Investigation of the reliability of the encapsulation system of photovoltaic modules

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Investigation of the Reliability of the Encapsulation System of Photovoltaic Modules

By

Dan Wu

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Abstract

Good reliability of the encapsulation system of Photovoltaic (PV) modules is crucial to ensure the long-term performance of PV modules. A carefully controlled lamination process is required to produce a reliable encapsulation system. To date, the influences of different lamination conditions on the reliability of the encapsulation system are poorly understood. To predict the performance of the encapsulation system, the correlation of the reliability of the encapsulation system with various stress levels is required, which is poorly developed. This thesis improves the understanding of these issues by investigating the correlation of different lamination conditions with the reliability of the encapsulation system and the degradation of adhesion strength under variable damp-heat conditions.

The influence of the curing temperature and curing time on the long-term reliability of the encapsulation system is investigated from various viewpoints such as curing level of EVA, chemical and optical stability of EVA and adhesion strength within the encapsulation system. The correlation of curing level and lamination quality has been identified. The effects of over-curing are demonstrated. Results show that the chemical stability, optical stability and the adhesion strength between encapsulant and backsheet increases with the increasing curing level. However, the best long-term adhesion performance at the glass-encapsulant interface is obtained at lower gel content. Too high curing can cause problems of bubble generation, discoloration and unstable interfaces. Among those identified degradation phenomena, interfacial adhesion strength demonstrates the fastest and the largest degradation.

The reliability of the adhesion strength is further examined under different stress levels. Among different environmental stress factors, moisture is considered to cause the greatest problems of adhesive interfacial stability.
Therefore, the adhesion strength is investigated under different damp-heat conditions. A methodology is developed that can be used to model the adhesion degradation induced by moisture at different humidity and temperature conditions. To do so, a stress model is established which enables a quantitative description of the moisture related stresses on PV modules. Based on this model, an exponential correlation is established between the adhesion strength and the humidity and temperature levels. This enables the comparison of adhesion strength of PV modules operating at different humid environments.
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6. Degradation of Interfacial Adhesion Strength within PV Modules during Damp-Heat
1. Introduction

The development of Photovoltaic (PV) devices has gained great improvement in the last few decades. One factor impeding greater deployment of PV technology is the higher cost of electricity generated by the devices compared to conventional energy such as fossil fuels. Levelised cost of electricity (LCOE) can be used to assess the cost-effectiveness of different technologies. It is the ratio of total life cycle costs of the system divided by the energy produced over the system life generating a value in $/kWh [1,2]:

\[
\text{LCOE} = \frac{\text{Total Life Cycle Cost}}{\text{Total Lifetime Energy Production}}
\]

From Eq 1.1, it can be seen that the total lifetime energy production is one of the important factors influencing the LCOE of the PV installation. It is the sum of electricity produced during the lifetime of the product. Energy production is mainly influenced by the amount of solar irradiance, the module rating, device power-to-energy performance and power degradation. It is shown that power degradation is the largest performance risk as is demonstrated in Figure 1.1 [3]. Therefore, the study of PV module degradation is of commercial importance to allow the correct estimation of energy output and lifetime and subsequently the financial feasibility of a PV system.

Figure 1.1 Relative lifetime energy production influenced by different factors (R, E and D stand for the module rating, the device power-to-energy performance and the power degradation, respectively) [3]
Field experience has shown that the degradation of PV modules is mainly caused by encapsulation related problems such as delamination, encapsulant material decomposition and interconnect issues etc. [4-6]. Good packaging is thus crucial to ensure the long-term reliability and lifetime of PV modules. For crystalline silicon (c-Si) PV modules, the cells are predominantly protected by polymeric encapsulant material that is sandwiched between a front cover (mostly glass) and a back cover (mostly polymeric backsheet) [7,8]. The encapsulant material together with the front glass and backsheet forms the most common encapsulation system of PV modules. Issues such as how to produce more reliable encapsulation systems and how the encapsulation systems perform under different environmental conditions are not well understood and the improvement in understandings on these issues is the aim of this thesis.

The encapsulation of PV modules is normally conducted through lamination process where temperature and pressure is applied upon modules during which the encapsulation materials experience chemical and physical changes to seal the solar cells and form a protective system with high weatherability. Carefully control of the lamination process can result in PV modules with more reliable encapsulation systems. A general review of the lamination procedures are given in Chapter 2.

The reliability of the encapsulation systems depends on various factors including the types of the encapsulation materials, chemical composition including the additives, the state of materials such as the thermal history, stress state and spatial structure, the properties of the materials as well as the environmental stresses. The state and the properties of the materials are mostly influenced by lamination processes. Issues such as how the lamination processes influence the quality of the encapsulation material, whether material with the same initial properties have the same long-term reliability are not well understood. These issues are the main focus of Chapter 5 which investigates the effects of different
curing temperature and time on the long-term reliability of the encapsulation system of PV modules from the viewpoints of the curing level of the encapsulant material, the chemical and optical stability of the encapsulant material and the adhesion strength between different layers within the encapsulation system.

The reliability of the encapsulation systems also depends on experienced stresses. There are different degradation mechanisms under different stress factors with different degradation rates under different stress levels. The influence of different stress factors on encapsulation system is reviewed in Chapter 3. There has been a lot of research investigating various degradation phenomena related to the encapsulation system such as delamination, material hydrolysis, discoloration and corrosion etc [9-11]. However, these studies are normally based on progressive uncontrolled ageing or carried out at a single controlled operating condition and cannot supply information of the correlation between degradation and environmental conditions. This correlation is studied in Chapter 6 with the focus on the interfacial adhesion strength. The adhesion strength is investigated under different well controlled damp-heat conditions with the aim to develop a methodology to compare the adhesion strength under different humidity and temperature conditions.

To carry out the studies in Chapter 5 and Chapter 6, different characterisation methods are required which are presented in Chapter 4.
2. Photovoltaic Module Manufacture

Manufacturing of PV modules generally incorporates a lamination process which is reviewed in this chapter. A PV module is a multilayer system and the lamination process is used to establish protection for the solar cells from the external environment by the use of encapsulation materials. The structure of the module is firstly introduced in section 2.1. Within the module structure, the encapsulant material is very important as it bonds together the cells with the front and back protection layers. As ethylene vinyl acetate (EVA) is the dominant material used in the PV industry, a detailed description on EVA is given in section 2.2 together with short introduction on several other encapsulant materials. Detailed procedures on lamination are given in section 2.3. During lamination, the EVA is crosslinked and the different layers are bonded together. The curing level of EVA and the adhesion strength between different interfaces within module structure are two of the most important factors used for quality control. This is discussed in section 2.4 with the analysis of the mechanisms of both crosslinking and adhesion formation.

2.1 Structure Configuration of PV Modules

Solar cells are generally fragile and if the cells are directly exposed to the atmosphere, the active circuitry will be damaged. Therefore, solar cells are generally encapsulated and packaged in a way to protect the cells from outdoor stresses and give structural support. Figure 2.1 shows a typical structure of a PV module. The cell matrix is enclosed by a polymeric encapsulant with a protective layer at both the front and the back of the cells. The modules generally incorporate a frame, which is used to give structural support and as a mounting point for the modules when incorporated in a system. Alternatively unframed laminates would either be incorporated as BIPV element in a building or use
back rail support structures for mounting. A junction box is glued on the back cover to protect the electrical connections which generally exit through the rear of the module.

![Figure 2.1 A typical PV module structure](image)

The top layer of the module must have a high light transmittance to maximise photon absorption of the cells. The most commonly used material is tempered low-iron glass with light transmission above 90% at wavelengths between 400-1100nm and a thickness around 4mm [12]. In order to reduce the influence of ultraviolet (UV) irradiance on the encapsulant beneath the glass, a UV screen may be applied, e.g. cerium dioxide to absorb UV. To reduce reflectance losses, the glass is sometimes coated with a layer of anti-reflective coating material. The front sheet can also be a transparent polymer such as polyethylene terephthalate (PET). The substitution of glass with PET can reduce the weight but the light transmittance of PET is smaller than glass which will lower the total energy generated. The other drawback of using a polymeric film as a front cover is that it is permeable to oxygen and water vapours and also to UV if the front-cover is non-UV screening. The mechanical strength is also less stable than the glass superstrate. The general weatherability is thus not as good as the design with a glass front sheet.
Encapsulant materials bond the cells with both the front and the back covers. The main functions of the encapsulant should include: providing mechanical support of solar cells; maximise optical coupling for different layers; separate cells from environmental stresses, like pollutants, rain, hail etc; and supply thermal conduction [8]. Various types of polymeric materials have been used as an encapsulant in the PV industry, such as silicone, EVA, polyvinyl butyral (PVB), polyurethane (TPU) and thermoplastic polyolefin (TPO). But 80% of the market is dominated by EVA as a result of good weathering resistance, high optical transparency, easy processing, low modulus and low cost [13]. EVA is also the only encapsulant material available for this study. Therefore, the encapsulant material used in this thesis is EVA.

The back supporting layer protects the module from UV, moisture and weather attack while acting as an electrical insulator. In most cases, it is multilayer polymeric laminate. Commonly used materials are TPT (Tedlar™/PET/Tedlar™), TPE (Tedlar™/PET/EVA), PPE (PET/PET/EVA), PVDF (Polyvinylidene fluoride) /PET/PVDF (Polyvinylidene fluoride). Glass can also be used as a back supporting layer. The advantages of using a double glass structure have been investigated to have better moisture barrier, and good UV resistance. However, the double glass encapsulation prevents the release of generated volatiles and other reaction products. These trapped products sometimes can lead to more degradation [14]. Besides, the double glass encapsulation system increases the cost and weight of the modules and adds difficulty for installation. Additional barrier layers can also be inserted into the design of the backsheet such as a metal foil which provides better isolation of cells from environmental stresses but meanwhile, just as the double glass encapsulation system, may trap the generated volatiles. The PPE material is one of the most popular backsheets in the PV market and is the only backsheet material available for this study. Thus, PPE is used as the backsheet in this thesis.
2.2 EVA and Several Other Encapsulant Materials for PV Modules

2.2.1 Introduction of EVA

EVA is currently the most widely used encapsulant material for PV modules. EVA is a copolymer of ethylene and vinyl acetate (VA) with VA groups randomly distributed along the backbone. Since the 1970s, the Jet Propulsion Laboratory (JPL) has conducted a series of experiments on the selection and development of encapsulant materials that would provide PV modules for a lifetime of more than 20 years [15,16]. It was found that EVA had the highest quality to cost ratio. Following this selection, several different EVA formulas from both Dupont (trade name Elvax) and U.S. Industrial Chemicals Inc. (trade name Ultrathene and Vynathene) were further examined for suitability. The best choice was the Elvax 150 from Dupont with a vinyl acetate content of 33% and a melting index of 43. The cost for the Elvax 150 resin pellets is around $0.55-$0.65/lb while the cost for EVA sheets is around $2.4-$3.5/m².

Elvax 150 has a molecular composition of -(CH₂-CH₂)₆₋₁₄-(CH₂-CHAc)-. Research has shown that Elvax 150 are block materials which has two blocks, i.e. the semi-crystalline polyethylene block (53 wt %) and the amorphous copolymer block of ethylene and vinyl acetate (47wt %) [16]. Figure 2.2 shows the structure of EVA. For Elvax 150, the vinyl acetate is found only in the amorphous block and accounts for 33 wt% of Elvax 150. The rest 67 wt% of Elvax 150 is ethylene content which is distributed in both semi-crystalline and amorphous blocks. The composition of the amorphous block includes 70 wt % vinyl acetate and 30 wt % ethylene.
The virgin type of EVA is not stable and different kinds of additives are needed to ensure stability. Firstly, it is susceptible to chain scission and crosslinking reactions under UV irradiance. Although it is protected by a UV screening front cover, some amount of UV light can still be transmitted into the EVA and cause photo degradation. This risk can be avoided by adding UV screening agents within EVA, i.e. UV absorber and UV stabiliser. Figure 2.3 shows the UV absorption spectrum of some components within EVA. It can be seen that the base material (Elvax 150) mainly absorbs UV light in the range of 260nm-360nm with peak absorption intensity at 280nm. To protect EVA from UV induced degradation, a UV absorbing agent is added in EVA resins. Cyasorb UV 531 is one of the UV absorbers in the early development and it has strong absorption between 275nm-370nm. Besides UV absorbers, a UV stabilizer is also compounded into EVA. The function of the UV absorber is to absorb UV light and quench the excited states of the reactant while the UV stabilizer is to scavenge free radicals. However, the problem of the UV absorber and stabiliser is that they tend to deplete with time.
 Except UV degradation, EVA can also deteriorate by thermal oxidation. Under an oxidative environment, alkoxy or alkyl peroxide radicals can be formed which can then extract hydrogen from other products resulting in more active free radicals. The reactions of these free radicals with the base material can lead to different polymer degradation such as chain scission, chain branching and crosslinking. To avoid these oxidation reactions, antioxidants are needed to inhibit the derivative reactions by decomposition of the peroxides or reacting with the active free radicals to generate inactive radicals.

Thirdly, basic EVA material melts to a viscous state at temperatures above 75°C while real operating temperatures of PV modules can be higher. Some roof-mounted and building-integrated photovoltaics (BIPV) modules in hot area can result in module operating temperature higher than 90°C [18,19]. If it is directly utilised for PV module encapsulation, it will soften to a viscous melt at high temperatures, while shrinking and stiffening under cold weather conditions. This kind of thermal expansion and contraction may result in cell cracking and
delamination. This can be prevented by EVA crosslinking reaction to form a temperature stable elastomer. Crosslinking is a process to convert a thermoplastic material into a network format thermosetting material so that the material will not flow under elevated temperatures. Therefore, peroxide is added within Elvax 150 to activate a cross-linking reaction in EVA. The peroxide is inactive below 90°C or with negligible activity, so that no curing reactions occur when EVA is extruded into a film format under temperatures lower than 90°C. Under high temperatures, above 100°C, the peroxide will decompose to produce radicals, which react with the polymer to form the cross-linking reaction. The degree of cross linking can be expressed as gel content which is the percentage by mass of the three-dimensional parts of EVA.

Another issue of basic EVA is that it does not readily adhere to glass and backsheet. As such, an adhesion promoter is added, normally in the form of trialkoxysilane to improve the adhesion between EVA and glass. Covalent bonds will be formed between EVA and glass rather than only physical connections.

From the above discussion, it can be seen that EVA contains a complex formulation of additives with different functionalities. A stabilised EVA used for PV module encapsulation material usually contains a mixed composition including the bulk EVA copolymer, an UV absorber, an UV stabilizer, an antioxidant, a curing agent and an adhesion promoter [15,17,20]. Table 2.1 lists the typical components for a type of EVA including the trade name, the concentration, their functions, manufacturers and the chemical name. Most of the EVA manufacturers in the PV industry followed this recipe until now, although a lot of research is conducted to further optimise the properties of EVA. The virgin EVA pellets together with the additives is firstly compounded together. Then, they are extruded to form a continuous film. The extruded film retains the thermoplastic properties of Elvax 150.
Table 2.1 Typical composition of EVA [15,17]

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Formulation</th>
<th>Function</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elvax 150</td>
<td>100 ppc</td>
<td>97.943% EVA Copolymer</td>
<td>Dupont</td>
</tr>
<tr>
<td>Cysorb UV 531</td>
<td>0.3 %</td>
<td>0.294% UV absorber</td>
<td>American Cyanamid</td>
</tr>
<tr>
<td>Tinuvin 770</td>
<td>0.1 %</td>
<td>0.098% UV stabiliser</td>
<td>Ciba-Geigy</td>
</tr>
<tr>
<td>Naugard-P</td>
<td>0.2 %</td>
<td>0.196% Anti-oxidant</td>
<td>Uniroyal</td>
</tr>
<tr>
<td>Lupersol TBEC</td>
<td>1.5%</td>
<td>1.469% Curing agent</td>
<td>Lucidol/Pennwalt</td>
</tr>
</tbody>
</table>

(Note: ppc represents parts per 100 parts of EVA, % is the percent of weight of each component as a ratio of the total weight)

2.2.2 Other Types of Encapsulants for PV Modules

In addition to EVA, there are also various other types of polymeric materials which have been considered as encapsulants for PV modules. Some general requirements for the encapsulant materials include good resistance against thermal and UV degradation, low water absorption and permeability, strong adhesion, good mechanical and electrical properties, thermally consistent with the cell and glass, and easy processability.

In the early days of PV, the main encapsulants used were silicones, e.g. polydimethyl siloxane (PDMS) with a backbone consisting of alternating atoms of Si-O and side groups of CH₃- connected with Si (Figure 2.4). PDMS has a good reputation of thermal and UV stability. The bond dissociation energy of Si-O is around 108 kcal/mol which is much higher than that of C-C bonds of 83 kcal/mol that is normally the backbone of other encapsulant materials such as EVA and PVB [20]. The corresponding wavelength of light for dissociate Si-O is around 263nm which seldom exists in terrestrial solar radiation and tends to be blocked by the glass anyway. This is also the reason for silicone's excellent stability against UV light. Silicone also has low moisture absorption, low dielectric
constant and good adhesion to multiple substrates [21]. However, its high cost has meant that it shares a very small portion of the market.

![Polydimethyl Silicone (PDMS)](image)

Figure 2.4 Structure of PDMS

In the beginning of the 1970s, PVB has been utilised as a solar cell encapsulant material. The structure of PVB is presented in Figure 2.5. It features high transparency and strong bonding properties. It has good adhesive strength with glass, metal, wood and other materials [22]. However, it shows high moisture and UV sensitivity which is not good for maintaining the reliability of PV modules. But today’s formulations of PVB have greatly improved UV stability and moisture resistivity [23]. A commercial double-glass PV module using PVB as encapsulant material has been shown to have better safety performance than those laminated with EVA [24]. PVB is popularly used in thin film PV modules which are normally encapsulated by double layers of glass and BIPV applications because it is the one of the only encapsulant fulfilling the building regulations. However, it is only used in a small scale for c-Si PV modules.

![Polyvinyl Butyral (PVB)](image)

Figure 2.5 Structure of PVB
TPU is a thermoplastic polymer and is a relatively new material for PV encapsulation. The structure of TPU is presented in Figure 2.6. It has mechanical and optical properties comparable to EVA. Because of its thermoplastic property, crosslinking is not needed which can greatly reduce the cycle time of lamination and subsequently the cost. It also allows a vacuum free lamination using a roll laminator or other faster procedures. Besides, thermoplastic packaging offers the possibility of replacing the defective or broken cells. Bayer material science has developed a product named ETIMEX TPU-FILM VISTASOLAR [25]. Good optical and electrical properties were maintained for PV modules encapsulated with this type of TPU.

![Structure of TPU](image)

**Figure 2.6 Structure of TPU**

Research on the invention, development and optimisation of encapsulant materials that are optically, electrically, chemically and mechanically stable and cost effective are still ongoing. At this moment, EVA is still the dominant material and most of the potential materials have been eliminated or are only used in small scale because of cost, manufacturing or performance issues. Even with better performance and lower cost, the success of the new encapsulant materials will depend on how easy it is for module manufacturers to transit from EVA to the new material.
2.3 Lamination of PV Modules

2.3.1 Lamination Overview

For most c-Si PV modules, the encapsulation process is performed on a flat-bed laminator. The laminator is a chamber that is divided by a flexible membrane into two chambers, i.e. the upper one and the lower one (Figure 2.7). The upper and the lower chamber can be evacuated and ventilated individually. Before lamination, a stack material of glass, encapsulant material, cells, another layer of encapsulant material and a backsheet will be placed on top of the heating plate. The essentials of ideal lamination are to evacuate the laminator at a lower temperature and then cure EVA at a higher temperature to achieve the purpose of sealing the solar cells. Figure 2.8 shows a typical curing profile. There are three main steps involved [26-28]:

(a) Heat the laminator to the curing temperature under a vacuumed environment. The upper chamber is in vacuumed condition before the sample lay-up is placed inside of the laminator and is kept vacuumed throughout this step. The lower chamber needs to be evacuated within a certain time to degasify the module stack and the laminator. The temperature gradually increases to the desired curing temperature. With the increasing temperature, EVA gradually melts and softens. The mobility will increase which enables it to embed the cells without curing.

(b) In the second step, the curing reaction happens. After step (a), the temperature is increased to the desired curing temperature. The peroxide is normally already activated before the curing temperature but it reaches the highest rate at the set point. At this stage, the lower chamber continues to maintain vacuum while the upper chamber starts ventilation which generates pressure upon the modules until 100 KPa pressure is achieved. After crosslinking, the structure of the EVA macromolecules is loose. The application of pressure enhances the structure compaction. Pressure also
ensures intimate contact between different layers within the PV modules, which contributes to strong adhesion. The pressure also results in a good contact between the modules and the hot plate leading to good heat transfer. The pressure and temperature is maintained until the desired curing state is achieved. This step is the longest process during lamination.

(c) After the curing process, samples are cooled down and taken out of the laminator. In the early days of production, modules were cooled in ambient air. Nowadays, laminators often have an embedded cooling chamber so that modules are cooled through the special cooling system. After cooling, the upper chamber is evacuated to release pressure while the lower chamber is ventilated. Laminator is opened and the modules are removed from the laminator.
These processes are only general overviews of lamination and will be different depending on the types of laminator and the types of material. For step (a), some of the production starts directly at the curing temperature to reduce curing time and cost. Some of the production starts at a lower temperature than the curing temperature to avoid bubble formation. Some laminators have the pressure exerted before the curing temperature is achieved and the optimum curing temperature is reached in a short time after applying pressure. In order to obtain the optimum production profiles, lots of trials are needed for each type of material.

