observed. Further testing is needed to determine what causes this outcome and if it can be reliably repeated. Some possible reasons for the difference in results can be proposed; a defect that occurred in the lamination process, minor variations in the test setup, a difference in guaiacol break down between tests or variation in the local EVA composition of polar elements could be possible reasons for the results. The amount of EVA removed by validation run 2 shows promising results for this process and use of guaiacol as a solvent. Test run 8 also suggests that the residence time of this chemical delamination process could achieve the same results in less time.

The continued investigation into this process should aim to reduce unknowns in the system. The test setup should transition to a closed system that reduces or prevents oxidization of the guaiacol during the test. More experiments should be conducted to get a more accurate observation of the variance in testing results and if the individual test results of note are outliers or if they regularly occur.

5 Conclusion and Recommendations

This chapter provides a summary the research conducted in this report and recommendation for continued research. Section 5.1 provides conclusions on the literature review study, solvent selection, solvent screening, and in depth studies into specific solvents. Section 5.2 recommends possible pathways for continued development of chemical delamination.

5.1. Conclusion

A literature review of existing research provided information on previous developments in chemical delamination and the current direction of research. The standard approach to chemical delamination has focused on c-Si photovoltaic modules encapsulated with ethylene vinyl acetate and laminated with glass and a composite plastic backsheet. The most popular solvent to delaminate modules is toluene, an abundant chemical produced with fossil fuels. Current research has focused on speeding up the delamination process by using different pretreatment methods on the photovoltaic module or using ultrasonic irradiation. One research paper performed a case study of a green solvent for chemical delamination indicating that the scientific community is aware that a more sustainable solvent is required for chemical delamination to be compatible with a circular economy. The criteria for evaluating the success of chemical delamination vary widely between studies. Coupled with the fact that these criteria often use similar nomenclature, careful consideration is required. Often times the final results of these research papers could not be directly compared.

Preliminary Testing was conducted on eleven solvents that were selected on the basis of a combination of factors: known reaction to EVA, a high boiling point, green solvent potential, minimal hazards and low cost. Four of the solvents, castor oil, cyrene, γ-valerolactone and pinacolone had little to no effect on the EVA and should not be considered as possible solvents for this process. Observations of both benzyl alcohol and xylene showed good reactions to EVA but both solvents are outperformed by similar solvents, benzaldehyde and toluene respectfully. Toluene and benzaldehyde were the best fossil fuel based solvents tested. Toluene served as a benchmark for comparing the other solvents. Toluene at 80°C separated the PV module layers but EVA remained on the sample indicating full dissolution was not achieved. Benzaldehyde did not dissolve the EVA but swelled it so that the adhesive bonding of the layers breaks down. Guaiacol, oleic acid and 2-MeTHF were found to be potential green solvents for chemical delamination. Guaiacol does not full dissolve EVA but separates the layers by breaking the bonds at the interfaces. Guiaiacol does not dissolve EVA because it is reacting with the minority polar elements that make up EVA. Utilizing temperatures near its boiling point (205 °C) guaiacol displays results comparable to toluene. Oleic acid is an extremely stable and safe solvent that is able to dissolve EVA. 2-MeTHF shows promising results and could be considered as a solvent for low temperature chemical delamination applications.

Guaiaicol and oleic acid were selected as solvents for further investigation. Testing was conducted for extreme experimental conditions using an open system. Guaiacol was found to be fast acting on the EVA at high temperatures. Under the extreme conditions the guaiacol test was stopped after 4 hours at 160°C when 53% of the weight of the solvent was evaporated. This suggests that guaiacol would benefit from a closed system were evaporated guaiacol is recaptured. The oleic acid test was carried out for 24 hours at 280°C with only a 24% change in the weight of the solvent during that time. The results of the oleic acid test indicate that oleic acid dissolves a large portion of the EVA but is unable to fully remove all of the EVA under these conditions. Additionally, the oleic acid dissolves the silicon in the PV material. The silicon leaching of oleic acid was not a desired outcome of this report, as intact cell material was the objective; however, the use of oleic acid may have applications in alternative photovoltaic recycling scenarios.