### 2.3.2 Factors Influencing Lamination Process

From the above described lamination processes, it can be seen that there are several parameters that need to be carefully controlled which influence the module quality:

(a) Temperature during Evacuation: if the temperature during the evacuation process is too low, the mobility of EVA will be too high when pressure is exerted in the curing step. This can result in shifting of cells and bending of busbar. However, if the temperature is too high, curing of EVA can occur in advance and gases may be trapped within EVA resulting in bubble generation and low adhesion strength.

(b) Curing Temperature: the curing rate of EVA increases with the increasing temperature. If the temperature is too high, curing occurs too quickly without completely removing the gases within the module structure and those generated during crosslinking. If the temperature is too low, curing rate will become slow, resulting in increased curing time and increased cost.

(c) Evacuation Time: this is to remove the gases within the construction to avoid the formation of bubbles. It also corresponds to the starting time of adding pressure. If the evacuation time is too short, it means pressure will be added upon the modules when the mobility of EVA is too high which can
result in shifting of cells and bending of the busbar. However, if the evacuation time is too long, the level of crosslinking of EVA will be too high.

(d) Ventilation Time: this determines how much pressure is applied upon the sample. With increasing ventilation time, pressure increases. If the pressure is too high, there will be higher risk of cell breakage. If the pressure is too low, the effectiveness of pressure to enhance adhesion is reduced.

(e) Dwell time: this is the dwell time for pressure applied upon the lay-up of PV modules. It is usually the longest time during lamination. A proper dwell time is needed to ensure crosslinking is neither too high nor too low.

(f) Cooling method: compared with the traditional natural cooling in the air, controlled cooling can accelerate the cooling rate which is good for reducing the potential of glass bending. There is also research which shows that the cooling process helps to reduce the residual thermal stresses within PV modules [29].

2.4 Quality Control of Lamination

2.4.1 Degree of Crosslinking

EVA needs to be cured to develop resistance towards melt, flow and creep. In order to assist the crosslinking reaction, peroxide is added in EVA to initiate the curing. Three major steps exist for the crosslinking reaction [30]. Firstly, the peroxide will decompose into free radicals which then extract hydrogen from the methyl group of vinyl acetate. This results in a methylene with a single electron. Two such methylenes can form a single C-C bond. Each of the methyl groups of vinyl acetate in EVA can contribute up to three free electrons and bond with three carbon atoms. A three dimensional network macromolecule is formed after crosslinking.
After crosslinking, the thermoplastic EVA is transformed into an elastomeric thermoset material. The hardness and tensile strength of EVA increases whereas the density and elongation-at-break decreases [16]. However, most of the properties of the base material are maintained after curing.

The degree of the crosslinking of EVA is often measured by Soxhlet extraction with the results expressed as gel content. There are no standardised requirements on gel content. Different EVA foil manufacturers have different recommended curing levels, ranging from about 60% to 90%. Gel content higher than 65% is claimed by the researchers from JPL as an acceptable level of curing [15]. This is because curing level higher than 65% ensures good mechanical-creep resistance. Photovoltaic Institute Berlin (PI Berlin) measured the gel content of 254 EVA sheets randomly extracted from 120 PV modules [31]. Results showed that over 65% of the EVA had gel content higher than 67%.

The curing level of EVA influences the mechanical, chemical and optical properties and thus the long-term reliability of the material. The curing level in the datasheet is the recommended level by the manufacturer which may change according to the lamination procedure. Careful control of the lamination process is important to achieve the best properties. However, there is a general lack of
understanding on how much gel content is needed to result in a reliable encapsulation system. This is discussed in this thesis by investigating the influence of different curing levels that are achieved by different lamination conditions on the long-term reliability of the encapsulation system.

2.4.2 Adhesion Strength

The PV module is a multilayer system with different interfaces. The interfaces are potential paths for contaminant ingress as well as leakage current [32]. Delamination can also happen within these interfaces, which has been observed in field exposed PV systems [33-35]. Delamination reduces the efficiency of the moisture barrier and results in further degradation mechanisms such as corrosion of metallic components, polymer decomposition, and light transmission losses [36]. The delaminated area will also suffer from reduced heat dissipation which has the potential to cause thermal fatigue and hot spotting [4]. Therefore, the interfacial adhesion strength is crucial for module reliability. These interfaces are bonded together during lamination with different mechanisms.

2.4.2.1 Adhesion Mechanism between Glass and EVA

A strong interfacial adhesion requires good wettability of the adhesive on substrate. Zisman [37] introduced the term of critical surface tension $\gamma_c$ to check the wettability of different liquids on solids. $\gamma_c$ is the value of the surface tension of a liquid, below which a drop of the liquid will wet and spread on the substrate, forming a zero contact angle so that any liquid having a surface tension lower than the critical surface tension can wet the surface. As a typical high energy surface, the critical surface tension of glass is on the order of thousands of dynes/cm while the surface tension of EVA is commonly within the range of tenth of dynes/cm, i.e melted EVA can wet the surface of glass [38]. Together with the applied pressure during lamination, the good wetting condition ensures
intimate contact of the molecules of EVA and glass.

For an adhesive-adherend system, it is often difficult to fully understand the mechanisms of the interactions at the interface. When the molecules of EVA meet the glass, there will be intermolecular interaction forces (van der Waals force). This force is inversely proportional to the seventh power of the distance between two molecules [39]. The intimate contact between EVA and glass maximises this force. The adhesion between EVA and glass may also receive contributions from mechanical interlocking. However, the dominant mechanism for the adhesion strength between glass and EVA is the silicon-oxygen covalent bonds that are formed between glass and the silane coupling agents within EVA.

2.4.2.1.1 Reaction of Silane with Glass

A most commonly used coupling agents for EVA in the PV industry is \( \gamma \)-hydroxy propylmethacrylic silane (\( \gamma \)-MPS) produced by Dow Corning with a trademark of “Z-6030”. The amount of silane used in EVA is preferably within the range of 0.1% to 1% phr (the weight ratio of the additives to Elvax 150 assuming the net weight of Elvax 150 is 100 pph) [40]. The silane coupling agent has a general form of \( X-(CH_2)_3-Si-(OR)_3 \). The silicon-oxygen bonds are formed through three main steps (Figure 2.10). Firstly, the alkoxysilane is hydrolysed to generate silanol. Each trialoxysilane molecule can generate mono-, di- and tri-silanols. The hydroxyl groups of the generated silanol can condense with each other to form oligomers with possible structures of dimer, linear and three dimensional siloxane. Then, when EVA meets glass, the uncondensed silanol from the first step will react with the hydroxyl groups at the surface of glass to form hydrogen bonds. After that, condensation reaction follows to eliminate a molecule of water and generate the siloxane (Si-O-Si) bonds between silane and glass. Some of the silanol may also react with each other to form siloxane bonds so that a three dimensional network is formed within silane. The dissociation energy of silicon-oxygen bond is around 453kJ/mol while that for the van der Waals' force is normally smaller.
than 5\textit{kJ/mol} [20]. Therefore, strong adhesion strength between glass and EVA is formed.

![Diagram of chemical reactions](image)

Figure 2.10 Steps for the formation of Si-O bond [41]

### 2.4.2.1.2 Graft of Coupling Agents onto EVA

The silane coupling agent is covalently bonded onto the EVA matrix through grafting reactions which is initiated by the peroxide (mostly TBEC) [41,42]. Figure 2.11 gives an example of the grafting reaction using γ-MPS as an example. The peroxide within EVA is first thermally decomposed to generate alkoxy free radicals. The alkoxy radical will either extract hydrogen from the backbone of EVA or share the free electron with the vinyl bond of silane coupling agents to generate alkyl radicals. The generated free radicals can then combine with each other so that the silane coupling agents can be grafted onto EVA. The generated free radicals can also combine with themselves and generate some byproducts. The peroxide added in EVA is also used to initiate the crosslinking reaction of EVA. Therefore, the crosslinking reaction and the grafting reaction occur at the same time during lamination. Normally, enough peroxide is added in EVA to complete the curing and grafting reaction so that some unused peroxide remains in the EVA after lamination.
2.4.2.2 Adhesion Mechanism between EVA and Backsheet

The backsheet of PV modules are typically three layers of polymers which are bonded together with adhesives (Figure 2.12).

- The outside polymer works as a protective layer to resist environmental attack such as moisture, oxygen and pollutants ingress and UV light deterioration.
- The middle layer is the core part supplying electrical insulation and mechanical support.
- The inner side of the backsheet is treated with primers often in the form of EVA with lower VA content than the bulk encapsulant EVA. This is to improve the adhesion strength between backsheet and encapsulant. The molecules of the two EVA can diffuse into each other and bond themselves together.
Figure 2.12 A typical structure of backsheet

The diffusion theory for adhesion was proposed by Voyutskii [43] who examined the adhesion between elastomers. They identified that the diffusion depends on factors like temperature, time and the properties of the diffusion molecules. Contact time between adhesive and adherend is one of the most important factors influencing polymer diffusion. The adhesion strength generally increases with the contact time. The mobility and diffusion coefficient of the polymer both increase with temperature so that the adhesion strength is sensitive to temperature. There are several models to describe the diffusion amongst which the most basic one is Fick’s Law [44]:

\[
\frac{dC(x,t)}{dt} = D \frac{d^2C(x,t)}{dx^2}
\]

(4.1)

\[
D = D_0 \exp \left( -\frac{E_d}{RT} \right)
\]

(4.2)

Where \(D\) is diffusivity at time \(t\), \(D_0\) is the pre-exponential factor, \(x\) is distance, \(t\) is time and \(C(x,t)\) is the material concentration at distance \(x\) in time \(t\), \(E_d\) is the diffusion activation energy, \(R\) is a constant and \(T\) is the absolute diffusion temperature.

2.4.2.3 Adhesion Requirements in PV Industry

In the PV industry, the adhesion strength is normally checked by a peel test. There are no standards on how much adhesion strength is needed. STR considers strength between EVA and glass greater than 53 N/cm measured by 180° peel test satisfactory. Pern and Glick [45] examined the adhesion strength between glass and EVA for samples of different types of EVA, different types of backsheet
and different glass cleaning methods. The measured 90° peel strength was in the range of 10 N/cm to 120 N/cm. The minimum adhesion should be higher than the weight of junction box and cables attached to the backsheet, i.e. larger than the predicted load. There currently is no agreement on the minimum adhesion strength and it remains an open question which requires a lot of further studies.

The value in the datasheet is often a minimum adhesion for any development and the adhesion can be improved by surface treatment and careful control of the production. This requires better understanding of the influences of lamination process on adhesion formation. Both curing level and adhesion strength are important for lamination quality. It is not known if there is a correlation between the two which will be studied in this thesis. Both properties are on the first approximation independent but both depend on the thermal regime the laminate has undergone, as curing and the effectiveness of adhesion promoter are both thermal active. The other issue for adhesion strength is that it decreases with time and delamination has been identified as a relevant failure mode for PV modules during outdoor operation. It is not clear how much adhesion is required to avoid delamination during outdoor operation. To do so, a correlation between adhesion degradation and environmental stress levels are needed. These issues will be studied in this thesis.

### 2.5 Conclusions

During lamination, EVA curing reactions occur and different layers within PV modules are adhered together. The curing level of EVA and the adhesion strength between different layers within PV modules are two of the most important quality control factors. Curing temperature and time have been identified as two of the major factors affecting the lamination quality. These different lamination conditions can result in encapsulation systems with different initial states and
properties which can further influence the long-term reliability. This triggers the aims of this thesis to investigate the influences of different lamination conditions on the reliability of the encapsulation systems of PV modules which is demonstrated in Chapter 5.
3. Degradation of Encapsulation System under Different Environmental Stress Factors

Investigation of the correlation of the reliability of the encapsulation system with environmental stresses requires understanding of the interaction between these different stress factors and the encapsulation system. Different stress factors cause different degradation mechanisms. Most of the time, they work cumulatively causing complex overall degradation.

The influencing stress factors mainly include irradiance, humidity and thermal stress. The effects of the three stress factors on the encapsulation system will be discussed separately in the following sections of this chapter. The reviewed degradation will focus on defects that have been identified during outdoor operation.

3.1 Irradiance Induced Degradation

For the influences of irradiance on encapsulation materials, UV light has the most destructive effects. UV light is a primary initiator for many reactions such as the photodecomposition, photo thermal and photo bleaching. Photons absorbed by the material can activate the polymer or the additives compounded into the polymer to create free radicals, initialising oxidation and other reactions.

Simulated photo degradation of the base EVA under UV light together with the effects of heat is demonstrated in Figure 3.1. The principal reactions are called Norrish I, Norrish II and Norrish III. In Norrish I, the side vinyl acetate group can dissociate from the main chain to form acetaldehyde followed by the formation of other gases, e.g., CO, CO$_2$ and CH$_4$ which have potential to further lead to bubbles in the module. In Norrish II, polyconjugated C=C bonds (polyenes) are
generated which have been widely considered as one of the most important chromophores causing EVA discoloration [9,46]. Besides polyenes, acetic acid is another product of Norrish II reaction which can catalyse the discoloration reaction and also act as one component to cause corrosion. The polyenes generated in Norrish II can further be oxidised to form α-β unsaturated carbonyl, which is another product leading to discoloration. In Norrish III, aldehyde is formed while the main chain becomes a ketone. In contrast to discoloration, there is another UV-light induced effect called photo-bleaching as a result of photo-oxidation. With sufficient oxygen and at a high enough temperature, the yellowed polyenes can be oxidised generating products that are more visibly clear. Photo-bleaching can lead to a colour changing of EVA from yellow back to clear.

Figure 3.1 Simulated photothermal degradation of EVA [17]

Besides the photodegradation of the base material, additives within EVA will decompose under UV light, generating free radicals that accelerate base EVA photodecomposition. The generated products may be chromophores that can
worsen EVA discoloration. As a result of low molecular weight, these additives can also deplete with time gradually losing their function of stabilising base EVA. Peike et al. [46] examined the discoloration rate of EVA with different additive formulations and found that EVA with a single additive whether it is a crosslinking agent or a UV stabiliser or a UV absorber or an antioxidant showed less discoloration than the EVA with combined additives. Pern [9] examined the discoloration of EVA with different formulations, curing conditions and different types of front covers under different UV light. It is found that a variety of factors influence the discoloration of EVA including the additives inside the EVA, depletion rate of the curing agent, UV absorber and UV stabiliser, UV light intensity, permeability of backsheet to allow oxygen ingress and causing photo-bleaching. Pern [47] also analysed the material properties of yellowed PV modules weathered outdoors for more than five years and found that with the darkening of EVA colour, the concentration of UV absorber (Cyasorb UV 531) decreased from 0.29wt% to nearly 0.15wt % while the gel content increased from 70% to 92%. The loss of UV absorber permits the penetration of UV light below 370nm to EVA causing more discoloration.

The main influences of the photo induced degradation on encapsulant properties are summarised in Figure 3.2. Discoloration is widely acknowledged and has been discussed a lot since the 1980s. Discoloured modules present colour change from clear to yellow to brown (Figure 3.3). EVA discoloration has the potential to reduce optical transmittance and thus module performance. A wide range of power losses of discoloured PV modules from nearly no degradation to around 40% power losses in 5 years was recorded. The most famous case is the browning of EVA within modules deployed in the Carrisa Plains PV power plant in central California. The overall module power performance losses are 35.9% from 1985 to 1990 while severe EVA browning occurred [48]. Berman et al. [49] tested 189 mirror-enhanced Solarex SX-146 modules which were in operation for five years in the Negev desert of Israel and extensive yellow-brown
appearance was reported. These browned modules have an average power
degradation rate of 1% per year. Springborn Laboratories [50] documented PV
module discoloration at different sites of California, New Mexico, Australia, Saudi
Arabia, Namibia, South Africa etc. from different manufacturers. However, these
documents are mostly incomplete and qualitative and it is difficult to get
information about the starting time of discoloration, dependence of discoloration
on environmental stresses, and induced power losses. More research is required
to understand the mechanisms and kinetics of PV module discoloration as well as
the induced power losses.

Figure 3.2 Irradiance induced degradation for Encapsulation materials

Besides discoloration, bubbles are another concern for encapsulant photo-
thermal degradation. In the process of photochemical degradation, gases of
different types can be generated with a potential to cause delamination which can enhance water ingress and cause further problems such as decoupling of light transmission and reduction of heat dissipation. Another problematic reaction product generated during photochemical ageing is acid such as acetic acid and carbon dioxides. The acidification may form electrolytes leading to metallisation corrosion. It may also cause increased conductivity of the encapsulant which can result in increase leakage current.

3.2 Humidity Induced Degradation

3.2.1 Moisture Ingress in PV Modules

The ingress of moisture into PV modules has been related to decreased performance and sometimes to accelerated degradation. Many degradation processes are moisture sensitive and the level of moisture content may vary by orders of magnitude from module surface to module interior. In order to understand the magnitude of humidity induced degradation, the first step is to quantify how much water can penetrate into modules under specific external environments with different encapsulation materials.

The ingress of moisture into PV modules occurs by diffusion. Miyashita et al. [51] inserted cobalt chloride (CoCl₂) paper into silicon solar cells with back materials of different water-vapour transmission rates (WVTR) to detect moisture ingress. Moisture ingress paths can be presented by Figure 3.4. Moisture ingress depends on the WVTR of the backsheet: moisture mainly permeates from the open edges when impermeable back material is used while moisture can diffuse from both backsheet and edges when permeable back material is utilised. Kempe [52] showed that moisture ingress from permeable backsheet is much quicker than that through edges. Moisture cannot penetrate through the cells but can move around the cells. Therefore, the outer area of the cells is more easily to be
corroded. Figure 3.5 is an electroluminescence (EL) image of a module before and after damp-heat exposure where darkening is observed to occur from the outer area of the cells towards the centre.

Figure 3.4 Schematic of moisture ingress route into PV modules

Figure 3.5 EL image of PV modules before (upper image) and after (lower image) damp-heat exposure

Water ingress is a moisture diffusion problem, which depends on the water concentration gradient and the diffusivity properties of the polymeric materials. It can be generally described by Fick’s law. According to Fick’s second law, the
water diffusion rate at certain time and certain distance through a thin membrane can be described as [44]:

\[
\frac{dC(x,t)}{dt} = D \frac{d^2C(x,t)}{dx^2} \tag{3.1}
\]

Where D is diffusivity, x is distance, t is time and C(x, t) is water concentration at distance x at time t. Based on Fick's law, Kempe [52,53] modelled the water ingress rate of different encapsulant materials for both glass-glass laminated and glass - (breathable) backsheet laminated modules. For modules laminated with impermeable superstrate and substrate, moisture enters into modules mainly through the sides of the encapsulant if there are no edge seals (Figure 3.4). The outer edge of the module was assumed to be in equilibrium with the surrounding environment. Assuming a one-dimensional model, the water concentration within the encapsulant material was calculated as following:

\[
C(x,t) = C_s + \frac{4C_s}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \sin \left( \frac{(2m+1) \pi x}{L} \right) \tag{3.2}
\]

Where \( C_s \) is the saturation concentration of encapsulant material, L is the thickness of the encapsulant material and m is the natural number used to solve the Fick's equation.

Besides Eq 3.2, moisture ingress can also be modelled as one-dimensional semi-infinite model which can generate the following equation if assuming an initial dry condition:

\[
C(x,t) = C_s \left( 1 - \text{erf} \left( \frac{x}{2\sqrt{D}t} \right) \right) \tag{3.3}
\]

Where \( \text{erf} \) is Gauss error function using \( \beta \) to represent the variables with the form as follows:

\[
\text{erf}(\beta) = \frac{2}{\sqrt{\pi}} \int_{0}^{\beta} e^{-\beta'^2} d\beta' \tag{3.4}
\]

This model is suitable for evaluation of short time moisture ingress at small distances (x) from the edge of a module while the trigonometrical series described in Eq 3.2 is more suitable for longer moisture ingress predictions. All of these models do not consider moisture ingress through cracks.
For modules with breathable backsheets, moisture ingress occurs mainly through the backsheet as shown in Figure 3.4. The water diffusion rate in encapsulants can be modelled using the following equation:

\[
\frac{dC_E}{dt} = \frac{WVTR_{BSat}}{C_{E, Sat}} (C_{E, Eq} - C_E)
\]  (3.5)

Integrating of Eq 3.5 yields:

\[
C_{(t)} = [1 - \exp\left(\frac{WVTR_{BSat}}{C_{E, Sat} t}\right)] \ast C_{E, Eq}
\]  (3.6)

Where the subscripts E, B and sat represent encapsulant, backsheet and saturated conditions. The development of these models is based on several assumptions. Firstly, uniform water concentration in the encapsulant is assumed because the encapsulant diffusivity is normally much greater than that of the backsheet. Secondly, the WVTR across the backsheet is supposed to be proportional to the concentration change.

Besides diffusion, moisture can also enter into modules through cracks by capillary action or through delaminated areas in which case the permeation can be very significant.

Measurement of moisture uptake within PV modules has been investigated by many researchers with the aim of developing non-destructive methods. This is complicated by the complex multi-layer structure of PV modules. Humidity sensors have been considered. Huyberechts and Frisson [54] laminated alumina electrodes within PV modules to measure the impedance changes of the encapsulant materials upon moisture ingress. Carlsson etc. [55,56] deposited a moisture-sensitive sensor of nanoporous TiO2 between the glass and encapsulant with a conductive coating electrode. The logarithm of the sensor’s resistance shows a linear dependence on water concentration. Lalaguna and the co-workers [57] investigated moisture absorption of laminates with back covers of different WVTR using a commercial capacitive humidity sensor. An integrated
circuit was incorporated in the sensor to translate the capacitive signal into voltage so that a proportional correlation was established between the voltage output and the relative humidity inside the modules. Besides sensors, the other popular way for moisture detection is using optical methods. Researchers from Dupont measured the moisture profiles within the structure of glass-polyvinylbutyral (PVB) - glass using fourier transform infrared (FTIR) spectroscopy techniques [58]. Moisture is infrared sensitive and the absorption peak is proportional to moisture concentration. Results also showed that the moisture ingress follows Fick’s diffusion law.

The absorbed water in polymers can exist in both mobile and bound phases [59,60]. In the mobile phase, moisture fills the free volume within the polymer. It can be transported through voids and become bonded with a certain likelihood. In the bound phase, chemical reactions occur and water molecules are bonded with the polymer. Iwamoto and Matsuda [61] studied the reaction of water in EVA and poly vinyl acetate by analysing the infrared spectrum within the range of 3300 cm\(^{-1}\) – 4000 cm\(^{-1}\) which is the absorption peak of the hydroxyl group. Four peaks were identified within this area corresponding to four different vibration modes of moisture that are hydrogen bonded to one or two C=O groups.

### 3.2.2 Effects of Moisture Ingress

Moisture can damage the packaging of PV modules in a number of different ways which are summarised in Figure 3.6.
Figure 3.6 Moisture induced degradation on the packaging system of PV modules

From the optical perspective, moisture ingress into encapsulants may cause light transmission reduction. McIntosh [62] analysed the optical degradation of encapsulants under damp heat condition of 85°C / 85% RH. Reduced light transmission of the encapsulants was observed. After drying out the samples, the absorption coefficient for both silicone and EVA increased, where small absorption shoulders were introduced at wavelengths of 250–500 nm; this translates to a 0.14% and 0.39% module efficiency losses for the silicone and EVA encapsulated PV modules, respectively. He pointed out that moisture can reduce material transmittance either by scattering the incident light or increasing the light absorption coefficient of the polymer.

Water absorption can also cause changes in the mechanical properties. With the uptake of moisture, molecule mobility will increase and thus plasticisation effects can occur [63,64]. This will further lower the glass transition temperature. A rule of thumb is that 1% of water absorption can lower the $T_g$ by 10°C for hydrophilic polymers [65]. Reduced tensile strength, elastic modulus and yield strength have been reported with the increasing of moisture absorption for different types of polymers [66-69]. Moisture absorption can also lead to
material swelling. Soles et al. [70] stated that moisture can reorganise the structure of flexible polymer to create more free volumes which can further enhance moisture absorption. Lin and Chen [71] identified faster and higher moisture re-sorption due to swelling effects. The swelling will introduce stresses to the material causing cracks, crazing and delamination [65].

Besides structural and mechanical degradation, moisture ingress will also decrease the insulation resistance of encapsulant causing safety issues. The conductivity values for bulk EVA, polymer/glass interfaces and surfaces have been modelled by Mon et al. [72] as a function of temperature, water concentration, and material permittivity which is also dependent upon moisture content. Increased leakage current was identified with increasing humidity levels [73].

Another concern of moisture ingress is the reaction between moisture and the encapsulation materials. Polymers such as EVA, PVB, TPE etc. that are used as encapsulation materials for PV modules often contain hydrolytic bonds which hydrolyse in the presence of moisture resulting in acidification and depolymerisation. The hydrolysis of encapsulation materials is widely reported [10,74-77]. Oreski and Wallner [10] examined the ageing of different types of backsheets and significant hydrolysis was observed for PET from ATR results. Chain scission was accompanied as a result of the hydrolysis. Acetic acid smell was noted for both outdoor and indoor exposed modules when they were disassembled [78,79]. Metallisation corrosion is another important issue related to water ingress. Corrosion can occur at cell grid lines, busbars and interconnects with a result of increased series resistance (Figure 3.7). The generation of acid can further catalyse corrosion. Kempe and the co-workers [77] measured the corrosion state using aluminum mirrors deposited on glass. They found that corrosion of the laminates with breathable backsheet is less than those protected
by impermeable backsheets which trapped the generated acetic acid inside the structure.

![Image](image.png)

Figure 3.7 Metallisation corrosion of PV modules [80]

In addition to the influences on bulk encapsulation materials, moisture uptake also deteriorates the joint strength. Firstly, moisture attack may cause bond decomposition, mostly in the form of hydrolysis, which in turn leads to reduced adhesion strength. Such a de-bonding reaction is normally accelerated by temperature [81]. The following is the hydrolysis case for siloxane bonds.

\[
M - O - Si + H_2O \leftrightarrow M - OH + HO - Si
\]  

(3.7)

Besides, due to the high permittivity of water, the presence of moisture will weaken the potential energy of ionic attraction [82]. These forces are inversely proportional to the relative permittivity of the medium. At room temperature, the typical relative permittivity (the ratio of the absolute permittivity of the material to that of the vacuum) of PET with a thickness of 5-50µm is around 2.5-4.5 while it is 80 for water, which means a small amount of water will lower the force significantly [83].

By displacing adhesives, moisture can also reduce the intermolecular forces such as van der Waals force and hydrogen bonds. Surface free energy can be used to determine the work of adhesion arising from interfacial molecular attractions.
The work of adhesion \( W_A \) to separate two interfaces in the medium of air can be expressed using the surface free energy of substrate \( \gamma_S \), surface free energy of adhesive \( \gamma_A \) and the interfacial free energy \( \gamma_{SA} \) [84]:

\[
W_A = \gamma_S + \gamma_A - \gamma_{SA}
\] (3.8)

Surface free energy can also be written as the sum of polar \( \gamma_p \) and dispersion \( \gamma_d \) components. Thus \( W_A \) can be rearranged as follows:

\[
W_A = 2(\sqrt{\gamma_S \gamma_A} + \sqrt{\gamma_p \gamma_p})
\] (3.9)

In the presence of moisture, \( W_A \) becomes:

\[
W_A = \gamma_{Sl} + \gamma_{Al} - \gamma_{SA}
\]

\[
= 2(\sqrt{\gamma_{Sl} \gamma_{Sl}} - \sqrt{\gamma_A \gamma_A} - \sqrt{\gamma_{Sl} \gamma_{Sl}} - \sqrt{\gamma_S \gamma_S} - \sqrt{\gamma_{Al} \gamma_{Al}} + \sqrt{\gamma_S \gamma_S} + \sqrt{\gamma_{Sl} \gamma_{Sl}}) \] (3.10)

Where \( \gamma_{Sl} \) and \( \gamma_{Al} \) are the interfacial free energies between substrate and water and that between adhesive and water respectively, \( \gamma_1 \) is the surface free energy of water. It can be seen from Eq 3.9, the work of adhesion is positive without the presence of moisture which means the adhesive system is stable. With the presence of moisture, the work of adhesion may turn into a negative value which indicates that the system is unstable and water can displace adhesive from the substrate [85]. The reduced adhesion strength can cause delamination of PV modules (Figure 3.8).

![Figure 3.8 Delamination of PV modules [35]](image-url)
3.3 Thermally Induced Degradation

Thermal effects on the encapsulation system of PV modules mainly come from changing temperature due to the mismatched coefficients of thermal expansion (CTE) between the assembly materials [84,86]. Under changeable temperature, materials will experience expansion and contraction. Due to the differences of CTE, the rates of material volumetric changes are different for different materials. Most of the time, these expansion and contractions are constrained due to material structure and properties. Thermal stresses are gradually built up which will eventually cause problems of creep, curvature, cracking and delamination. This kind of stress is especially defective for adhesive joints where delamination can occur to release the strains. Delamination can happen at the glass/encapsulant, encapsulant/cell and encapsulant/backsheet interfaces for c-Si modules while in a-Si module, extra adhesive and cohesive failure can occur between the encapsulant and back metallization layer [87]. It is reported that thermal cycling is responsible for most of the connection failures in PV modules [88].

Another important effect of temperature on the encapsulation system is the acceleration or reduction function on other degradation processes. Temperature usually works together with UV light accelerating various photo-thermal reactions. The water diffusion rate through encapsulants has been reported to be accelerated by temperature [52,58]. Other processes like corrosion, leakage current, diffusion of dopants, impurities etc. all occur more rapidly at higher temperatures.
3.4 Conclusions

The performance of the encapsulation systems of PV modules decreases under stress. Understanding the degradation of encapsulation systems under different environmental conditions can provide more information on PV module lifetime under specific conditions and what kind of quality is needed for modules before exposure so that long enough protection can be maintained.

Each of the degradation formats is often caused by multiple stress factors. Understanding of one degradation phenomenon can be achieved by investigating the contributions from each factor separately and then combine together. Among the discussed stress factors in this chapter, humidity is considered to cause the greatest and the most diverse problems which are accelerated by temperature. UV will cause different degradation mechanisms. And there are no available chambers for UV test. According to the history of the published qualification testing, failure rates for both c-Si modules and thin film module were highly related to damp heat and thermal cycling tests while the failure rate due to UV test is very low [89,90]. Therefore, this thesis only focuses on humidity and
thermal effects. Delamination is one of the most commonly identified defects for PV modules. The degradation of adhesion strength under humidity induced stresses is investigated in Chapter 6 with the aim to develop a methodology to correlate the degradation of encapsulation systems with different stress levels.
4. Experimental Development

4.1 Introduction

This chapter describes the experimental tools used in this thesis. There are two main experimental parts in this thesis which is outlined in Figure 4.1. The first part is the reliability study of bespoke laminates in dependence of lamination conditions. The aim of this part is to understand the influence of different lamination conditions on the performance of the encapsulation system of PV modules. The performance of the encapsulation system is assessed from chemical, morphological, optical, and mechanical viewpoints. Material characterisation methods of soxhlet extraction, differential scanning calorimetry study (DSC), fourier transform infrared (FTIR) – attenuated total reflectance (ATR) spectroscopy, transmittance measurements and peel tests are conducted. Soxhlet extraction is used to measure the gel content of EVA, DSC can also measure the curing level of EVA but also shows some morphology properties, FTIR-ATR is needed for chemical stability monitoring, transmittance measurement is to evaluate the optical property of the EVA and peel testing is used to measure the adhesion strength at different interfaces of the encapsulation system. The performance of the encapsulation systems is evaluated from both initial properties and long-term reliability through accelerated aging tests.

After having observed the general degradation behaviours of the encapsulation systems from the first part of the experiments, the second part of the experiments focusses on more detailed investigations of the interfacial adhesion strength degradation, focusing at the encapsulant-backsheet interface. The aim is to model the adhesion strength degradation of commercial mini-modules to withstand moisture ingress under different temperature conditions. Commercial modules are subjected to different damp-heat stress levels. In the second part, as
the main interest is on interfacial adhesion strength, experimental work mainly requires peel tests.

In the following sections of this chapter, each of these characterisation methods are discussed in detail including the soxhlet extraction test, DSC measurement, infrared spectroscopy test, transmittance tests and peel tests. Besides the different characterisation methods, the environmental stress tests are also introduced.

### 4.2 Soxhlet Extraction Test

#### 4.2.1 Apparatus and Reagents

Uncrosslinked EVA can be dissolved in some organic solvents such as xylene, toluene, and decalin. The solubility depends on the content of vinyl acetate (VA) and the rate of dissolution can be enhanced by heating or stirring. However, after
crosslinking, the macromolecule EVA is insoluble in any solvent. This is why the crosslinking degree of EVA can be measured by Soxhlet extraction method.

In this thesis, the gel content of EVA is measured through conventional solvent extraction method according to standard ASTM D2765-11 [91] using reagent grade xylene as solvent which has a boiling point of around 140°C. The testing apparatus is shown in Figure 4.2. It is a typical extraction kit with a 500mL round-bottom flask, a coil borosilicate condenser, and a heating mantle with sufficient capacity to boil xylene. Besides xylene, toluene is another widely used solvent but it is more toxic than xylene and that is why xylene is chosen here.

During the extraction, an anti-oxidant is required to inhibit further crosslinking or the formation of other free radicals which can degrade EVA. 2, 6 di-tert-butyl-4-methylphenol (butylated hydroxytoluene, “BHT”) is utilised as an antioxidant. The antioxidant is added to the reaction with a concentration of 1% wt.

![Figure 4.2 Extraction apparatus](image)

### 4.2.2 Testing Procedure

The extraction procedure is presented in Figure 4.3. An amount of EVA around 0.3g is tested and weighed to the nearest 0.001g. The amount is selected according to the standard ASTM D2765-11. The EVA is taken from different parts
of the sample and is cut into small pieces of approximately 2 X 2 mm², which is then placed into a cleaned, dry 120-mesh stainless steel pouch (weight \(m_1\)) followed by the determination of the weight of \(m_2\). The pouch is folded and submerged in the solvent. Then, 1% of antioxidant (3.5g) is dissolved in the xylene. The sample is extracted in xylene for 12 h. A rule of thumb for the solvent amount is 350 g xylene for a 500-mL flask or 500 g xylene for a 1000-mL flask or 1000 g xylene for a 2000-mL flask. After extraction, the cross-linked macromolecules of EVA cannot dissolve in xylene but will remain in the pouch while the uncrosslinked molecules can be extracted and dissolved in xylene. The remaining insoluble residue, together with the mesh, is dried at 150 °C in the oven for 4 h, then cooled in a desiccator and weighed (\(m_3\)). Xylene is reused until it darkens. The gel content of EVA can be expressed as the mass ratio of the undissolved part of EVA to the initial EVA mass:

\[
gel \ content = \frac{m_3-m_1}{m-m_1} \%
\]  

(4.1)

Figure 4.3 General procedures for EVA gel content test

Besides the solvent extraction, there are also other recently developed methods for EVA gel content measurement, such as DSC. The extraction method is time
consuming but more accurate, easy to operate and relatively inexpensive. The DSC method will be discussed in the following section.

4.2.3 Uncertainty Analysis of the Soxhlet Extraction Test

The major sources of uncertainty for the soxhlet extraction measurement are presented in Figure 4.4. The measurement uncertainty mainly comes from the instability of sample weighting, the non-uniformity of the sample, measurement processes and environmental effects. The expanded relative uncertainty of gel content measurement is calculated to be around ±0.9%. This uncertainty is stated as the standard uncertainty multiplied by a coverage factor k=2, which corresponds to a probability of approximately 95%. The uncertainty calculations are based on the ISO standard JCGM 100 [92]. The contributions of each component on the total uncertainty are described in details as follows:

Figure 4.4 Sources of uncertainty in soxhlet extraction test

4.2.3.1 Relative standard uncertainty due to $m_1$, $m_2$ and $m_3$, $u_r(m_1, m_2, m_3)$

4.2.3.1.1 Instability of the scale $u$(scale)
The scale used is Mettler Toledo AG245. The specification of the scale is listed in Table 4.1. All of the measurements are below 41 g for the soxhlet extraction test. Therefore, the readability is 0.01 mg. According to the uniform distribution, uncertainty due to the readability of the scale is:

\[
\begin{align*}
\text{u(readability)} &= \frac{0.01}{2\sqrt{3}} = 0.00289 \text{ mg} \\
\end{align*}
\]

Within the range of 0 - 41 g, the repeatability of the scale is 0.02 mg and the linearity is 0.03 mg. The standard uncertainty of the scale can be calculated by combining the three effects:

\[
\text{u(scale)} = \sqrt{\text{u(readability)}^2 + \text{u(repeatability)}^2 + \text{u(linearity)}^2} = \sqrt{(0.00289)^2 + 0.02^2 + 0.03^2} = 0.03617 \text{ mg}
\]

| Table 4.1 Specification for the Mettler Toledo AG245 scale |
|---------------------------------|------------------|
| Range                           | 210g/41g         |
| Readability                     | 0.1 mg/0.01 mg   |
| Repeatability                   | 0.1 mg/0.02 mg   |
| Linearity                       | ±0.2 mg/±0.03 mg |

4.2.3.1.2 Relative standard uncertainty of \( m_1 \), \( m_2 \) and \( m_3 \)

The standard uncertainty of \( m_1 \), \( m_2 \) and \( m_3 \) equals to the standard uncertainty of the scale.

\[
\text{u}(m_1) = \text{u}(m_2) = \text{u}(m_3) = \text{u}(\text{scale}) = 0.03617 \text{ mg} 
\]

The average of \( m_1 \), \( m_2 \) and \( m_3 \) are computed from measurements of 15 different samples, generating values of 2234 mg, 2565 mg and 2520 mg. The relative uncertainty of \( m_1 \), \( m_2 \) and \( m_3 \) can then be calculated as follows:

\[
\begin{align*}
\text{u}_r(m_1) &= \frac{\text{u}(m_1)}{m_1} = \frac{0.03 \, 617}{223 \, 4} = 0.001619\% \\
\text{u}_r(m_2) &= \frac{\text{u}(m_2)}{m_2} = \frac{0.03 \, 617}{2565} = 0.001410\% \\
\text{u}_r(m_1) &= \frac{\text{u}(m_1)}{m_1} = \frac{0.03 \, 617}{2520} = 0.001435\%
\end{align*}
\]
4.2.3.1.3 Combined relative uncertainty of \( m_1, m_2 \) and \( m_3 \) \( u_r(m_1, m_2, m_3) \)
The sources of uncertainty of \( m_1, m_2 \) and \( m_3 \) are not independent but are fully correlated. According to the standard JCGM 100:2008 [92], the combined standard uncertainty of fully correlated quantities is the linear sum of each component. The combined relative uncertainty of \( m_1, m_2 \) and \( m_3 \) can be expressed as:

\[
u_r(m_1, m_2, m_3) = u_r(m_1) + u_r(m_2) + u_r(m_3) = 0.004464% \quad (4.8)\]

4.2.3.2 Relative uncertainty due to the non-uniformity of EVA \( u_r(M) \)
Non-uniformity of cured EVA comes from two main sources. One is the non-homogeneity of the polymer due to production. The other one is the lamination processes due to the non-uniform distribution of temperature and pressure. The non-uniform curing level of EVA induced from lamination processes depends on the lamination conditions. It will be shown in chapter 5 that gel leakage will happen when the curing level is too low and the extraction method will no longer be suitable for these materials. For the investigated lamination conditions, the standard uncertainties due to the non-uniformity of EVA are obtained by repeating the measurement at nine different locations of EVA sheets, which generate uncertainties in the range of 0.002 to 0.004. The largest uncertainty of 0.004 is used to represent the worst case of the uncertainty due to material non-uniformity. This absolute uncertainty corresponds to an average gel content of 90%. The relative uncertainty due to material non-uniformity can then be calculated as:

\[
u_r(M) = \frac{0.004}{0.9} = 0.4444% \quad (4.9)\]

This uncertainty also includes the effects of environment and operation which are considered to be very small.
4.2.3.3 Expanded and standard relative uncertainty of the soxhlet extraction measurement

The standard relative uncertainty of the soxhlet extraction test is calculated as follows by combining the uncertainty due to weighting and material non-uniformity:

\[ u_r(\text{extraction}) = \sqrt{u_r(m_1, m_2, m_3)^2 + u_r(M)^2} = \sqrt{0.004464^2 + (0.4444)^2} = 0.44\% \quad (4.10) \]

For a coverage factor \( k=2 \), multiplying the combined relative uncertainty by 2, gives an expanded relative uncertainty of around 0.9\%. This gives a level of confidence of about 95\%. The calculation of uncertainty is summarised in Table 4.2.

<table>
<thead>
<tr>
<th>Sources of uncertainty</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combined uncertainty of ( m_1, m_2 ) and ( m_3 )</td>
<td></td>
</tr>
<tr>
<td>( u_r(m_1, m_2, m_3) )</td>
<td></td>
</tr>
<tr>
<td>Instability of the scale ( u(\text{scale}) )</td>
<td>0.03617mg</td>
</tr>
<tr>
<td>Relative uncertainty of ( m_1 )</td>
<td>0.001619%</td>
</tr>
<tr>
<td>Relative uncertainty of ( m_2 )</td>
<td>0.001410%</td>
</tr>
<tr>
<td>Relative uncertainty of ( m_3 )</td>
<td>0.001435</td>
</tr>
<tr>
<td>( u_r(m_1, m_2, m_3) )</td>
<td>0.004464%</td>
</tr>
<tr>
<td>Uncertainty due to EVA non-uniformity ( u_r(M) )</td>
<td>0.4444%</td>
</tr>
<tr>
<td>Standard relative uncertainty</td>
<td>0.44%</td>
</tr>
<tr>
<td>Expanded relative uncertainty</td>
<td>0.9%</td>
</tr>
</tbody>
</table>

From the above calculations, it can be seen that the uncertainty of the soxhlet extraction test mainly comes from the uncertainty due to material non-uniformity. The uncertainty due to sample weighting is not significant.
4.3 Differential Scanning Calorimetry Study (DSC)

4.3.1 DSC Principle
Differential scanning calorimeter (DSC) is a thermal analysis technique for material characterisation. The principle of DSC is to evaluate the temperature differences between a sample crucible and a reference crucible during heating up or cooling down processes [93,94]. Both the specimen and the reference crucibles are maintained at nearly identical temperature throughout the experiment. Thermal effects are generated from the sample when it is heated up or cooled down where physical or chemical changes happen. The difference in the energy input required to match the temperature of the sample to that of the reference is the amount of heat absorbed or released by the sample. The heat flow in or out of a sample vs. temperature is then determined. In this way, DSC can detect thermal transitions of polymers, such as melting or crystallisation as well as chemical reactions, like crosslinking or oxidation. In addition, when the mechanical state of the sample changes during thermal process, such as glass transition, although there are no endothermic or exothermic phenomena, a sudden change of the specific heat will happen which corresponds to baseline shift in the thermal curve.

4.3.2 Testing Procedure
In this study, the curing state and the morphological properties of EVA is characterised by DSC (TA Instrument Q2000 DSC). The machine has a temperature accuracy of ±0.1°C and a calorimetric precision of ±0.05% which is calibrated using indium. Standard aluminium pans are used with around 7 mg sample weighed to the nearest 0.001 mg measured each time. A hole-punch with a diameter of 4 mm is used to cut a round piece of sample to minimise sample variation. The thermal tests are conducted under nitrogen (N₂) flow to create an
inert and dry atmosphere with a constant flow rate of 50 ml/min. The heating and cooling rate is 10°C/min throughout the test.