An optimization was conducted using a simple testing setup with guaiacol as the solvent. The success of a test run was primarily evaluated by isolating the weight of EVA removed during the test. This evaluation was possible due to strict documentation of the weight of all the materials in the sample prior to lamination. Secondary evaluations on the amount of backsheet removed and the silicon content in the resulting aqueous solvent solution provide context for the sample condition after the test. The result of the optimization found that the predicted optimum test condition were at the boundary conditions of the test at 160°C for 3 hours. The driving test factor in the system was found to be temperature, residence time did have an effect but was much less significant. This suggests that increasing temperatures further could lead to faster and more complete delaminations. For guaiacol this would require a pressurized environment with a non reactive gas to avoid oxidation of the solvent.

The validation tests of the optimization model indicated that the model is notably conservative. This is likely due to two distinct scenarios being present in the testing results; lower temperature tests where the backsheet remains intact and higher temperature tests that dissolve the backsheet and expose more EVA area to the solvent. The design of experiment method used targets the minimal number of test runs required to define a predictive equation for a result. In this case the low number of tests was not compatible with the discontinuity present in the system and notable deviation of results at high temperatures. The highest amount of EVA removed during the testing was in validation run 2 when 60% of the EVA was removed in 3 hours.

5.2. Recommendation

The objective of this report was to further the collective knowledge of chemical delamination as a method for PV recycling, to recommend alternative solvents and to change the established methodology.

Guaiacol, oleic acid, and 2-MeTHF are solvents that are useful for chemical delamination and have the potential for sustainable green production. Guaiacol has the most promising reaction to EVA, and results showed that the best delamination results occurred at the upper range of the solvents' ability under atmospheric conditions. Testing guaiacol in an environment that inhibits oxidization and allows for higher temperatures with pressurization is recommended.

Different solvents allowed different responses to be measured. It is recommended that initial screening of solvents remains broad and qualitative in order to not unduly reject a solvent. When the chemical delamination method is optimized, the measured responses should conform to what the solvent allows rather than a standard set of responses. A final test format should be adopted by the chemical delamination research community which clearly defines the testing procedure, the sample condition, the solvent used and response measured. Standardization of a final test would allow for a more direct comparison of solvents and methods between studies and reduce the amount of repeated research.

Multi-step chemical delamination processes should be considered to utilize the strengths of different solvents. The testing of a mixture indicated that the combined solvent performed worse than the solvents individually. By splitting the delamination process into multiple steps the benefits of each solvent could be fully utilized. An example of a multi-step process could be: an initial step using a polar solvent (e.g. guaiacol) to dissolve the backsheet and separate glass. A nonpolar solvent (E.g. toluene or oleic acid) could then be used to dissolve the remaining bulk EVA and free the cell material. The multi-step process could be changed to best suit the properties of the solvents and optimize the speed of delamination and the energy use in the recycling system.

Scalability and cost of the chemical delamination process requires further research. The experiments carried out in this report illustrated the importance that the initial sample condition played in the chemical delamination process. The experiments were conducted on a laboratory scale and indicated that under atmospheric conditions without supplementary equipment the chemical process will not be sufficient for the required throughput and speed of industrial recycling but may be applicable for small scale applications. For larger modules, processes that require diffusion of the solvent through an intact module will encounter significant challenges in the speed of delamination and the throughput of the system. Intact glass sheets reduce the speed of delamination, when applicable, consideration should be given to shattering the glass prior to delamination. It is recommended that dissolution of the backsheet be considered in future chemical delamination research. Sacrificing the backsheet during the process allows larger amounts of EVA to be exposed to the solvent allowing for faster and scalable delamination. The results of this report suggest that conducting chemical delamination at higher temperatures and pressures are required, this could be achieved through the use of a pressure vessel to allow for more extreme conditions in the entire system or ultrasonic irradiance which produce localized high temperature and pressure conditions. A cost comparison and analysis between the strengths of ultrasound and a pressurized system would be beneficial for future studies.

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A

Result Data and Solvent Information

Table A.1: Optimization and validation test sample material weights.