The thermal process for testing EVA is as follows:

1. Heat up from ambient temperature to 250°C at a constant heating rate of 10 °C/min;
2. Cool down to -60°C at a cooling rate of 10 °C/min;
3. Heat up to 250°C at a constant heating rate of 10 °C/min (repeat the first run to check if the curing is complete or not)

4.3.3 Typical DSC Results of EVA

A typical DSC thermogram of the EVA used in this study is shown in Figure 4.5. Several transition peaks can be observed. Between 40-70 °C, there are two endothermic peaks which are due to EVA melting. The first melting peak corresponds to the imperfect crystalline phase while the second one reflects the primary crystallites of polyethylene [95]. In the second cycle, i.e. after recrystallisation, only the 2nd melting peak can be observed. At near 35°C, an exothermic peak appears which is known to be the re-crystallisation peak. A broad transition at -30°C is also identified which corresponds to the glass transition of EVA. The curing of EVA occurs in the region of 100-225 °C where a broad exothermic peak can be seen [96,97]. The enthalpy of this peak is proportional to the amount of residual peroxide in the EVA that is not contributing to the curing process during lamination. It can then be related to the peroxide that is used for crosslinking and thus the crosslinking degree. At the second cycle, this peak disappears which indicates that all of the unused peroxide has been consumed in the first heating up cycle. This method is used as a quick checking of the curing state of EVA and the results can be calculated based on the following equation:
curing state = \left( 1 - \frac{H_{\text{cured}}}{H_{\text{un-cured}}} \right) \% = \left( 1 - \frac{\left( \int_{T_s}^{T_e} \frac{\partial H}{\partial T} dT \right)_{\text{cured}}}{\left( \int_{T_s}^{T_e} \frac{\partial H}{\partial T} dT \right)_{\text{un-cured}}} \right) \% \quad (4.11)

Where $T_s$ and $T_e$ are the starting and ending temperature for crosslinking, $H$ is the enthalpy of the crosslinking reaction, $T$ is the temperature.

![Figure 4.5 DSC thermogram of EVA](image)

**4.3.4 Uncertainty Analysis of the DSC Measurement**

The possible sources of uncertainty of the DSC test for curing level measurement are illustrated in Figure 4.6.
4.3.4.1 Relative uncertainty of enthalpy measurement of cured EVA $u_r(H_{cured})$

The uncertainty of enthalpy measurement of cured EVA mainly comes from two main sources including the enthalpy calibration uncertainty and the uncertainty due to the non-uniformity of the cured EVA.

4.3.4.1.1 Relative uncertainty of enthalpy calibration $u_r(C)$

There are two main components contributing to the uncertainty of enthalpy calibration, i.e. the uncertainty of the standard reference material and the measurement repeatability.

4.3.4.1.1.1 Relative uncertainty due to standard reference material $u_r(S)$

The enthalpy and temperature of the DSC is calibrated using standard melt of indium by deterring its melting energy and temperature. The procedure is heating the material from 100°C to 180°C with a temperature ramp rate of 10°C/min under nitrogen environment. According to the manufacture’s calibration certificate, the certified value of indium melting enthalpy is 28.51 J/g ± 0.19 J/g. The uncertainty is defined under a coverage factor of 2 with a confidence level of 95%. Therefore, the standard uncertainty due to the
instability of the standard reference material is 0.08 J/g (0.19/2 = 0.08). The relative uncertainty can then be computed as:

\[ u_r(S) = \frac{0.08}{28.51} = 0.002806 \]  \hspace{1cm} (4.12)

4.3.4.1.2 Relative uncertainty due to enthalpy measurement repeatability \( u_r(R) \)

The uncertainty due to the repeatability of the enthalpy determination is obtained by measuring the melting enthalpy of the standard indium according to the procedure described in 4.3.4.1.1 by 10 times. The obtained mean value of the melting enthalpy of indium is 27.867 J/g with standard deviation of 0.5428 J/g (n=9). Thus, the uncertainty due to the repeatability of enthalpy determination is calculated as follows:

\[ u(R) = \frac{s}{\sqrt{n}} = \frac{0.5428}{\sqrt{10}} = 0.1716 \text{ J/g} \]  \hspace{1cm} (4.13)

The relative uncertainty can be calculated as:

\[ u_r(R) = \frac{0.1716}{27.867} = 0.006158 \]  \hspace{1cm} (4.14)

4.3.4.1.3 Relative uncertainty of enthalpy calibration \( u_r(C) \)

The relative uncertainty of enthalpy calibration can be obtained by combining the above two components using the following equation:

\[ u_r(C) = \sqrt{u_r(S)^2 + u_r(R)^2} = \sqrt{0.002806^2 + 0.006158^2} = 0.006767 \]  \hspace{1cm} (4.15)

4.3.4.1.2 Relative uncertainty of \( H_{\text{cured}} \) due to the non-uniformity of cured EVA \( u_r(M_{\text{cured}}) \)

The non-uniformity of \( H_{\text{cured}} \) of the cured EVA depends on the lamination conditions. For each lamination condition, it is obtained by measuring the curing enthalpy of 5 different cured EVA sheets. For the investigated lamination conditions, the obtained mean value of the melting enthalpy of the cured EVA ranges from 2.7 J/g to 11.2 J/g with standard deviation of 0.37 J/g to 0.77 J/g (n=4). The largest standard deviation of 0.77 J/g (n=4) is chosen to calculate the uncertainty due to the non-uniformity of the cured EVA.
\[ u(M_{\text{cured}}) = \frac{0.77}{\sqrt{5}} = 0.344 \, J/g \]  \hspace{1cm} (4.16)

The relative uncertainty can be calculated as:
\[ u_r(M_{\text{cured}}) = \frac{0.344}{11.2} = 0.0307 \]  \hspace{1cm} (4.17)

4.3.4.1.3 Relative uncertainty of enthalpy measurement of cured EVA \( u_r(H_{\text{cured}}) \)

The uncertainty of the enthalpy measurement of the cured EVA is a combination of the uncertainty due to enthalpy calibration and the uncertainty due to non-uniformity of the cured EVA.
\[ u_r(H_{\text{cured}}) = \sqrt{u_r(C)^2 + u_r(M_{\text{cured}})^2} = \sqrt{0.006767^2 + 0.0307^2} = 3.1437\% \]  \hspace{1cm} (4.18)

4.3.4.2 Relative uncertainty of enthalpy measurement of uncured EVA \( u_r(H_{\text{uncured}}) \)

4.3.4.2.1 Relative uncertainty of \( H_{\text{uncured}} \) due to the non-uniformity of uncured EVA \( u_r(M_{\text{uncured}}) \)

The uncertainty of \( H_{\text{uncured}} \) due to the non-uniformity of uncured EVA is obtained by measuring the curing enthalpy of the uncured EVA taken from 10 different parts of the rolls. The obtained mean value of the melting enthalpy is 20.473 J/g with standard deviation of 0.6071 J/g (n=9). Thus, the uncertainty due to the non-uniformity of uncured EVA is calculated as follows:
\[ u(M_{\text{uncured}}) = \frac{s}{\sqrt{n}} = \frac{0.6071}{\sqrt{10}} = 0.1920 \, J/g \]  \hspace{1cm} (4.19)

The relative uncertainty can be calculated as:
\[ u_r(M_{\text{uncured}}) = \frac{0.1920}{20.473} = 0.009377 \]  \hspace{1cm} (4.20)

4.3.4.2.2 Relative uncertainty of enthalpy measurement of uncured EVA \( u_r(H_{\text{uncured}}) \)

The uncertainty of the enthalpy measurement of the uncured EVA is a combination of the uncertainty due to enthalpy calibration and the uncertainty due to non-uniformity of the uncured EVA.
\[ u_r(H_{\text{uncured}}) = \sqrt{u_r(C)^2 + u_r(M_{\text{uncured}})^2} = \sqrt{0.006767^2 + 0.009377^2} = 1.1564\% \]  \hspace{1cm} (4.21)
4.3.4.3 Combined relative uncertainty of DSC measurement $u_r(DSC)$

According to the equation 4.11, the uncertainty of the curing state measurement using DSC method includes uncertainty due to enthalpy of both cured and uncured EVA. The sources of uncertainty for $H_{\text{cured}}$ and $H_{\text{uncured}}$ are correlated. To estimate the uncertainty of DSC measurement, fully correlation between $H_{\text{cured}}$ and $H_{\text{uncured}}$ are assumed to represent the worst case, which gives the combined relative uncertainty as follows:

$$u_r(DSC) = u_r(H_{\text{cured}}) + u_r(H_{\text{uncured}}) = 3.1437\% + 1.1564\% = 4\% \ (4.22)$$

For a coverage factor $k=2$, multiplying the combined relative uncertainty by 2, gives an expanded relative uncertainty of around 8%. This gives a level of confidence of about 95%. The uncertainty calculation of DSC is summarised in Table 4.3.

<table>
<thead>
<tr>
<th>Source of uncertainty</th>
<th>Cured EVA</th>
<th>Uncured EVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncertainty of enthalpy calibration $u_r(C)$</td>
<td>$u_r(S)$</td>
<td>0.002806</td>
</tr>
<tr>
<td></td>
<td>$u_r(R)$</td>
<td>0.006158</td>
</tr>
<tr>
<td></td>
<td>$u_r(C)$</td>
<td>0.006767</td>
</tr>
<tr>
<td>Uncertainty due to EVA non-uniformity $u_r(M)$</td>
<td>0.0307</td>
<td>0.009377</td>
</tr>
<tr>
<td>Uncertainty of enthalpy measurement $u_r(H)$</td>
<td>3.1437%</td>
<td>1.1564%</td>
</tr>
<tr>
<td>Standard uncertainty of DSC $u_r(DSC)$</td>
<td>4%</td>
<td></td>
</tr>
<tr>
<td>Standard uncertainty of DSC ($k=2$)</td>
<td>8%</td>
<td></td>
</tr>
</tbody>
</table>
4.4 Infrared Spectroscopy Test

4.4.1 Transmittance and Absorbance

When infrared radiation is passed through a sample, some of the radiation is absorbed by the sample and some is passed through. Each of the absorption peaks at a particular energy level corresponds to a vibration and rotation mode of the molecules. This enables the infrared spectroscopy to analyse material structures.

![Figure 4.7 Absorption of radiation](image)

The light absorption through a substance can be explained using Figure 4.7. When radiation of intensity \( I_0 \) passes through an absorbing species with a concentration \( c \) for a path length of \( b \), the intensity of light transmitted through this material will reduce to \( I_t \). The transmittance (T) of a sample is defined as the fraction of light that passes through the sample which can be described by the following equation [98,99]:

\[
T = \frac{I_t}{I_0}
\]  
(4.23)

Transmittance is linked with absorbance as follows:

\[
A = -\log(T) = -\log\left(\frac{I_t}{I_0}\right) = \log\left(\frac{I_0}{I_t}\right)
\]  
(4.24)

According to the Lambert–Beer law, the absorbance (A) is linearly related to concentration (c), sample thickness (d) and molar absorption coefficient (\( \varepsilon \)):

\[
A = \varepsilon bc
\]  
(4.25)
This equation enables the calculation of the concentration of a substance by measuring its absorbance at specific wavelength as long as the sample thickness and the molar absorption coefficient are known. Due to material variation, multiple measurements are needed to reduce the uncertainty caused by material non-uniformity.

A special case of FTIR is the ATR sampling. In the ATR test, samples are in intimate contact with an optically dense crystal. IR radiation is directed into this crystal at a certain angle so that when the beam is in contact with the sample, it is totally internally reflected (Figure 4.8) [100]. The reflectance creates an evanescent wave which extends beyond the surface of the crystal into the sample that is in intimate contact with the crystal. The evanescent wave will be attenuated where it is absorbed by the sample. The attenuated radiation is reflected and then passed to the detector to generate an ATR spectrum.

The main difference for ATR and FTIR is the sampling path length. FTIR works in transmission mode that IR radiation penetrates through the whole sample. In ATR, light does not go through the whole sample but is totally reflected after
penetrating a certain depth of the sample that is in contact with the crystal. The sample thickness for ATR is the penetration depths \( (d_p) \) of IR radiation which is a function of wavelength \( (\lambda) \), angle of incidence of light \( (\theta) \), refractive index of the crystal \( (n_1) \) and refractive index of the sample \( (n_2) \):

\[
d_p = \frac{\lambda}{2\pi n_2 \sqrt{n_1^2 \sin^2 \theta - n_2^2}}
\]  \hspace{1cm} (4.26)

As long as the crystal is fixed, the incident angle of light and refractive index of the crystal is constant so that the penetration depth at specific wavelength is fixed. According to the Lambert–Beer law, ATR measurement also allows quantitative and semi-quantitative analysis.

### 4.4.2 Interpretation of the Spectrum

In this thesis, FTIR-ATR is used to monitor chemical changes of the encapsulant materials during different stress exposure processes. The spectrum of the samples is recorded using a FTIR machine (Perkin Elmer Spectrum One) with ATR sampling accessory. The crystal of the ATR is Diamond/ZnSe. The spectrum is obtained in the range of 4000 cm\(^{-1}\) – 400 cm\(^{-1}\) by averaging 16 scans with a resolution of 4 cm\(^{-1}\). A baseline correction is performed to remove the influences of testing environment and measurement artefacts, using air as the baseline correction measurement. An example of the ATR spectrum of EVA at both dry and hydrated conditions is shown in Figure 4.9 and the assignment of the major peaks is listed in Table 4.4 [101-103].
Table 4.4 IR peaks of EVA

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Vibration Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>3200-3600</td>
<td>Hydroxyl stretching O-H</td>
</tr>
<tr>
<td>2918</td>
<td>Asymmetric vibration of –CH(_2)</td>
</tr>
<tr>
<td>2849</td>
<td>Symmetric vibration of –CH(_2)</td>
</tr>
<tr>
<td>1735</td>
<td>Ketone (C=O) Stretching</td>
</tr>
<tr>
<td>1235</td>
<td>Ester (C-O) Stretching</td>
</tr>
<tr>
<td>1019</td>
<td>Ester (C-O-C) Stretching</td>
</tr>
<tr>
<td>1464, 1370</td>
<td>–CH(_2) bending</td>
</tr>
<tr>
<td>1641, 1545</td>
<td>Polyene (C=C) vibration</td>
</tr>
</tbody>
</table>

FTIR test in transmission mode can also be conducted for EVA. Figure 4.10 presents the spectrum obtained from FTIR and FTIR-ATR. Noisy peaks are observed from the results of FTIR measurement especially in the wavelengths of strong absorption while narrow, sharp and distinguishable peaks can be identified in ATR spectrum. This is because the EVA sheet is too thick for FTIR. In transmission mode, the light beam passes through the entire sample where
absorption happens. If the sample is too thick, all the radiation will be absorbed before passing through the sample to be detected which produces noisy peaks.

To obtain the absorbance, there are two major ways, i.e. the peak height and the peak area [99]. Peak area method is chosen here. The reason for this is that peak shoulders sometimes appear which may cause biased calculation if peak height method is used. As is shown in Figure 4.11, to obtain the peak area, a straight line XY is first drawn by connecting the troughs of each peak. Then a second line AB which is perpendicular to the 0% absorption line is draw. The length of AB is the height of the peak while the integrated area of this peak under the line XY is the peak area. The peak area is calculated to represent the absorbance and according to the Lambert–Beer law, semi-quantitative analysis is conducted.
4.4.3 Uncertainty Analysis for the FTIR-ATR Test

The possible sources of uncertainty in the FTIR-ATR absorbance measurement are illustrated in Figure 4.12. The uncertainty mainly comes from the uncertainty due to testing repeatability, the non-uniformity of the material and the uncertainty due to data analysis with details described in the following section. The uncertainty is wavelength dependent. Only the peaks that will be used in this thesis are analysed which include the vibration of $\text{–CH}_2$ at 2918 cm$^{-1}$ and 2849 cm$^{-1}$, the carbonyl stretching at 1735 cm$^{-1}$, the ester C-O stretching at 1235 cm$^{-1}$ and the ester C-O-C stretching at 1019 cm$^{-1}$. There are also some other effects which will influence the absorbance measurement, such as the drift of the machine and the testing environment. The drift of the machine is cancelled out by taking baseline measurement before spectrum measurement. All the tests are conducted by the same operator under laboratory conditions. The effects of environment are included in the repeatability measurement.
Figure 4.12 Sources of uncertainty in FTIR-ATR absorbance measurement based on peak area

4.4.3.1 Relative uncertainty due to testing repeatability \( u_r(R) \)

The testing repeatability is evaluated from the average of 10 measurements of an EVA sheet at the same location and calculating the peak area according to section 4.4.2. The results of the mean, the standard deviation, the standard uncertainty of the mean and the relative uncertainty for the investigated peaks are listed in Table 4.5.

Table 4.5 Data used to obtain the repeatability uncertainty of ATR measurement

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>2918</th>
<th>2849</th>
<th>1735</th>
<th>1235</th>
<th>1019</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td>Mean</td>
<td>Standard deviation</td>
<td>Degree of freedom</td>
<td>Standard uncertainty of the mean ( u(R) )</td>
<td>Relative uncertainty ( u_r(R) )</td>
</tr>
<tr>
<td></td>
<td>7.672</td>
<td>0.1082</td>
<td>9</td>
<td>0.034215</td>
<td>0.446%</td>
</tr>
<tr>
<td></td>
<td>3.329</td>
<td>0.02685</td>
<td>9</td>
<td>0.00849</td>
<td>0.255%</td>
</tr>
<tr>
<td></td>
<td>2.857</td>
<td>0.0386</td>
<td>9</td>
<td>0.012207</td>
<td>0.4273%</td>
</tr>
<tr>
<td></td>
<td>3.89</td>
<td>0.12526</td>
<td>9</td>
<td>0.039609</td>
<td>1.0182%</td>
</tr>
<tr>
<td></td>
<td>0.942</td>
<td>0.01398</td>
<td>9</td>
<td>0.004422</td>
<td>0.4694%</td>
</tr>
</tbody>
</table>
4.4.3.2 Relative uncertainty due to material non-uniformity $u_r(M)$

Uncertainty due to material non-uniformity is evaluated from the average of the measurements of 15 different EVA sheets. Data used to obtain the uncertainty due to material non-uniformity is documented in Table 4.6.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>2918</th>
<th>2849</th>
<th>1735</th>
<th>1235</th>
<th>1019</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>7.777333</td>
<td>3.319333</td>
<td>2.896</td>
<td>3.997333</td>
<td>0.943333</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.199981</td>
<td>0.132313</td>
<td>0.14126</td>
<td>0.132421</td>
<td>0.021269</td>
</tr>
<tr>
<td>Degree of freedom</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>Standard uncertainty of the mean $u(M)$</td>
<td>0.051635</td>
<td>0.034163</td>
<td>0.036473</td>
<td>0.034191</td>
<td>0.005492</td>
</tr>
<tr>
<td>Relative uncertainty $u_r(M)$</td>
<td>0.6639%</td>
<td>1.0292%</td>
<td>1.2594%</td>
<td>0.8553%</td>
<td>0.5822%</td>
</tr>
</tbody>
</table>

4.4.3.3 Relative uncertainty due to baseline selection $u_r(B)$

The absorbance is influenced by the selection of the baseline. The effects of baseline selection on the uncertainty of absorbance measurement are obtained by computing the peak area of one EVA spectrum by 10 times with 10 different baseline selections. The results are listed in Table 4.7.
Table 4.7 Data used to obtain the uncertainty due to baseline selection

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Wavenumber 2918</th>
<th>2849</th>
<th>1735</th>
<th>1235</th>
<th>1019</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumber</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>7.768</td>
<td>3.257</td>
<td>2.89</td>
<td>3.75</td>
<td>0.967</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.079415</td>
<td>0.048316</td>
<td>0.006667</td>
<td>0.009428</td>
<td>0.00483</td>
</tr>
<tr>
<td>Degree of freedom</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Standard uncertainty of</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>the mean u(B)</td>
<td>0.025113</td>
<td>0.015279</td>
<td>0.002108</td>
<td>0.002981</td>
<td>0.001528</td>
</tr>
<tr>
<td>Relative uncertainty u_r(B)</td>
<td>0.3233%</td>
<td>0.4691%</td>
<td>0.0729%</td>
<td>0.0795%</td>
<td>0.158%</td>
</tr>
</tbody>
</table>

4.4.3.4 Combined relative uncertainty of absorbance measurement u_r(A)

The total uncertainty of absorbance measurement can be obtained by combing the above major three effects using the equation below:

\[ u_r(A) = \sqrt{u_r(R)^2 + u_r(M)^2 + u_r(B)^2} \]  

(4.27)

The results for the investigated peaks are listed in Table 4.8. The expanded relative uncertainty is obtained by multiplying the combined relative uncertainty by 2 to give a confidence level of 95%. The expanded relative uncertainty is in the range of 1.5% - 2.7%.
Table 4.8 Uncertainty for ATR-FTIR absorbance measurement

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>2918</th>
<th>2849</th>
<th>1735</th>
<th>1235</th>
<th>1019</th>
</tr>
</thead>
<tbody>
<tr>
<td>uᵣ(R) %</td>
<td>0.446</td>
<td>0.255</td>
<td>0.4273</td>
<td>1.0182</td>
<td>0.4694</td>
</tr>
<tr>
<td>uᵣ(M) %</td>
<td>0.6639</td>
<td>1.0292</td>
<td>1.2594</td>
<td>0.8553</td>
<td>0.5822</td>
</tr>
<tr>
<td>uᵣ(B) %</td>
<td>0.3233</td>
<td>0.4691</td>
<td>0.0729</td>
<td>0.0795</td>
<td>0.158</td>
</tr>
<tr>
<td>Combined relative uncertainty uᵣ(A) %</td>
<td>0.86</td>
<td>1.16</td>
<td>1.33</td>
<td>1.33</td>
<td>0.76</td>
</tr>
<tr>
<td>Expanded relative uncertainty %</td>
<td>1.72</td>
<td>2.32</td>
<td>2.66</td>
<td>2.66</td>
<td>1.52</td>
</tr>
</tbody>
</table>

4.5 Transmittance Test

4.5.1 Measurement of Transmittance

To maximise light absorption of solar cells, EVA needs to have high optical transparency in the visible spectrum. The capability of EVA to transmit visible light is characterised by its transmittance. According to Section 4.4, transmittance is a ratio between the transmitted irradiance to the injected irradiance. But unlike Section 4.4 in which infrared light is used, the light source in this test needs to have a capacity to generate visible light.

The transmittance of EVA is measured using a Cary 5000 spectrophotometer (Agilent Technologies, USA) equipped with an integrating sphere. The measurement is conducted under transmittance mode by directly placing the sample in the transmittance test sample compartment which is just over the integrating sphere. The transmittance spectra are obtained in the spectral range 200–1200 nm at 1 nm resolution and an average integrating time of 0.1 s. To reduce the measurement errors, a zero baseline correction is conducted using air as the correction measurement and the 100% baseline correction is carried out using a black body mask.
4.5.2 Calculation of Yellowing Index and Whiteness Index

Based on the measured transmittance results, the yellowing index (YI) and whiteness index (WI) of EVA is calculated based on the standard ASTM E313 – 10 [104].

\[ YI = 100 \frac{C_X X - C_Z Z}{Y} \]  \hspace{1cm} (4.28)

\[ WI = Y + (W_{lx}, x)(x_n - x) + (W_{ly}, y)(y_n - y) \]  \hspace{1cm} (4.29)

Where X, Y, Z are tristimulus values of the measured object; \( C_X, C_Z, W_{lx}, x \) and \( W_{ly}, y \) are numerical coefficients used for calculation and their values depend on the types of standard illuminant and observer; \( x_n, y_n \) are the chromaticity coordinates of the CIE standard illuminant and source. The calculation of the tristimulus values of the object is based on CIE standards [105,106]:

\[ X = k \int \varphi(\lambda) \bar{x}(\lambda) \, d\lambda = k \int R(\lambda) S(\lambda) \bar{x}(\lambda) \, d\lambda \]  \hspace{1cm} (4.30)

\[ Y = k \int \varphi(\lambda) \bar{y}(\lambda) \, d\lambda = k \int R(\lambda) S(\lambda) \bar{y}(\lambda) \, d\lambda \]  \hspace{1cm} (4.31)

\[ Z = k \int \varphi(\lambda) \bar{z}(\lambda) \, d\lambda = k \int R(\lambda) S(\lambda) \bar{z}(\lambda) \, d\lambda \]  \hspace{1cm} (4.32)

Where \( \varphi(\lambda) \) is the relative colour stimulus function, \( R(\lambda) \) is the measured spectral reflectance, transmittance, or radiance factor, \( S(\lambda) \) is the relative spectral power of a CIE standard illuminant, \( \bar{x}(\lambda), \bar{y}(\lambda), \bar{z}(\lambda) \) is the colour-matching functions of one of the specified CIE standard observers and \( k \) is a normalizing constant. The constant \( k \) is chosen so that \( Y \) equals 100 when \( R(\lambda) \) is 1 for all wavelengths. It can be obtained using the following equation:

\[ k = \frac{100}{\int S(\lambda) \varphi(\lambda) \, d\lambda} \]  \hspace{1cm} (4.33)

The integration needs to be carried out in the wavelength range of 360 nm to 830 nm. To simplify the calculation, the integration in Eq 4.30 to Eq 4.32 can be approximated by numerical summation from 360 nm to 830 nm at certain wavelength intervals (\( \Delta\lambda \)):

\[ X = k \sum_\lambda \varphi(\lambda) \bar{x}(\lambda) \Delta\lambda = k \sum_\lambda R(\lambda) S(\lambda) \bar{x}(\lambda) \Delta\lambda \]  \hspace{1cm} (4.34)

\[ Y = k \sum_\lambda \varphi(\lambda) \bar{y}(\lambda) \Delta\lambda = k \sum_\lambda R(\lambda) S(\lambda) \bar{y}(\lambda) \Delta\lambda \]  \hspace{1cm} (4.35)

\[ Z = k \sum_\lambda \varphi(\lambda) \bar{z}(\lambda) \Delta\lambda = k \sum_\lambda R(\lambda) S(\lambda) \bar{z}(\lambda) \Delta\lambda \]  \hspace{1cm} (4.36)
Since EVA is a transparent polymer, transmittance is used in Eq 4.34 to Eq 4.36 to calculate the tristimulus of EVA and then the YI and WI. As mentioned in section 4.5.1, the measurement of the transmittance is carried out with 1 nm wavelength intervals. The light source of the spectrophotometer is a tungsten halogen lamp which has a correlated colour temperature that is approximating CIE standard illuminant A. However, all the calculations are based on CIE standard illuminant D65. Other CIE specified standard illuminants can also be utilised but since CIE D65 represents daylight conditions, it is the most widely utilised illuminant for calculating colour. It is selected here. In addition, CIE 1931 standard colorimetric system is chosen so that the observer is the CIE 1931 standard colorimetric observer whose colour-matching properties correspond to the CIE 1931 colour-matching functions. The parameters used to measure the transmittance spectrum and those constants for calculating the YI and WI are summarised in Table 4.9.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Selections</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colorimetric system</td>
<td>CIE 1931 standard colorimetric system</td>
</tr>
<tr>
<td>Colour-matching functions</td>
<td>CIE 1931 colour-matching functions</td>
</tr>
<tr>
<td>Observer</td>
<td>CIE 1931 standard colorimetric observer (2°)</td>
</tr>
<tr>
<td>Illuminant Measurement Calculation</td>
<td>CIE Standard A</td>
</tr>
<tr>
<td>Calculation</td>
<td>CIE Standard D65</td>
</tr>
<tr>
<td>Measurement Interval</td>
<td>1nm</td>
</tr>
<tr>
<td>$C_X$</td>
<td>1.2985</td>
</tr>
<tr>
<td>$C_Z$</td>
<td>1.1335</td>
</tr>
<tr>
<td>$x_n$</td>
<td>0.3127</td>
</tr>
<tr>
<td>$y_n$</td>
<td>0.3290</td>
</tr>
<tr>
<td>$W_{I,x}$</td>
<td>800</td>
</tr>
<tr>
<td>$W_{I,y}$</td>
<td>1700</td>
</tr>
</tbody>
</table>
4.5.3 Uncertainty Analysis of the Transmittance Measurement

The possible sources of uncertainty in the transmittance measurement are illustrated in Figure 4.13. The uncertainty mainly comes from the uncertainty due to testing repeatability and the non-uniformity of the material. There are also other factors contributing to the uncertainty of transmittance measurement, such as the drift of the machine and the operating environment. Before the transmittance is measured, baselines for 100% transmittance and 0% transmittance are conducted. This baseline correction has cleared out the effects of the drift of the machine. The measurement is done at room temperature and the effects are included in the repeatability measurement. Details of each of the main components on uncertainty contribution are described in the following section.

4.5.3.1 Uncertainty due to measurement repeatability $u(R_\lambda)$

The repeatability of transmittance measurement is evaluated from the average of 10 measurements of 100% transmittance and 50% transmittance. 100% transmittance is achieved by placing empty samples in the sample compartment while 50% transmittance is achieved using neutral density filter as the specimen.

---

**Figure 4.13 Sources of uncertainty in transmittance measurement**
The uncertainty is wavelength dependent with the results shown in Figure 4.14 for both 100% and 50% transmittance.

![Figure 4.14 Absolute uncertainty due to repeatability of both 100% and 50% transmittance measurement](image)

It can be seen that the uncertainty of 100% transmittance and 50% transmittance are similar to each other with uncertainty in most of the wavelength smaller than 0.02. There are two exceptional wavelength ranges, i.e. around 300nm and 800nm where large variation is demonstrated. This is because the spectrophotometer changes lamp at these two wavelength ranges.

### 4.5.3.2 Uncertainty due to the non-uniformity of EVA \( u(M_i) \)

Uncertainty due to material non-uniformity is evaluated by measuring the transmittance at six different locations of three different EVA sheets for each lamination conditions. The absolute uncertainty for the five investigated lamination conditions is shown in Figure 4.15. The largest uncertainty within the five conditions is selected to represent the uncertainty due to material non-uniformity.
4.5.3.3 Combined uncertainty of transmittance measurement $u(T_{\lambda})$

The combined uncertainty of transmittance measurement can be obtained by combing the uncertainty due to repeatability and uncertainty due to material non-uniformity using the following equation:

$$u(T_{\lambda}) = \sqrt{u(R_{\lambda})^2 + u(M_{\lambda})^2}$$  \hspace{1cm} (4.37)

The uncertainty is wavelength dependent with the results shown in Figure 4.16. It can be seen that the uncertainty at most of the wavelength are below 0.2 and the uncertainty is mainly induced by the non-uniformity of the material.

Figure 4.15 Absolute transmittance uncertainty due to material non-uniformity for different lamination conditions
4.5.4 Uncertainty Analysis of the YI and WI Measurement

As is shown in Section 4.5.2, the value of YI and WI are functions of the tristimulus value of the colour. The sources of uncertainty for YI and WI mainly come from the uncertainty of tristimulus measurement and the uncertainty due to material non-uniformity (Figure 4.17).

![Figure 4.16 Combined absolute uncertainty for transmittance measurement](image)

![Figure 4.17 Sources of uncertainty in YI and WI measurement](image)
4.5.4.1 Relative uncertainty due to tristimulus $u_r(X)$, $u_r(Y)$, $u_r(Z)$ and chromaticity coordinates $u_r(x)$, $u_r(y)$, $u_r(z)$

The tristimulus is calculated according to Eq 4.34 - Eq 4.36 which is a function of the integration of transmittance in the wavelength range of 360 nm to 830 nm. Therefore, uncertainty of the tristimulus is mainly due to the uncertainty of transmittance which is shown in section 4.5.3. Seen from section 4.5.3, the uncertainty of transmittance measurement includes the uncertainty of repeatability and material non-uniformity; here only uncertainty of repeatability is considered. That is because the uncertainty due to material non-uniformity will be calculated in the next part. The uncertainty of transmittance repeatability is wavelength dependent. The relative uncertainty of the tristimulus values can be calculated using the following equation:

$$u_r(X) = u_r(Y) = u_r(Z) = \sqrt{\sum_{\lambda=360}^{830} \left( \frac{u_r(T(\lambda))^2}{60} \right)} = 0.7752\% \quad (4.38)$$

Besides the tristimulus value, the WI is also a function of the chromaticity coordinates ($x$, $y$, $z$). The chromaticity coordinates are functions of the tristimulus values in the following format:

$$x = \frac{X}{X+Y+Z} \quad (4.39)$$

$$y = \frac{Y}{X+Y+Z} \quad (4.40)$$

$$z = \frac{Z}{X+Y+Z} \quad (4.41)$$

The sources of uncertainty of the chromaticity coordinates come from the uncertainty of the tristimulus values of $X$, $Y$ and $Z$ which are correlated. The worst case of fully correlation is assumed here to represent the worst case. For a full correlation, the uncertainty is the linear summation of each uncertainty component. Therefore, the relative uncertainty of $x$, $y$ and $z$ can be obtained as the follows:

$$u_r(x) = u_r(y) = u_r(z) = u_r(X) + u_r(Y) + u_r(Z) = 2.33\% \quad (4.42)$$
4.5.4.2 Relative uncertainty due to material non-uniformity $u_r(M_{YI})$ and $u_r(M_{WI})$

Uncertainty due to material non-uniformity is obtained by calculating the YI and WI values of six samples at each lamination conditions. The largest standard deviation of the YI is $0.08964$ (n=6) corresponding to the mean value of 0.5657. This largest variation is taken to represent the worst case of uncertainty. Therefore, the uncertainty due to the non-uniformity of EVA for YI measurement is calculated as follows:

$$u(M_{YI}) = \frac{0.08964}{\sqrt{6}} = 0.03660$$  \hspace{1cm} (4.43)

The relative uncertainty can be calculated as:

$$u_r(M_{YI}) = \frac{0.03660}{0.5657} = 0.06470 = 6.47\%$$  \hspace{1cm} (4.44)

Similar to the YI, the largest standard deviation of the WI measurement is $1.2821$ (n=6) which corresponds to a mean value of 89.99. This largest variation is taken to represent the worst case of uncertainty. The uncertainty due to the non-uniformity of EVA for WI measurement is calculated as follows:

$$u(M_{WI}) = \frac{1.2821}{\sqrt{6}} = 0.5234$$  \hspace{1cm} (4.45)

The relative uncertainty can be calculated as:

$$u_r(M_{WI}) = \frac{0.5234}{89.99} = 0.005816 = 0.58\%$$  \hspace{1cm} (4.46)

4.5.4.3 Combined uncertainty of YI and WI measurement $u_r(YI)$ and $u_r(WI)$

The YI are direct function of the tristimulus value of X, Y and Z while WI are function of both the tristimulus value of Y and the chromaticity coordinates of x and y. The uncertainty sources of X, Y and Z as well as the uncertainty sources of x and y are correlated and full correlation is assumed to represent the worst case. The combined relative uncertainty of YI and WI can then be obtained using the following equations:
\[ u_r(YI) = \sqrt{u_r(X, Y, Z)^2 + u_r(M_{YI})^2} = \sqrt{(u_r(X) + u_r(Y) + u_r(Z))^2 + u_r(M_{YI})^2} = \]
\[ \sqrt{(0.7752 + 0.7752 + 0.7752)^2 + 6.47^2} = 6.9\% \quad (4.47) \]
\[ u_r(WI) = \sqrt{(u_r(Y) + u_r(x, y))^2 + u_r(M_{WI})^2} = \]
\[ \sqrt{(u_r(Y) + u_r(x) + u_r(y))^2 + u_r(M_{WI})^2} = \sqrt{(0.7752 + 2.33 + 2.33)^2 + 0.58^2} = 5.5\% \quad (4.48) \]

From the above calculations, it can be seen that the major sources of uncertainty for YI and WI are different. For YI, the uncertainty mainly comes from the uncertainty due to material non-uniformity and the uncertainty due to the tristimulus is insignificant. For WI, the uncertainty is mainly due to the uncertainty of the chromaticity coordinates while the uncertainty due to material non-uniformity is insignificant.

### 4.5 Adhesion Strength Test

The peel test is widely used in the PV industry to measure the adhesion strength of different layers within PV modules [11,14,107,108]. It is performed by applying force at certain angles to a narrow strip so that two bonded substances are separated at a constant rate. The peel test measures the force needed to cause such separation of the two substances. The measured force describes the interfacial adhesion. There are also other methods for characterising interfacial adhesion strength, which mainly include double cantilever beam (DCB) test, wedge test, indentation test and blister test (Figure 4.18) [109-111].
Figure 4.18 Schematic diagram of (a) DCB test, (b) wedge test, (c) indentation test and (d) blister test [109-111]

The DCB test is used to measure the cleavage de-bonding. The sample configuration is standardised in ISO 25217 [112]. Two identical beams of adherent are bonded together with the adhesive (Figure 4.18 (a)). An initial crack is introduced at one edge of the specimen where tensile load is applied by pulling the adherent apart at a constant rate. The load-displacement behaviour is recorded which is used to calculate the fracture energy. This method allows an elementary analysis based on elementary beam mechanics and is easy to operate. However, the specimen for the DCB test requires two identical adherents which cannot represent the structure of PV modules. Besides, the DCB test is suitable for rigid adherent while the backsheet of PV modules are mostly polymeric materials. Therefore, the DCB test is not suitable for the application in this thesis.

The wedge test is a systematically developed method and has been standardised as ASTM D3762 [109]. It is suitable for assessing the performance of metal-adhesive joints where two rigid adherents are bonded together. In this test, a wedge is forced into one end of the sandwiched samples to initiate the crack. The separation of bonded surfaces occurs as the crack releases energy. The crack extension at various time intervals is recorded. Surface fracture energy can be obtained using fracture mechanical analysis. The driving force for the de-bonding propagation mainly comes from the stiffness of the deformed adherent. The
application of this test is based on the assumption that adherent do not deform plastically which is suitable for thick and stiff adherent. However, in PV modules, most of the back covers are soft material which is not suitable for the wedge test.

As is illustrated in Figure 4.18 c, the indentation test involves compressing an indenter with a hemispherical point against the adhesives adhered on a rigid substrate [113]. The centre contact area is subjected to high compressive indenter stress which causes the material to be extruded and piles up at the edge of the indenter. The compressive strains of the underlying substrate are transferred to the adhesive through the entire thickness of the adhesive as normal tensile stress. De-bonding occurs if the adhesion strength between the adhesive and the substrate is lower than the developed tensile stress creating a delamination area. A microscope is required to monitor the delamination and measure the de-bonded area. This test is widely used for qualitative analysis of adhesion. It is easy to conduct and is applicable to a wide variety of adhesion system. The de-bonding area can be readily used for qualitative analysis. There are also models developed by researchers to extract the adhesion energy but all involves complex mechanical analysis [110,114]. The other drawback of this test is the complex loading system which also involves shear stress to be generated by the extrusion process. This shear stress can be very large for soft adhesive material such as the encapsulant material of PV modules. The other issue to be aware of is that the compression of the hard indenter into the substrate with high force which may cause glass cracking in PV modules and is thus not quite suitable for the application in this thesis.

Figure 4.18 d shows the schematic diagram of a blister tests. The blister test creates a blister within the bonding system. Firstly, a hole needs to be produced at the adherent layer through which pressures is applied to the adhesive in a controlled manner causing propagation of a delamination [111]. Pressure is normally applied by entering gases through the hole at a controlled rate. The
motion of the crack front is observed using a microscope. The pressure at which the blister just progresses is the critical pressure $P_c$. The interfacial fracture energy ($\gamma$) can be obtained from the following equation by multiplying the blister height ($h$) and $P_c$ [115]:

$$\gamma = hP_c$$

(4.49)

The advantage of the blister test is that it imposes a low strain on adhesive materials, thus avoiding the viscoplastic deformation. However, the drawbacks are also obvious. Firstly, the sample preparation is complex and time consuming. One of the processes is the hole drilling which is often achieved using etchants. Besides, there is a lack of standardisation on the testing process so that some of the operations such as the pressure ramp rate and when the crack propagates are determined by experience. Considering the large number of samples in this thesis and the time scale, this method is discarded.

Compared with the other testing methods, the peel test requires a simple sample preparation which enables large number of samples to be tested. The fracture rate and failure locus can be controlled. Furthermore, the testing process is quick and straightforward and the testing equipment is easy to access with various kinds of commercial equipment available. The obtained data can be readily used for ranking and quality control. The problem for the peel test is that it may induce viscoplastic deformation at the peeling tips which can give misleading results if the measured force is directly used for the calculation of fracture energy or used for the prediction of realistic delamination. This material deformation is a common issue for adhesion test that also exits in other testing methods such as DCB test, wedge test and indentation test. In this thesis, only relative changes of the measured peel force are of interest. The nonlinear viscoplastic strains are assumed to be constant for the same type of material under the same set of tests. During stress testing, the properties of the material are changing gradually which may also cause changes of the deformation. Results show that the tested materials become more brittle during stress exposure. The
viscoplastic deformation reduces with the material becoming more brittle [84]. Therefore, the measured peel force for samples that have undergone stress exposure and have become more brittle can represent more accurately the intrinsic adhesion strength than fresh samples. The relative changes calculated from the measured peel strength represent some upper limit of the real situation. Considering the wide application, easy operation and material suitability, the peel test is utilised in this thesis to characterise the adhesion strength of the encapsulation materials at different interfaces within PV modules.

Two types of peel tests are carried out: 90° peel test and 180° T-peel test, as shown in Figure 4.19. The 90° peel test is used to measure the adhesion strength at the glass-EVA interface when the backsheet is strongly bonded to EVA (Figure 4.19 (a)). Or it can measure the adhesion strength at EVA-backsheet interface when EVA can strongly bond to glass (Figure 4.19 (b)). If the EVA fails to be bonded with the glass when peeling the backsheet from the EVA layer, the 90° peel test cannot be used. Instead, the T-peel test is selected for adhesion strength measurements at the EVA-backsheet interface (Figure 4.19 (c)). Both tests are destructive and samples can only be used a single time. The tests are conducted according to standards ISO 8510-1:2006 and ISO 11339:2010 [116,117].

![Schematic diagram of 90° peel test and T-peel test](image)
4.5.3 Equipment

The apparatus for the peel test is a tensile testing machine capable of applying the peel force with constant speed. A commercial testing stand (Chatillon LTCM-500) is used. It has a capacity of 2.5 kN with a speed range of 5-500 mm/min and a crosshead length of 750 mm. To measure the force, a DFS-500 series digital force gauge is connected to the test stand with an accuracy of 2.5 N. Self-aligning grips are used to hold the sample strips so that the force is loaded normally to the bonding plane. For the 90° peel test, a self-adjusting platform is required to hold the rigid substrate of the sample. It needs to be able to move smoothly in a horizontal direction at the same speed as the vertical crosshead so that a 90° angle is maintained during peeling.

The two types of peel test settings are shown in Figure 4.20. For the 90° peel test, the flexible strip of backsheet or backsheet together with the EVA strip is held by a grip that is driven vertically while the glass is fastened by the 90° peel table which moves horizontally. For the T-peel test, both the peeling arms are flexible. Each of the peeling arms is held by one of the jigs and the two peeling arms need to be maintained coaxially.

Figure 4.20 Peel test setup: 90° peel test (left) and T-peel test (right)
4.5.4 Sample Preparation

4.5.4.2 Sample Preparation for 90° Peel Test

In order to do the peel test, strips with certain widths are needed. For the 90° peel test in this thesis, a precise cutting depth is required to avoid damaging the base material. This is especially important when measuring the adhesion strength between backsheet and EVA. If the EVA is destroyed, there will be a risk of EVA deformation resulting in jumping failure interfaces. When measuring the adhesion between EVA and glass by peeling the backsheet together with the EVA from the glass, if the glass is scored, it may break during cutting or peeling when stress is applied.