Run Number	Sample Number	Glass Weight (g)	Backsheet Weight (g)	Average Wafer Weight (g)
Run 1	14	3.342	0.889	0.385
Run 2	18	3.327	0.886	0.385
Run 3	34	3.359	0.904	0.385
Run 4	26	3.373	0.890	0.385
Run 5	27	3.331	0.893	0.385
Run 6	17	3.306	0.921	0.385
Run 7	20	3.347	0.906	0.385
Run 8	32	3.332	0.901	0.385
Run 9	13	3.366	0.892	0.385
Run 10	38	3.328	0.906	0.385
Run 11	12	3.306	0.899	0.385
Run 12	9	3.326	0.907	0.385
Run 13	29	3.331	0.893	0.385
Run 14	35	3.334	0.903	0.385
Run 15	31	3.322	0.913	0.385
Run 16	24	3.373	0.865	0.385
Val 1	37	3.321	0.905	0.385
Val 2	33	3.360	0.906	0.385
Val 3	11	3.325	0.913	0.385

Table A.2: Hazards of selected solvents from Chemwatch Gold.[24]

Solvent	Pictograms	Hazards
Benzaldehyde		H302 - Harmful if swallowed.
Benzyl Alcohol		H302 - Harmful if swallowed. H302 - Harmful if inhaled.
Castor Oil		H315 - Causes skin irritation. H319 - Causes serious eye irritation. H335 - May cause respiratory irritation.
Cyrene		H315 - Causes skin irritation. H319 - Causes serious eye irritation. H335 - May cause respiratory irritation.
γ-Valerolactone		H302 - Harmful if swallowed. H315 - Causes skin irritation. H317 - May cause an allergic skin reaction. H319 - Causes serious eye irritation. H335 - May cause respiratory irritation.
Guaiacol		H302 - Harmful if swallowed. H315 - Causes skin irritation. H319 - Causes serious eye irritation.
2-MeTHF		H225 - Highly flammable liquid and vapour. H302 - Harmful if swallowed. H315 - Causes skin irritation. H318 - Causes serious eye damage. H335 - May cause respiratory irritation. H336 - May cause drowsiness or dizziness.
Oleic Acid	None	Not Applicable.
Pinacolone		H225 - Highly flammable liquid and vapour. H302 - Harmful if swallowed. H304 - May be fatal if swallowed and enters airways.
Toluene		H225 - Highly flammable liquid and vapour. H304 - May be fatal if swallowed and enters airways. H315 - Causes skin irritation. H336 - May cause drowsiness or dizziness. H361d - Suspected of damaging the unborn child. H373- May cause damage to organs through prolonged or repeated exposure.
Xylene		H226 - Flammable liquid and vapour. H312 - Harmful in contact with skin. H315 - Causes skin irritation. H332 - Harmful if inhaled.

Table A.3: Optimization and validation test result data.

Run Number	Sample Number	Initial Weight (g)	Final Weight (g)	Initial EVA Weight (g)	Final EVA Weight (g)	EVA Removed (%)
Run 1	14	6.032	6.001	1.415	1.384	2.2
Run 2	18	6.008	5.905	1.410	1.307	7.3
Run 3	34	6.045	5.008	1.397	1.264	9.5
Run 4	26	6.051	6.042	1.403	1.393	0.7
Run 5	27	6.010	6.005	1.400	1.395	0.4
Run 6	17	6.036	5.906	1.424	1.294	9.1
Run 7	20	6.021	4.683	1.383	0.951	31.2
Run 8	32	6.014	4.667	1.395	0.950	31.9
Run 9	13	6.068	6.067	1.425	1.424	0.1
Run 10	38	5.980	4.732	1.360	1.018	25.2
Run 11	12	5.993	5.961	1.403	1.371	2.3
Run 12	9	6.064	5.983	1.446	1.365	5.6
Run 13	29	6.071	5.979	1.461	1.370	6.3
Run 14	35	6.033	5.032	1.411	1.313	6.9
Run 15	31	6.067	5.930	1.447	1.311	9.5
Run 16	24	5.991	4.688	1.368	0.930	32.0
Val 1	37	6.013	4.718	1.403	1.012	27.9
Val 2	33	6.089	4.321	1.438	0.576	60.0
Val 3	11	5.992	4.523	1.368	0.812	40.6