For the purpose of accuracy and safety, the strip cutting is done through an automated laser system (Synrad CO₂ Laser). The relevant materials (backsheet only if backsheet-EVA interfacial adhesion strength is needed or backsheet together with EVA if EVA-glass interfacial adhesion strength is needed) are cut by the CO₂ laser into strips of 10 mm width. The transition wavelength of the laser is 10.6 microns (943 cm⁻¹) where high absorption occurs for most plastics. According to the FTIR spectrum of EVA shown in section 4.4, there is high absorption in that wavelength range. The cutting speed, power and number of passes are adjusted according to the material properties so that the desired cutting depth is achieved.

Laser cutting has many advantages compared with other alternative cutting methods such as blade or disc-based cutting. The quality of the cutting is shown in Figure 4.21 which presents an image of one of the typical strip cuts measured by a coherence correlation interferometer (CCI). This cut is made in the backsheet layer only in order to measure the adhesion at EVA-backsheet interface. The left figure is the 3-D image of the surface profile near the cut while the right one is the corresponding 2-D image. The colour scale indicates the
depth of the scanned surface. The trench Figure 4.21 (a) is the cut. A depth of 250 µm is observed, which is equal to the thickness of the backsheet (roughly 250 µm). Compared with commonly used blade cutting, laser cutting is quicker and more precise in terms of parallelness and control of cutting depth.

![Figure 4.21 Interferometer image of the cutting of the backsheet](image)

(a) 3-D image of the peel strip cutting   (b) 2-D image of the peel strip cutting

However, it also has some disadvantages. Laser cutting relies on photothermal ablation to cut materials. As EVA is thermoset plastic after curing, chemical degradation happens to break down chemical bonds during laser cutting releasing carbon smoke. Therefore, discoloration and charring of the cutting edge is often observed. For thermoplastic materials, such as PET backsheets, thermal damage of the edge material is unavoidable as melting dominates the cutting process. Figure 4.22 is a microscopic image of cutting edges cut by sharp blades and laser. Compared with blade cutting, the kerf width caused by laser cutting is wider and less uniform and the surrounding material appears more damaged. However, this damage is only tens of microns in width for the materials investigated in this thesis. Compared with the width of the whole strip (1 cm), it accounts for several tenth of a percent of the strip width. Therefore, it is assumed that damage incurred by the laser cutting will not have significant influence on the measurement results.
Figure 4.22 Microscopic image of the cutting edge: knife cut (left image) and laser cut (right image)

4.5.4.3 Sample Preparation for T - Peel Test

For the T-peel test between the encapsulant and backsheets, separated strips with a structure of backsheet-encapsulant-backsheet are required. This means the cut should go through the entire cross section of the samples instead of having strict depth control. This favours blade cutting. Therefore, strips of 1 cm width are cut using sharp blades for the T-peel test.

4.5.5 Typical Peel Test Results

The peel test measures forces vs. time or displacement. One of the typical results is demonstrated in Figure 4.23. Three stages can be defined as follows:

1. Loading of the peeling arm as it takes up slack. The pull force increases sharply until the strip is fully tensioned to the peel tip where peeling starts.

2. Propagation of the interface separation. Data from this area gives the adhesion strength sought. In this thesis, the first 1-2 cm peeling after fully tensioning is discarded as the adhesion strength is not reliably measurable in this region. Data of the last 1-2 cm which is not stable and normally show much higher values than the rest is not used either. Therefore, the edges had slightly different properties with the rest of the
sample. The average value of the remaining data is used. In addition, extreme high peaks and valleys need to be excluded. In most cases, the high peak is caused by deformation of the adhesive or adherent while valleys represent bubbles or bad adhesion.

(3) Completion of the separation. A sudden drop of the peel strength to zero is characterised in this stage.

The measured peel force fluctuates and the quality of the data depends on the properties of the adhesive and adherent as well as the quality of the bonding.

![Typical peel test results](image)

Figure 4.23 Typical peel test results

### 4.5.6 Influence of Peel Speed on Peel Strength

The other issue of the peel test is the selection of the peel rate which is often based on experience or convenience in industry. The peel test is very sensitive to peel speed and it appears justified to have a scientific understanding on the influence of peel rate on measured peel strength in the case of the encapsulation materials of PV modules in order to derive a reasonable peeling speed for the measurement system.
In order to investigate these influences, laminates of the size 10 cm X 10 cm with a structure of Glass - EVA – (PET/PET/EVA) are cured at 145°C for 11 min under a pressure of 100 KPa. 90° peel tests between glass and EVA of these laminates are examined at ambient temperature with varied crosshead speeds of 10 mm/min, 50 mm/min, 100 mm/min and 150 mm/min that are commonly used in the PV industry [45,118]. Two specimens are produced for each speed condition. Before peeling, the backsheet together with EVA is cut by laser into strips of 1 cm width. The cutting speed is 762 mm/s with a power of 32 W and 10 passes. Each sample generated 8 strips so that 16 strips are assessed for each speed condition.

Figure 4.24 presents the measured peel strength under these different peel rates. The error bar within the figure represents the standard deviation of the total measurement. This is to give an indication of the sample variation. It is observed that the peel strength increases almost linearly with peeling rates within the investigated speed range. This can be attributed to the viscoelastic nature of the polymer.

Figure 4.24 Effects of peel speed on peel strength (error bar represent the standard deviation)
As is shown in Figure 4.25, when the flexible polymer is subjected to peeling, the peel force will exert a bending moment at the peel tip with a moment arm of \( m \). In addition, tension will stretch the material. These deformations result in extra strains and once the strain exceeds its yield strain, a zone of viscoelastic or plastic deformation at the crack tip is created. Thus, the measured peel force not only includes the fracture energy to create the new surfaces but also the work due to irreversible viscoelastic and plastic deformation at the crack tip. According to the first law of thermodynamics, Kinloch et al. [119] analysed the peel of flexible laminates and developed numerical formulas for calculating the energy of the different deformation formats included in a typical peel test:

\[
P = \frac{b}{1 + \varepsilon_a - \cos \theta} (G_0 + G_t + G_b) = \frac{b}{1 + \varepsilon_a - \cos \theta} (G_0 + h \int_{0}^{\varepsilon_a} \sigma \, d\varepsilon + G_b)
\]  

(4.50)

Where \( P \) is the peel strength, \( G_0 \) is the intrinsic deboning energy at the interface, \( G_t \) and \( G_b \) is energy dissipated during tensile and bending of the peel arm respectively, \( \theta \) is the peel angle, \( b \) is width of the peel arm, \( h \) is thickness of peel arm, \( \sigma \) is the stress under the peel force and \( \varepsilon_a \) is the produced strain under the stress. These kinds of fracture analysis enable the calculation of the intrinsic de-bonding energy. However, even with these formulas, it is still complex and sometimes impossible to obtain the de-bonding energy.

---

Figure 4.25 Deformation zone near crack tip
The rate of these deformations increases with increasing crack velocity, which causes increased peel strength with the increasing peel rate [37]. Therefore, lower peel speed is preferable to more closely represent the thermodynamic work of adhesion. In this thesis, 50mm/min is selected as it is a relatively low rate among those commonly used peel rates in the PV industry. This thesis is only interested in the relative changes of the measured peel force after exposure to different stresses or the differences between samples produced at different conditions rather than the absolute values. The required comparability is achieved by keeping the peel angle, crosshead rate, material type and testing temperature the same. The deformation is assumed not to be too different and the relative changes or differences can represent the differences of the intrinsic adhesion strength.

### 4.5.7 Uncertainty Analysis of the Peel Test

The major sources of uncertainty for the peel test are shown in Figure 4.26 including the uncertainty due to strip width, the uncertainty of measured forces and the uncertainty due to material non-uniformity. Calculation of the uncertainty contribution from each of the main components is described as follows.

![Figure 4.26 Sources of uncertainty in peel test](image)
4.5.7.1 Relative standard uncertainty due to the strip width \( u_r(w) \)

The width of the strip varies which is checked by a 0-25 mm micrometer. The uncertainty of the strip width mainly comes from two sources, i.e. the strip width variation \( u(V) \) and the calibration uncertainty of the micrometer \( u(C) \).

4.5.7.1.1 The strip width variation \( u(V) \)

The strip width variation is evaluated by measuring 30 strips under repeatable conditions. The mean of the 30 measurements for laser and knife cutting is 0.98 cm and 1.029 cm respectively. The corresponding standard deviation is 0.071 cm and 0.284 cm. Therefore, the standard deviation of the mean for laser and knife cutting is:

\[
u(V_{\text{laser}}) = \frac{0.071}{\sqrt{30}} = 0.013 \text{ cm} \quad (4.51)
\]

\[
u(V_{\text{knife}}) = \frac{0.284}{\sqrt{30}} = 0.052 \text{ cm} \quad (4.52)
\]

4.5.7.1.2 Calibration uncertainty of the micrometer \( u(C) \)

For 0-25 mm micrometer, the expanded uncertainty is typically 0.004 mm according to the standard ISO 3611 with a coverage factor of 2 \([120]\). This yields a standard uncertainty of 0.002 mm \((0.004/2=0.002 \text{ mm})\).

4.5.7.1.3 Relative standard uncertainty of the strip width \( u_r(w) \)

The standard uncertainty of the strip width for both laser and knife cutting can be calculated by combining the above two components.

\[
u(w_{\text{laser}}) = \sqrt{(u(V_{\text{laser}}))^2 + u(C)^2} = \sqrt{0.013^2 + 0.0002^2} = 0.013 \text{ cm} \quad (4.53)
\]

\[
u(w_{\text{knife}}) = \sqrt{(u(V_{\text{knife}}))^2 + u(C)^2} = \sqrt{0.052^2 + 0.0002^2} = 0.052 \text{ cm} \quad (4.54)
\]

The relative standard uncertainty of the strip width can then be obtained.

\[
u_r(w_{\text{laser}}) = \frac{u(w_{\text{laser}})}{w_{\text{laser}}} = \frac{0.013}{0.98} = 1.326\%
\quad (4.55)
\]

\[
u_r(w_{\text{knife}}) = \frac{u(w_{\text{knife}})}{w_{\text{knife}}} = \frac{0.052}{1.029} = 5.045\%
\quad (4.56)
\]
It can be seen that the uncertainty of the strip width mainly comes from the strip width variation for both knife and laser cutting. The uncertainty due to the micrometer's reading is insignificant.

### 4.5.7.2 Relative standard uncertainty due to the measured forces $u_r(F)$

Uncertainty due to the measured force mainly comes from two main sources, i.e. the uncertainty due to the machine’s accuracy $u(A)$ and the uncertainty due to measurement repeatability $u(R)$.

#### 4.5.7.2.1 Relative uncertainty due to the machine’s accuracy $u_r(A)$

The force gauge used for the peel test carries an accuracy of ±0.10% of the full scale which is 2.5 kN for the machine used in this study. This yields an absolute accuracy of 2.5N. According to the rectangular distribution, the absolute standard uncertainty due to the force gauge accuracy is:

$$u(A) = \frac{2.5}{\sqrt{3}} = 1.443 \text{ N}$$

(4.57)

The average peel strength measured for the samples in this thesis is around 85N which generate the relative uncertainty to be:

$$u_r(A) = \frac{u(A)}{F} = \frac{1.443}{85} = 1.697\%$$

(4.58)

#### 4.5.7.2.2 Relative uncertainty due to measurement repeatability $u_r(R)$

The repeatability of the peel strength measurement is checked by measuring the gravity of a known weight of 700 g by 20 times. The average value of the 20 times measurement is 6.69 N with standard deviation of 0.1019 N (n=19). Therefore, the standard and relative uncertainty of the mean is:

$$u(R) = \frac{0.1019}{\sqrt{20}} = 0.02173 \text{ N}$$

(4.59)

$$u_r(R) = \frac{0.0217 \times 3}{6.69} = 0.3248\%$$

(4.60)

#### 4.5.7.2.3 Relative standard uncertainty of the measured force $u_r(F)$

The relative standard uncertainty of the measured force $u_r(F)$ can be calculated by combining the above two effects.
\[ u_r(F) = \sqrt{u_r(A)^2 + u_r(R)^2} = \sqrt{1.697^2 + 0.3248^2} = 1.728\% \quad (4.61) \]

It can be seen that the major source of uncertainty for the measured force comes from the accuracy of the measured machine. The uncertainty due to repeatability is insignificant.

### 4.5.7.3 Relative standard uncertainty due to material non-uniformity \( u_r(M) \)

The non-uniformity of the material depends on lamination conditions. It is estimated by measuring the peel strength of multiple strips of samples cured at each condition. For 90° peel test, 24 strips are measured for each lamination condition while for T-peel test, 6 strips are measured (results shown in Chapter 5). For 90° peel test, the standard uncertainty of the mean ranges from 4 N/cm to 8 N/cm for the investigated lamination conditions while that for T-peel test ranges from 0.5 N/cm to 2.2 N/cm. The worst case of 8 N/cm and 2.2 N/cm for 90° peel test and T-peel test is taken respectively as an indication of the effects of material non-uniformity on peel strength uncertainty. They correspond to the measured mean value of 86 N/cm and 43 N/cm respectively. The relative uncertainty can then be calculated as:

\[
u_r(M_{90^\circ}) = \frac{u(M_{90^\circ})}{F(90^\circ)} = \frac{8}{86} = 9.302\% \quad (4.62)
\]

\[
u_r(M_T) = \frac{u(M_T)}{F(T)} = \frac{2.2}{43} = 5.116\% \quad (4.63)
\]

The obtained uncertainty due to material non-uniformity not only accounts for the effects of non-uniformity but also includes the effects of environment and operation.

### 4.5.7.4 Combined and expanded relative uncertainty of the peel test

The combined relative standard uncertainty for the peel test can be calculated using the following equation by combining the uncertainty of strip width, the
uncertainty of force measurement and the uncertainty due to material non-uniformity:

\[ u_r(S) = \sqrt{u_r(w)^2 + u_r(F)^2 + u_r(M)^2} \]  

(4.64)

For 90° peel test,

\[ u_r(S_{90°}) = \sqrt{u_r(w_{laser})^2 + u_r(F)^2 + u_r(M_{90°})^2} = \sqrt{1.326^2 + 1.728^2 + 9.302^2} = \sqrt{1.758 + 2.9860 + 86.5272} = 9.5 \% \]  

(4.65)

For T-peel test,

\[ u_r(S_T) = \sqrt{u_r(w_{knife})^2 + u_r(F)^2 + u_r(M_T)^2} = \sqrt{5.045^2 + 1.728^2 + 5.116^2} = \sqrt{25.452 + 2.9708 + 26.173} = 7.3 \% \]  

(4.66)

For a coverage factor of 2, multiplying the combined standard uncertainty by 2, gives the expanded uncertainty with a level of confidence of 95%.

\[ U(S_{90°}) = \pm 2 \times 9.5 \% \times S = \pm 19 \% \times S \]  

(4.67)

\[ U(S_T) = \pm 2 \times 7.3 \% \times S = \pm 14.6 \% \times S \]  

(4.68)

The calculation of uncertainty for the peel test is summarised in Table 4.10.

<table>
<thead>
<tr>
<th>Sources of uncertainty</th>
<th>90° peel</th>
<th>T-peel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative uncertainty of the strip width ( u_r(w) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strip width variation ( u(V) )</td>
<td>0.013 cm</td>
<td>0.052 cm</td>
</tr>
<tr>
<td>Calibration uncertainty of the micrometer ( u(C) )</td>
<td>0.0002 cm</td>
<td>0.0002 cm</td>
</tr>
<tr>
<td>( u_r(w) )</td>
<td>1.326%</td>
<td>5.045%</td>
</tr>
<tr>
<td>Relative uncertainty of the measured force ( u_r(F) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative uncertainty of the machine’s accuracy ( u_r(A) )</td>
<td>1.697%</td>
<td>1.697%</td>
</tr>
<tr>
<td>Relative uncertainty of measurement repeatability ( u_r(R) )</td>
<td>0.3248%</td>
<td>0.3248%</td>
</tr>
<tr>
<td></td>
<td>1.728%</td>
<td>1.728%</td>
</tr>
<tr>
<td>-----------------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>Relative uncertainty due to material non-uniformity $u_r(M)$</td>
<td>9.302%</td>
<td>5.116%</td>
</tr>
<tr>
<td>Relative uncertainty of the peel test</td>
<td>9.5%</td>
<td>7.3%</td>
</tr>
<tr>
<td>Expanded relative uncertainty of the peel test</td>
<td>19%</td>
<td>14.6%</td>
</tr>
</tbody>
</table>

From the above calculation, it can be seen that for 90° peel test, the measurement uncertainty mainly comes from the material non-uniformity. Strip width variation and force gauge uncertainty are relatively minor contributions to the uncertainty. However, for T-peel test, the strip width and the material non-uniformity have similar magnitude contribution to measurement uncertainty while the uncertainty from force gauge reading is very small. This indicates the importance of the control of strip cutting which reduces the measurement uncertainty.

### 4.6 Stressing Test

Ageing of the samples is achieved through various accelerated stress tests. Both damp-heat and thermal cycling are used. Conditions are selected according to the IEC 61215 standard [121]. Damp-heat is a steady state condition with constant temperature and humidity levels. This is to investigate the ability of the samples to withstand moisture ingress. This is accelerated by temperature. In the IEC 61215, the damp-heat condition is set to 85°C – 85% RH. In this thesis, adjustments are made on the temperature and relative humidity levels to create different damp-heat levels.

For thermal cycling, temperature is cycled from -40°C to 85°C with detailed procedures shown in Figure 4.27. The aim of thermal cycling is to exam the ability of the samples to withstand thermal mismatch and thermal fatigue.
4.7 Conclusions

The performance of the encapsulation system is assessed from chemical (soxhlet extraction, DSC and FTIR-ATR), morphological (DSC), optical (transmittance measurement) and mechanical (adhesion strength at different interfaces) viewpoints. Soxhlet extraction for measuring the gel content of EVA is accurate (uncertainty around 0.9% for a coverage factor k=2) and an easy operation, but it is time consuming while DSC is quick but less accurate (uncertainty around 8% for a coverage factor k=2). FTIR-ATR and spectrophotometer are well developed methods for polymer characterisation. Peel tests can be noisy and need to be carefully controlled. This chapter only focuses on the principles, processes, and data analysis methods of each characterisation method. Detailed experimental flow including material, geometry and results of each part of the experiment is presented in the following chapters.

The lamination process of PV modules influences its financial feasibility. How different lamination conditions influence the overall reliability of the
encapsulation materials has not been well understood. The first part of the experimental work is to investigate these influences and also obtain a general understanding of different degradation phenomena of the encapsulant system. This will be discussed in Chapter 5. The reliability of PV modules is not only determined by the production quality but also varies at different locations of different environmental stress levels. Adhesion is one of the major degradation mechanisms and is poorly understood. The second part of the experimental work focuses on the reliability of adhesion strength to withstand moisture ingress under different temperature conditions. The details of this part are documented in Chapter 6.
5. Effects of Different Lamination Conditions on the Reliability of the Encapsulation System of PV Modules

5.1 Introduction

Lamination of PV modules requires a flat-bed laminator where temperature, pressure and time are controlled to achieve ‘optimum’ quality. As is discussed in section 2.4, the main processes during lamination are curing reaction and adhesion formation. The variation of lamination parameters will change the speed and magnitude of chemical reactions as well as phase transitions of the polymers within the encapsulation systems. This will influence the chemical, mechanical, optical and electrical properties of the encapsulation materials and thus the durability of PV modules.

In commercial production, deviations from lamination recipes can happen in several different ways. The starting temperature or curing temperature can be increased in attempts to accelerate the production processes. Lower temperatures may be experienced in the area where glass bending happens due to thermal stresses. Different deviations may also happen due to minor issues of the production equipment. The influences of the variation of these different lamination conditions on the reliability of encapsulation systems are not well documented. Understanding of these influences can help quality control of PV modules and supply more information on lamination. Besides, increased lifetime of PV modules is needed to improve the energy yield. A 30 year lifetime warranty has been proposed for future PV modules [122]. To achieve this, reliable encapsulation systems are required. Understanding how different lamination conditions influence the long-term performance of the encapsulant systems is crucial to improve the reliability of the encapsulation systems, which is the aim
of this chapter. In this chapter, the influence of different curing temperature and curing time on the long-term performance of the encapsulant systems of PV modules has been investigated.

Samples are produced using EVA as the encapsulant and PPE (PET-PET-EVA) as the backsheet. Three different curing temperatures of 125°C, 135°C and 145°C (for a curing time of 10min) and three different curing times of 5min, 10min, 20min (@145°C curing temperature) are investigated. The influence of these different lamination conditions on the properties of encapsulant materials is first analysed. Then, the influence on the long-term durability of the encapsulation systems is investigated through accelerated damp-heat and thermal cycling exposure. The properties that examined mainly include the curing level of EVA, chemical stability, optical changes of EVA and the adhesion strength at different interfaces within the encapsulation systems.
5.2 Experimental Design

Figure 5.1 Testing programme for laminates
A general testing programme of this chapter is depicted in Figure 5.1. Five different lamination conditions are investigated. EVA is the encapsulant material and PET/PET/EVA (PPE) is the backsheet. Specimens with three types of structure are laminated, i.e. backsheet-EVA-backsheet, glass-EVA-backsheet and free standing cured EVA. The properties examined include the adhesion strength at the glass-EVA interface (GEI) and EVA-backsheet interface (EBI), the gel content of EVA, the morphology, the chemical stability and the optical stability of EVA. The initial properties of un-aged samples are first measured followed by the reliability examination through damp-heat and thermal cycling tests. Ageing of the sample is achieved through damp-heat and thermal cycling exposure. Damp-heat is conducted at the condition of 85°C / 85% RH for an extended period of 2000h. Measurements are conducted at each 500 h time intervals, i.e. 500 h, 1000 h, 1500 h and 2000 h. For thermal cycling, laminates are tested after 200 cycles and 400 cycles, respectively. Details about the material, sample configuration and lamination processes are described in the following subsections.

5.2.1 Material

EVA used in this study is a fast curing EVA available from Evasa, Spain. It has a vinyl acetate content of 34%, a density of 0.96 g/cm³, a melting point of 63°C, a glass transition temperature of -25°C, and a UV cut off at 360 nm. Manufacturer recommended curing condition is 145°C to 150°C for a total time of 15 min.

The backsheet is a multilayer polymer. Figure 5.2 shows the microscopic image of the cross-section of the backsheet. The centre part is a modified PET and is the core part of the backsheet carrying the major protective electrical and mechanical functions. The outside is another layer of modified PET working as a protective layer. The cell side is an EVA layer providing high bonding strength to
the encapsulant. The three layers are bonded together using adhesives. The thickness of the backsheet is around 0.4mm.

![Cross Section Image](image)

Figure 5.2 Microscopic image of the cross section of backsheet (magnification X10)

Glass used is a low iron un-tempered float glass from Saint-Gobain with a thickness around 3.4 mm. As it is float glass, one side of it is tin rich. The tin side of the glass is identified by illuminating the glass with a UV lamp which emits brighter fluorescent. The non-tin side is used as the contact surface with the encapsulant materials. The glass is firstly submerged in deionised water for 5 min and then cleaned in an ultrasonic tank with isopropanol solution for 20 min and is dried by air gun.

### 5.2.2 Geometry

As is shown in Figure 5.1, samples of three types of configuration are produced, i.e., laminates with the structure of backsheet-EVA-backsheet, laminates with the structure of glass-EVA-backsheet, and free standing cured EVA sheets. For the free standing EVA, samples of two thicknesses are produced, the first is two layers of EVA and the second is one layer EVA. For the laminates, the EVA all consisted of two layers of EVA. This is to simulate the real condition of PV
modules where two layers of encapsulants is needed with one on top of the cells and the other on back of the cells. The geometries of the three kinds of samples are illustrated in Figure 5.3.

Figure 5.3 Sample configurations

Laminates of glass/EVA/backsheet are used to measure the adhesion strength at GEI. The size of the laminates is 100 mm X 125 mm. Silicone coated release papers are inserted between the EVA and the glass at one end of the samples to initiate the crack. For each laminate, the backsheet together with EVA is cut by a CO₂ laser system into strips of 10mm width. The cutting speed is 400 mm/s with a power of 50 W and 10 passes. After cutting, eight strips are generated for each sample. 90° peel test is conducted on each of the strip. The reliability of the adhesion strength at this interface is checked through both damp-heat and thermal cycling exposure. Three samples are produced at each degradation time interval for each lamination condition. The strip cutting is conducted after stress exposure and it is assumed that the stress exposure does not have significant influences on the edge of the cutting strip. 24 strips are measured at each testing point from which the average peel strength is calculated. After peeling off the strips from glass, FTIR-ATR tests are conducted on the surface of EVA that is in contact with glass. Three of the eight strips of each laminate are checked.

In order to measure the adhesion strength at EBI, laminates with the structure of backsheet/EVA/backsheet of 100 mm X 150 mm are produced. Failure locus is initiated by inserting a release paper at the very beginning of the sample between EVA and backsheet. The sample is cut into strips of 10mm width with a
sharp knife and T-peel tests conducted. Six strips are measured for each lamination condition from which the average adhesion strength is calculated.

In addition to the laminates, six free stand EVA sheets of 10 cm X 10 cm are cured at each condition. Three of the EVA sheets (one layer EVA) are used for crosslinking measurements which are measured through both conventional solvent extraction and DSC measurement. The other three (double layer EVA) are used for transmittance test. The ideal condition for both crosslinking measurements and transmittance tests is using the extracted EVA from the above laminates after peel test. It was firstly tried with the extracted EVA for DSC measurement, strange and inaccurate heat peaks appeared. DSC is very sensitive to material purity and states, however, after extraction, the EVA will be deformed and contaminated. The stress during the extraction of EVA may also change EVA crystallinity by exerting orientation upon the molecular chain. The deformation of EVA will also influence the results of transmittance measurements. Furthermore, the 1 cm strip after peel test is too narrow for the sample compartment of the spectrophotometer. Thus, free standing EVA sheets are used to represent the worst case during damp-heat exposure. Since two layers of EVA are too thick for the sample pans of DSC, only one layer EVA is used for DSC measurements.

5.2.3 Curing and Lamination

5.2.3.1 Lamination Profile

The curing of EVA and lamination of samples are performed using a 2BG laminator L176A (Figure 5.4). Figure 5.5 shows the lamination profile used in this chapter by taking the condition of 145°C curing temperature and 10 min dwell time as an example.
The vacuum of the laminator is established within 1 min followed by a 4 min hold time to degasify the laminator and samples. Lamination does not start with the required curing temperature but 15°C lower than the curing temperature to avoid too much and too quick curing during the vacuum stage. The temperature does not increase directly to the curing temperature but to a stage which is 10°C lower than the curing temperature. This increase of temperature is achieved within 1-2 min and temperature is maintained at this level for the rest of the vacuum hold time.

Figure 5.4 Laminator

Figure 5.5 Lamination profile
Following the vacuum hold time, a pressure of 100 KPa is applied within 1 min to the upper chamber. During the application of pressure in the upper chamber the temperature continues to increase to the curing temperature within 1-2 min. The intermediate temperature stage in the vacuum process is to avoid overshooting of temperature. The heating plate of this laminator is a thick copper layer with thermocouples installed underneath. The resistance between the heating plate and the thermocouples due to imperfect contact leads to the real plate temperature being hotter than indicated by the thermocouples. In the curing process, when pressure is applied, the contact between the heating plate and the thermocouples will be improved, and the indicated temperature will jump to a level which is higher than the set curing temperature. The intermediate temperature stage minimises this overshooting. Pressure is applied at the intermediate temperature which is 10°C lower than the curing temperature. There will still be a temperature increase after applying pressure but to a level that is not higher than the curing temperature. The increasing temperature in the following step is thus more controllable. In this thesis, the time of this stage is called "curing time", i.e. it includes the time of temperature increase from the intermediate temperature to the curing temperature as well as the time of maintaining constant curing temperature and pressure.

After curing, the lower chamber of the laminator is ventilated and reaches atmospheric pressure within 1 min while the upper chamber is evacuated. Samples are taken out of the laminator and cooled in ambient conditions.

5.2.3.2 Lamination Conditions

The lamination is conducted at five conditions as listed in Table 5.1. This includes three different temperatures of 125°C, 135°C, 145°C and three different curing times of 5 min, 10 min, and 20 min.
### Table 5.1 Lamination conditions

<table>
<thead>
<tr>
<th>No.</th>
<th>Curing temperature (°C)</th>
<th>Curing time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>125</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>135</td>
<td>10</td>
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<td>3</td>
<td>145</td>
<td>10</td>
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<tr>
<td>4</td>
<td>145</td>
<td>5</td>
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<tr>
<td>5</td>
<td>145</td>
<td>20</td>
</tr>
</tbody>
</table>

5.3 Effects of Different Curing Temperature and Time on the Reliability of the Encapsulation Systems of PV Modules

This section presents the results of the different properties examined for the laminates. During the damp-heat exposure, due to the malfunction of different equipment, some of the measurements are not possible to conduct. There will be some blank data points, but this does not influence the general trend of the results.

#### 5.3.1 Bubble Formation

In order to identify the critical temperature from which bubbles start to appear, laminates with the structure of glass-EVA-backsheet are first produced at the higher temperature of 160°C with 10 min curing time. Figure 5.6 shows that two types of bubbles are observed. The first type of bubbles is located at the interface between the EVA and the backsheet and is relatively large in size. At the temperature of 160°C, these type of bubbles are often connected together covering almost the entire area of the laminates. It can directly result in delamination. The other type of bubble is trapped within the EVA layer and is much smaller than the first type of bubble. It is spherical in shape, with a
diameter mostly less than 2 mm. It leads to reduced adhesion at the interfaces of both glass-EVA and EVA-backsheet. The possible mechanisms for bubble generation are trapped air due to inefficient evacuation as well as evolved volatiles during lamination. 160°C is too high a temperature for this lamination design, and curing occurs too quickly before air and generated volatiles are removed from the laminator.

Figure 5.6 Bubbles formed at the curing temperature of 160 °C

Since 160°C is too high, the curing temperature is reduced down to 155°C. Fewer bubbles are produced. Bubbles at the backsheet disappear with only the small bubbles within EVA left. A further reduction of temperature of 5°C, i.e. to 150°C yields almost bubble-free laminates with only a few small bubbles trapped within the EVA. Laminates at 150°C are also produced but the adhesion after lamination is very weak as will be shown in the section 5.3.7. Therefore, 150°C is considered as the critical temperature for the lamination system used in this chapter.
5.3.2 Effects of Different Curing Temperature and Time on EVA Gel Content

5.3.2.1 Gel Content of EVA Cured at Different Temperature and Time

Two samples of EVA are measured for gel content at each lamination condition with the results shown in Figure 5.7. In general, the gel content increases with both curing temperature and dwell time. With increasing of curing temperature, the gel content increases gradually from around 70% at 125°C – 10 min to over 90% at 145°C – 10 min. However, at 125°C – 10 min, on the surface of the flask and the surface of the mesh, small sticky particles are identified in a molten state, i.e. gel leakage could have happened (Figure 5.8). The gel leakage indicates that the EVA is not well cured at 125°C – 10 min. To obtain a proper curing with the curing temperature of 125°C, a longer dwell time is required. For a curing time of 10 min, a temperature higher than 135°C is required to achieve gel content above 85%.

With the increasing of curing time from 5 min to 20 min at 145°C, the measured gel content increases with a quicker rate from 5 min (80% gel content) to 10 min (90% gel content) and slows down afterwards until it stabilises at 92%. More than 5 min dwell time is needed at the curing temperature of 145°C to achieve gel content higher than 85%.

Another observation is that at lower gel content, the deviation of the results is larger and at higher gel content, the deviation is smaller. This is because with increasing gel content, the crosslinking reaction tends to be more complete, which result in smaller deviation.
Figure 5.7 Gel content of EVA cured at different temperatures for a curing time of 10 min (upper figure) and at different times at curing temperature of 145°C (lower figure).

Figure 5.8 Gel leakage during extraction.
5.3.2.2 Changes of EVA Gel Content during Damp-Heat Exposure

In order to see the influence of humidity and temperature on gel content from long-term aspects, EVA sheets are exposed to damp-heat condition and gel content is measured at different time intervals during exposure. Figure 5.9 shows the changes of EVA gel content during damp-heat exposure for samples cured at different temperatures and time conditions. No obvious changes are observed for EVA cured at 135°C – 10 min, 145°C – 10 min, 145°C – 5 min and 145°C – 20 min where gel content around 85%, 90%, 80% and 90% is maintained respectively even after 2000 h exposure. This indicates that there is no further on-site curing during damp-heat exposure. For the condition of 125°C – 10 min, gel leakage still happened even after 2000 h damp-heat degradation and results are not reliable.

Figure 5.9 Changes of gel content during damp-heat exposure
5.3.3 Effects of Different Curing Temperature and Time on DSC

Results

Besides the soxhlet extraction method, the curing of EVA is also checked using DSC measurement. In order to distinguish the results from extraction, the results obtained from DSC is defined as curing state. The aim of this comparison is to show the correlation between the two methods. Other information such as the crystallinity and melting temperature of EVA can also be obtained from the DSC curves. During degradation, the results from DSC can also give information of peroxide within EVA.

5.3.3.1 Curing State of EVA Cured at Different Temperature and Time

The curing state of EVA is obtained according to the method described in section 4.3 with the results plotted in Figure 5.10. Similar trends compared to the Soxhlet extraction are observed. The curing state increases with the increasing of curing temperature and curing time. From 125°C to 145°C, the curing state increases from approximately 50% to 85%. At the curing temperature of 145°C, with the increasing of curing time from 5 min to 20 min, the curing state increases from 57% to 90%. The increasing rate is quicker from 5 min to 10 min and slower afterwards. To achieve a curing state above 85%, a residual enthalpy less than 3 J/g is needed. Same as the extraction method, the variation reduces with the increasing of curing state.
Figure 5.10 Curing state of EVA cured at different temperatures for a curing time of 10 min (upper figure) and at different times at curing temperature of 145°C (lower figure).

A correlation curve between the gel content measured from soxhlet extraction and the curing state measured from DSC is presented in Figure 5.11. A non-linear correlation is observed. The results measured from DSC are lower than that obtained from extraction. For different types of EVA, this correlation is different depending on the types of peroxide and needs to be estimated for each type of EVA.
5.3.3.2 Changes of EVA Curing State during Damp-Heat Exposure

Figure 5.12 shows the changes of curing state during damp-heat exposure. During exposure, the curing state for samples laminated at all the five conditions increases gradually until it stabilises at around 90%. The largest increase happens within the first 500 h exposure.

From the gel content results shown in section 5.3.2, no further crosslinking occurred during degradation. This indicates that the increasing of curing state measured by DSC is caused by the depletion of the peroxide either through physical release or decomposition. None of these processes contribute to the crosslinking of EVA. The decomposition of peroxide can generate high energy free radicals which can participate in other reactions such as deacetylation, creating polyenes which can be detected by ATR spectrum. This will be discussed in section 5.3.5.

The variation of the results increases from 0 h to 1000 h and then decreases until 2000 h. This is because the peroxide starts decomposition during damp-heat exposure. The decomposition is more completed throughout the whole sample.
with the increasing exposure time. At 500 h and 1000 h, the consumption of the peroxide is not homogenous while after 1500 h, the consumption tends to be complete.

![Curing state changes under damp-heat exposure](image)

**Figure 5.12 Curing state changes under damp-heat exposure**

### 5.3.4 Effects of Different Curing Temperature and Time on EVA Melting Temperature

The curing state of EVA is expected to influence its physical properties. Therefore, the melting transitions are analysed for the various curing conditions. As is discussed in section 4.3, the first melting peak in thermograms of EVA is caused by the imperfect crystallisation while the second melting peak reflects the primary crystallites of polyethylene within EVA. The melting point reflects the size of the crystals, i.e. larger crystals result in higher melting temperature and smaller size result in lower melting points. The maximum temperature of the second melting peak (\(T_{m,max}\)) is expected to represent the average size of the primary crystals within EVA [123].
5.3.4.1 Melting Temperature of EVA Cured at Different Temperatures and Times

Figure 5.13 shows the correlation of the T$_{m,\text{max}}$ of EVA with different curing temperature and time. The T$_{m,\text{max}}$ decreases with the increasing curing temperature and curing time. With increasing of lamination temperature and time, the curing degree of EVA increases. As a result of the increased curing degree, the structure of EVA becomes more compact and the freedom of motion of EVA macromolecules is reduced. Thus, the structure rearrangement and folding is hindered during the cooling processes, resulting in smaller crystals.

Figure 5.13 $T_{m,\text{max}}$ of EVA cured at different temperatures for a curing time of 10min (upper figure) and at different times at curing temperature of 145°C (lower figure)
The above analysis indicates that there is a correlation between $T_{m,max}$ and the curing degree of EVA. The relationship between the $T_{m,max}$ and the curing state of EVA is presented in Figure 5.14. It exhibits a strong dependence of the melting position on the curing state. With the increasing curing state, the value of $T_{m,max}$ decreases. To achieve a curing state above 85%, a $T_{m,max}$ of less than 57°C is required whereas a curing state less than 60% result in a $T_{m,max}$ higher than 59°C. This result indicates another method for calculating the curing of EVA through the measurement of the melting points.

![Figure 5.14](image)

Figure 5.14 The maximum temperature of the 2nd melting peak vs. the curing state of EVA for all the investigated lamination conditions

5.3.4.2 Changes of EVA Melting Temperature during Damp-Heat Exposure

The changes of $T_{m,max}$ during the damp-heat exposure are demonstrated in Figure 5.15. No obvious changes are observed during degradation for samples cured at all the five investigated conditions. This corresponds to the unchanged gel content of EVA during damp-heat exposure.
5.3.5 Effects of Different Curing Temperature and Time on EVA

Chemical Stability

EVA is not stable under environmental stresses and is sensitive to moisture. The vinyl acetate part of EVA is susceptible to hydrolysis under humidity. With the presence of oxygen, thermo oxidation degradation may occur. The chemical changes of EVA of the laminates during damp-heat exposure are examined through an infrared spectrometer. After peeling off the strips, EVA is extracted and the surface in contact with glass is tested using FTIR-ATR according to the method described in section 4.4.

The FTIR-ATR spectra of EVA cured at different conditions during damp-heat exposure is shown in Figure 5.16. In general, with the increase in exposure time, the absorption of hydroxyl peaks (3200 cm\(^{-1}\) – 3800 cm\(^{-1}\)) increases. This can be due to moisture ingress that is hydrogen bonded to the acetate groups or vinyl acetate hydrolysis which generates a molecular hydroxyl group and acetic acid. In fact, the hydrolysis of vinyl acetate is also a result of moisture ingress as water...
is one of the reactants of hydrolysis. The acetate C=O peak (1735 cm⁻¹), the ester C-O (1236 cm⁻¹) peak and C-O-C peak (1018 cm⁻¹) all decrease with damp-heat exposure which implies progressing hydrolysis of EVA. The absorbance at 2918 cm⁻¹ and 2950 cm⁻¹ represent the asymmetrical and symmetrical stretching of methylene groups in the backbone of EVA, which decreases during degradation. This may be caused by deacetylation reactions with the formation of ethylene bonds. This reaction is known as “Norrish II” which transfers the alkyl into alkene (see Figure 3.1). The methylene peak reduction may also be resulted from the methylene oxidation with the formation of carbonyls. For the two reactions, one generates polyenes while the other generates unsaturated carbonyls, both of which are widely considered as chromophores of EVA discoloration [17]. After degradation, two new peaks appeared around 1640 cm⁻¹ and 1560 cm⁻¹. The two new formed peaks generally increase with ageing time which are assigned to the olefins C=C stretching.
In order to rank the stability of samples cured at the different conditions, absorbance of some of the main functional groups during damp-heat exposure...
are calculated by computing the peak area with the results shown in Figure 5.17–Figure 5.20. The examined peaks include the hydroxyl groups (3200–3800 cm⁻¹), the ester groups (1735 cm⁻¹ and 1236 cm⁻¹) and the methylene group (2918 cm⁻¹).

The hydroxyl absorption in the range of 3800–3200 cm⁻¹ reflects the moisture absorption capability of EVA. EVA cured at 125°C for 10 min shows the largest and the quickest absorption. The peak increases from 0 h to 500 h, after which it maintains stable until 2000 h degradation. This is followed by EVA cured at 145°C – 5 min. No obvious differences are identified for the other three conditions, i.e. 135°C – 10 min, 145°C – 10 min and 145°C – 20 min where absorption increases continuously with a lower rate before 500 h and a higher rate thereafter. After 2000 h, they reach the same level of that of the 125°C – 10 min condition. Moisture absorption rate for EVA cured at these three conditions is much slower than that cured at 125°C – 10 min. Saturated moisture ingress is achieved within 500 h for 125°C – 10 min whereas approximately 10% of the maximum moisture is absorbed at the other three conditions. When the peak area increases, the standard deviation becomes larger. This is because the moisture absorption is uneven throughout the whole sample.

EVA cured at lower temperature and shorter dwell times are more hygroscopic than that cured at higher temperature and longer time especially at the condition of 125°C – 10 min. This can be explained by the curing level of EVA. With the increasing degree of crosslinking, structural compaction of EVA is improved with reduced free spaces within EVA, which results in reduced water absorption capacity. According to the measured curing level in section 5.3.2, EVA cured at 125°C – 10 min and 145°C – 5 min has the lowest gel content of around 65% and 80% while the other three conditions all have gel content above 85%. The low gel content at 125°C – 10 min and 145°C – 5 min results in faster moisture ingress.
Figure 5.17 ATR absorbance changes of hydroxyl groups during damp-heat exposure

The two peaks at 1736 cm$^{-1}$ and 1236 cm$^{-1}$ are due to ester absorption. They can represent EVA hydrolysis. For all the conditions, the peak area of both peaks declines continuously. EVA cured at 125$^\circ$C – 10 min shows the fastest and most significant decline, followed by the laminates prepared at 145$^\circ$C – 5 min. There are not too many differences between the other three conditions of 135$^\circ$C – 10 min, 145$^\circ$C – 10 min and 145$^\circ$C – 20 min. Comparing the absorbance drop between 125$^\circ$C – 10 min and 145$^\circ$C – 5 min, although similar levels are reached after around 1000 h damp-heat exposure, 125$^\circ$C – 10 min shows quicker degradation between 0-500 h while quicker decreasing occurs at 500-1000 h for 145$^\circ$C – 5 min. This is because the moisture absorbed in EVA cured at 125$^\circ$C – 10min has already reached its maximum absorption within 500 h while for the condition of 145$^\circ$C – 5 min, very limited amount of moisture is absorbed after 500 h exposure but it increases greatly between 500-1000 h (Figure 5.17).

The above analysis demonstrates that cleavage of the ester group shows dependence on lamination conditions with higher degradation at lower curing
temperatures and shorter dwell times. This dependence is due to different moisture absorption capacities which are influenced by the degree of curing. Therefore, curing is one of the dominant influencing factors on EVA hydrolysis.

Figure 5.18 ATR absorbance changes of 1736 cm\(^{-1}\) during damp-heat exposure

Figure 5.19 ATR absorbance changes of 1236 cm\(^{-1}\) during damp-heat exposure
The absorption at 2918 cm$^{-1}$ exhibits trends similar to the ester related peaks. No obvious differences are identified for the conditions of 135$^\circ$C – 10 min, 145$^\circ$C – 10 min, and 145$^\circ$C – 20 min. 125$^\circ$C – 10 min shows the largest and fastest decreasing followed by the condition of 145$^\circ$C – 5 min.

Figure 5.20 ATR absorbance changes at 2918 cm$^{-1}$ during damp-heat exposure

As can be seen from the above analysis, chemical stability of EVA is dependent on EVA curing degree. Figure 5.21 gives an example of the correlation between the moisture peak area after 1000 h damp-heat exposure and the gel content of EVA. With increasing gel content, the area of moisture peak decreases until the gel content is over 85% where the moisture absorption area stabilises. With increasing crosslinking, the spatial structure of the three dimensional molecular network of EVA becomes more compact and thus is less susceptible to moisture and oxygen ingress. Therefore, reactions such as hydrolysis and thermal oxidation will slow down leading to less degradation. For the investigated EVA, gel content above 85% insures good stability while those less than 70% shows high risk of moisture ingress, hydrolysis and backbone breakage.
5.3.6 Effects of Different Curing Temperature and Time on EVA

Optical Stability

5.3.6.1 Transmittance of EVA Cured at Different Temperature and Time

The transmittance results for EVA cured at different temperature and time conditions are shown in Figure 5.22. No obvious differences can be seen at different curing conditions. The spectrum has a UV cut-off around 360nm. This is due to the UV absorber added in EVA formulation which has strong absorption of UV irradiance in the range of 270nm-360nm. In the visible range, transmittance is approximately 93% for all the conditions.
5.3.6.2 Changes of EVA Transmittance during Damp-Heat Exposure

As is demonstrated in Figure 5.22, different lamination conditions result in near identical transmittance. This may change with ageing, as is investigated here. Figure 5.23 shows the transmittance changes of EVA during damp-heat exposure for different lamination conditions in the wavelength range between 200nm-1200nm.

Three areas can be identified. The first area is 200 nm – 270 nm where a slight increase can be seen. The second area is 270 nm – 360 nm where except 145°C – 5 min, no obvious changes are observed. The third area is the visible range 360 nm – 800 nm where non-uniform decreases are seen. UV absorber mainly functions in the range of 270 nm – 360 nm where it has strong UV absorption so that EVA base material is protected from UV deterioration. The stable condition in area (2) indicates that there is no depletion of the UV absorber within the EVA. The increasing transmittance at 200 nm – 270 nm and the decreasing transmittance at 360 nm – 800 nm are due to the discolouring chromophores formed during damp-heat exposure. It is noticed that in the visible region, the transmittance reduction is especially high in the range of 400 nm to 500 nm.
which corresponds to blue light absorption. The loss of light transmittance in this region leads to irradiance domination of mixing green and red light making EVA appears more yellow. As is reviewed in section 3.1, EVA discoloration is mainly caused by the appearance of chromophores including polyenes (C=C bonds) and the α-β unsaturated carbonyl groups. According to the results in section 5.3.5, polyenes are identified in the infrared spectrum for all the five conditions with the absorption peaks at around 1640 cm⁻¹ and 1560 cm⁻¹.

For the transmittance degradation in area (3), the degradation becomes smaller with the increasing of curing temperature and time in the investigated ranges. Samples cured at 125°C – 10 min present the worst optical stability. The transmittance keeps a downward tendency from 0 h to 1000 h, after which it gradually increases until 2000 h exposure. This is followed by the condition of 145°C – 5 min. 145°C – 20 min shows similar degradation level with that of 145°C – 5 min which implies that too much curing does not improve the optical stability. Samples cured at 135°C – 10 min shows much better optical stability but are still worse than that at 145°C – 10 min which presents the best stability with the majority of the reduction occurs in the region of 400 nm – 500 nm. The recovery happened at 125°C – 10 min is also identified in the curing conditions of 135°C – 10 min, 145°C – 5 min and 145°C – 20 min.

The transmittance degradation at 145°C – 20 min demonstrates different behaviour than the other conditions in the range of 380 nm – 500 nm. There is a sharp peak at around 390 nm for the conditions of 145°C – 5 min, 145°C – 10 min, 135°C – 10 min and 125°C – 10 min while the peak is much broader at 145°C – 20 min. Transmittance in this range has smaller changes during damp-heat exposure than the other conditions. This may be caused by over-cooking of the EVA where additives are over consumed triggering reactions that generate more types of chromophores.
The relationship of the transmittance changes during damp-heat exposure at the different conditions can be more quantitatively observed by plotting the relative changes of the integrated transmittance (integrated from 360 nm to 800 nm) with that before exposure vs. the exposure time which is shown in Figure 5.24. The 145°C – 10 min condition presents the best optical stability with around 5% reduction within 2000 h damp-heat exposure. This is followed by the condition of 135°C – 10 min where the lowest point is at 500 h after which recovery occurs. 125°C – 10 min demonstrates the largest optical degradation with around 13% continuous reduction from 0 h to 1000 h and then gradually recovers about 10% afterwards. But even after recovery, the transmittance is still lower than that at 145°C – 10 min. 145°C – 5 min follows the similar trend of 125°C – 10 min with degradation stops after 1000 h and recovers afterwards. 145°C – 20 min shows comparable degradation with that of 145°C – 5 min but unlike the other conditions where large degradation happens, optical reduction at 145°C – 20 min shows less fluctuation after 500 h.
The unexpected improvement of optical transmission may be caused by the oxidation of the generated chromophores with the presence of oxygen under high temperature. For the free standing cured EVA, FTIR-ATR tests are also conducted. The area of peak at 1560 cm\(^{-1}\) which corresponds to the polyenes is presented for the different lamination conditions during damp-heat exposure in Figure 5.25. The peak area shows similar increasing and decreasing trend with the transmittance for EVA cured at 125\(^\circ\)C – 10 min and 135\(^\circ\)C – 10 min. At 125\(^\circ\)C – 10 min, this peak area increases until 1000 h followed by a gradual decrease until 2000 h exposure. At 135\(^\circ\)C – 10 min, it increases from 0 h to 500 h when the highest intensity is seen and then the absorption starts decreasing until 1500 h. The peak area at 145\(^\circ\)C – 20 min is similar to that at 145\(^\circ\)C – 10 min while the transmittance reduction at 145\(^\circ\)C – 20min is larger than that at 145\(^\circ\)C – 10 min. This indicates that there are other chromophores contribute to the transmittance reduction at 145\(^\circ\)C – 20 min.
Figure 5.25 ATR absorbance changes of 1560 cm\(^{-1}\) during damp-heat exposure

5.3.6.3 Changes of Whiteness Index (WI) and Yellowness Index (YI) during Damp-Heat Exposure

From the above analysis, it can be seen that EVA tends to become yellow under damp-heat exposure. To further investigate the degree of yellowness, the whiteness index (WI) and yellowness index (YI) is calculated with the results shown in Figure 5.26 and Figure 5.27. WI indicates the degree of the material departures from a preferred white while YI indicates how much of these change from a preferred white towards yellow. With the increasing of exposure time, WI decreases while YI increases, which means EVA becomes less colourless during exposure.

Seen from Figure 5.26, samples cured at 145\(^o\)C – 20 min demonstrate the largest WI reduction followed by 125\(^o\)C – 10 min and then 145\(^o\)C – 5 min. 135\(^o\)C – 10 min and 145\(^o\)C – 10 min show the smallest decline with 135\(^o\)C – 10 min slightly larger than that at 145\(^o\)C – 10 min. At 125\(^o\)C – 10 min, the average value of WI reduces from around 90 to 72 within 1000 h exposure after which, just as the recovery of transmittance, the value of WI increases back to 80% at 1500 h and
stays stable after 2000 h exposure. The reverse increase of WI is also identified for the condition of 135°C – 10 min at 1000 h. This reverse of WI is consistent with the changes in transmittance curves. This is because the general reduction and increase of transmittance leads to reduction and increase of WI.

For the YI, the largest increase occurs for the condition of 145°C – 20 min followed by 145°C – 5 min and 125°C – 10 min. 135°C – 10 min and 145°C – 10 min shows the smallest increase. The recovery of transmittance and WI is also reflected in the YI results. There is a continuous increase of YI for the condition of 125°C – 10 min from 0.5 at 0 h to 3.5 at 1000 h followed by a drop from 1000 h to 1500 h. At 135°C – 10 min, the YI increases from 0 h to 500 h and then slightly decreases but is not obvious. This is because the changes of transmittance at 135°C – 10 min are in very small scale.

Figure 5.26 Changes of the whiteness index of EVA during damp-heat exposure
Samples cured at 145°C – 20 min shows the largest deviation from colourless. However, the transmittance values for this condition are much higher than that at 125°C – 10 min. An example of the T% comparison of the two conditions is shown in Figure 5.28 for EVA exposed in damp-heat conditions for 500 h. 145°C – 20 min has higher transmittance than 125°C – 10 min in the range of 460 nm – 800 nm but the YI of 145°C – 20 min is higher than 125°C – 10 min. This is because the decreasing of transmittance at 145°C – 20 min is much steeper with significant drops between 460 nm and 510 nm than that at 125°C – 10 min. This uneven transmittance deviation from the un-aged samples leads to more departure of colour from the given preferred white.
5.3.7 Effects of Different Curing Temperature and Time on Peel Strength

This section aims to understand the dependence of adhesion strength at the glass-EVA interface (GEI) and the EVA-backsheet interface (EBI) on different lamination conditions. The reliability is checked for both damp-heat and thermal cycling stress tests.

5.3.7.1 Peel Strength of Laminates Cured at Different Temperature and Time

For each of the investigated lamination conditions, trials are conducted before full experiments are carried out to check the fracture interfaces within the laminates. Laminates of glass-EVA-backsheet is preferred as it represents the structure of PV modules. A fracture is initiated at EBI by placing a release paper at the beginning of one end of the samples and then peeling the backsheet from EVA at 90°. For most of the conditions, the failure locus jumps to the GEI after a few seconds of fully loading of the peel arms and maintains at GEI for the
remaining peeling. This indicates that GEI is the critical failure interface. However, there are two exceptional conditions, i.e. 125°C – 10 min and 145°C – 5 min where failure alternates between EBI and GEI. To obtain the adhesion strength at EBI, a T-peel test is conducted. The measured peel strength at GEI and EBI for samples laminated under different temperatures and times is demonstrated in Figure 5.29.

There is large variation for the results at GEI. For the different temperatures of 125°C, 135°C and 145°C, no statistical differences can be seen for the results at GEI with average values in the range of 80 N/cm to 100 N/cm. The major contribution of adhesion at GEI is the siloxane (Si-O-Si) bonds formed between the silane coupling agents and glass. Possible reasons for the similarity of peel strength at the three temperature conditions is that the reaction between glass and silane coupling agents starts at a very low temperature and 10 min is enough for the reaction to achieve similar level under all the three investigated temperature regimes. However, at 125°C – 10 min, the reliability of the results is suspect. Not too many data are collected at this condition because the failure tends to happen at EBI although the fracture is initiated at GEI. The peel strength at EBI at 125°C – 10 min measured under 90° is around 50 N/cm which is much lower than that at GEI. It is also noted that for the curing condition of 150°C – 10 min, the measured strength at GEI is in general lower than 5 N/cm and can be peeled off manually. As is pointed out in section 5.3.1, 150°C is a critical temperature at which bubbles start to generate. With increasing curing temperature to 150°C, the starting temperature also increases which accelerates crosslinking during EVA melting. Like most polymers, the wettability of EVA reduces with increasing crosslinking [124]. Reduced wettability will lead to bad contact between EVA and glass and thus reduces the adhesion strength. Together with the formation of bubbles, lamination at 150°C results in samples with low adhesion strength. For the lamination system used in this chapter, 150°C is too high to generate strong adhesion strength and samples cured at this condition
are not subjected to accelerated ageing tests. It should be noted that this kind of critical temperature varies with laminator, sample geometry and lamination procedure.

In contrast to the peel strength at the GEI, peel strength at the EBI illustrates an obvious increasing trend with curing temperature from approximately 7 N/cm at 125°C to 42 N/m at 155°C. The adhesion at the EBI mainly comes from the mutual diffusion of the inner side of the backsheets which are coated with EVA compatible film and the encapsulant EVA. The diffusion rate constant follows the Arrhenius behaviour which is exponentially proportional to temperature. The mobility of the molecular chains also increases with temperature. The positive dependence of diffusion with temperature is the main reason for the increased adhesion strength at EBI with curing temperature.
Figure 5.29 Peel strength at GEI and EBI for laminates cured at different temperatures for a curing time of 10min (upper figure) and at different times at curing temperature of 145°C (lower figure)

In the case of laminates cured at different times of 5 min, 10 min, 15 min and 20 min, the peel strength at GEI increases from 5 min to 10 min and stays at a similar level for longer time duration. Even with 5 min curing time, the peel strength is over 40 N/cm. There are two possible reasons for the lower peel strength at 5 min. Firstly, intimate contact between EVA and glass is achieved by applying pressure upon laminates. Samples cured at 5 min have the pressure maintaining time of 5 min which is much shorter than the other three conditions. Besides, with the shortening of curing time, the formation of silane-oxygen bonds between glass and the coupling agents is less complete than the other three conditions. It is suggested to ensure enough pressure maintaining time to allow good adhesion at the GEI.

As the curing time increases from 5 min to 20 min, peel strength at the EBI more than doubles from 19 N/cm to 45 N/cm. The increase is quick at the beginning and stabilises after 15 min. The diffusion between the EVA compatible material at the inner side of backsheet and the bulk EVA increases with curing time.
Therefore, stronger adhesion is achieved with longer curing time. The stabilization after 15 min may indicate that the diffusion has almost completed within this time duration and longer time does not contribute more to the adhesion strength.

Comparing the two sets of results, as the measurement set up's are different; it is difficult to obtain quantitative correlations. However, it can still be inferred that peel strength above 20 N/cm (generated from samples cured at 135°C) measured by T-peel test can result in adhesion strength much higher than that of 90 N/cm obtained from 90° peel tests.

For the laminates of glass-EVA-backsheet, failure interface varies with the lamination conditions. The fracture locus is recorded during peel test with the distributions presented in Figure 5.30. Glass-EVA and EVA-backsheet represent fracture that occurs at the GEI and the EBI, respectively, while mixed mode means the fracture changes between the two interfaces. As the curing temperature increases from 125°C to 150°C, the failure shifts from the dominant EBI to predominantly the GEI and then completely GEI. With the increasing curing temperature, the mutual diffusion of EVA and EVA compatible materials in the inner side of the backsheet increases. At 125°C, the temperature is too low for the diffusion to result in adhesion strength higher than that between glass and EVA under a dwell time of 10 min. Therefore, the weakest point for samples laminated at 125°C – 10 min is at the EBI, where failure happens predominantly. Similar trends are observed when the curing time increases from 5 min where failure happens almost equally at the EBI and the GEI to 10 min where fracture mainly happens at the GEI and then to 15 min and 20 min where de-bonding is completely at the GEI. This indicates that the lamination time of 5 min at 145°C is too short for the mutual diffusion to generate an interfacial strength that is higher than that between glass and EVA.
5.3.7.2 Changes of Peel Strength during Damp-Heat Exposure

The degradation of peel strength at GEI for laminates cured at different temperature and time conditions is shown in Figure 5.31. For all five lamination conditions, similar degradation behaviour is identified. The measured peel strength starts at a similar level and then degrades by approximately 75% within 300 h and remains constant at around 10-20 N/cm afterwards until 2000 h. The stabilised peel strength at 125°C – 10 min is about 10 N/cm higher than the other conditions. The possible reason for this is that at 125°C – 10 min, EVA is not well
cured and still has strong viscous properties. At damp-heat test of 85°C, it can soften to a viscous melt and wet the glass to re-build up more secondary forces resulting in improved adhesion. However, this flowing also increases the risk of cell moving, crack and breakage and should be avoided for PV modules.

![Graph of degradation of peel strength between glass and EVA for samples](image)

Figure 5.31 Degradation of peel strength between glass and EVA for samples cured at different temperatures for a curing time of 10min (upper figure) and at different times at curing temperature of 145°C (lower figure)
After 2000 h damp-heat exposure, peeling of laminates cured at 125°C – 10 min, 145°C – 10 min and 145°C – 20 min is impossible as the strip broke. This indicates that the cohesive strength of the strip became smaller than the adhesion strength after ageing. The snap firstly happens at the outside layer of the backsheet, i.e. the first PET layer, while the other two layers of the backsheet stays together and bonded with EVA very well (Figure 5.32). Continued peeling causes the other two layers of the backsheet to break together with the EVA. The reason for the breakage is that the material becomes brittle after degradation. EVA cured at 145°C – 10 min and 145°C – 20 min has a high curing degree which is good for creep resistance and chemical stability but meanwhile increases material stiffness making it more susceptible to embrittlement. Samples laminated at 125°C are less chemically stable with more hydrolysis and chain broken. It also has higher crystallinity. These make the material vulnerable for embrittlement.

![Figure 5.32 Breakage of the peeling strip after 2000h damp-heat exposure](image)

During damp-heat exposure, failure does not always happen at the GEI but shifts during degradation. The pattern depends on lamination conditions. The development of the distribution of fracture interfaces at each lamination condition is presented in Figure 5.33. With the increasing of stress application, the failure area for laminates cured at 125°C – 10 min changes from dominant
EBI to a combination of both EBI and GEI failure. As temperature increases to 135°C, peeling occurs mostly at GEI throughout the 2000 h damp-heat exposure. When temperature further increases to 145°C, the fracture pattern changes from predominantly GEI failure to the combined failure of both GEI and EBI after 1000 h exposure. At 145°C – 5 min, the changes are in contrast with that of 145°C – 10 min. Fracture shifts from jumping GEI and EBI failure before stress testing to dominantly GEI failure after stress exposure. For samples cured at 145°C – 20 min, the adhesion strength at the EBI is higher than that at the GEI so that failures occur at the GEI before stress testing and this fracture locus is maintained for the whole damp-heat exposure.
Figure 5.33 Distribution of the identified failure locus during damp-heat exposure
5.3.7.3 Changes of Peel Strength during Thermal Cycling

The reliability of adhesion at the GEI is also checked through thermal cycling tests with the results shown in Figure 5.34. In general, the peel strength decreases continuously from 0 cycles to 400 cycles. The mechanisms of interfacial strength degradation under thermal cycling are different from those of damp-heat. As is discussed in section 3.3, under thermal cycling, material expansion and contraction occurs and thermal stress is built up due to mismatched CTE of the different components. In the laminates, due to the stiffness of the front glass, EVA volumetric changes are strongly constrained. When temperature increases, compression thermal stress towards EVA is developed at the interface between glass and EVA. Irreversible plastic deformation can happen once the generated compression thermal stress exceeds the yield strength of EVA. In contrast, when the laminates are cooled down, shrinkage happens. Compressive thermal stress created during heating up will gradually change to tensile thermal stress. Irreversible plastic deformation occurs when the tensile stress exceeds EVA yield strength. The change of thermal stress continues with the cyclic temperature until failure happens.

![Figure 5.34 Degradation of peel strength between glass and EVA under thermal cycling](image_url)
Seen from Figure 5.34, for laminates cured at the three different temperature conditions, the degradation follows similar trends. After 200 cycles, those cured at 145°C-10min shows the highest peel strength followed by 125°C – 10 min and then 135°C – 10 min. After 400 cycles, they achieve the same level of around 30 N/cm. During thermal cycling, the amount of material expansion and shrinkage is proportional to the differences of the CTEs. For crosslinked polymers, research shows that the expansion coefficient reduces with the increasing of crosslinking degree [125,126]. Therefore, the amount of expansion and contraction declines with the increasing crosslinking degree and the generated residual stresses is reduced. However, as discussed in the previous section, samples with much lower curing state will benefit from their viscous properties which help the formation of stronger secondary forces after softening. It is thus not surprising that samples cured at 125°C – 10 min have higher peel strength than that at 135°C – 10 min after 200 cycles exposure.

For the three different curing time conditions, laminates cured at 10min shows the best stability. Those cured at 145°C – 5 min witnesses slight increasing at 400 cycles after reduction from 0 cycle to 200 cycles. Samples with the longest curing time of 20 min degrade quickest which lost adhesion after 200 thermal cycles. In fact, among the investigated five lamination conditions, 145°C – 20 min demonstrates the lowest stability under cyclic thermal stresses. This is due to its high crosslinking degree of EVA. Too fast curing, especially throughout evacuation process during lamination, can result in imperfect interfaces in the form of voids and bubbles which delaminate quicker. Furthermore, the higher crosslinking also results in higher polymer shrinkage during curing which means more residual thermal stress within EVA will be developed during the following cooling process [127]. With more residual stress, debonding occurs more easily. This increasing trend of residual stress and crosslinking degree has been experimentally detected by Li [29].
5.4 Optimum Lamination Condition

The performance of the different properties are summarised in Table 5.2 for the investigated five lamination conditions.

Samples cured at 125°C – 10 min represent the situation of insufficient curing and bad backsheet-encapsulant adhesion. It shows problems of unstable chemical properties, obvious optical yellowing and haze, weak adhesion between EVA-backsheet. This instability can be explained by the low curing level. With the decreasing degree of crosslinking, EVA structure compaction is reduced with more free spaces which result in more water absorption. The low backsheet-encapsulant adhesion also supports moisture and oxygen ingress. However, looking at the adhesion strength at the GEI, it demonstrates the best stability. They show especially good moisture resistance with adhesion strength after 1000 h damp-heat exposure almost double of the other four conditions. They also show very strong adhesion after 200 thermal cycling tests. The high adhesion strength at 125°C – 10 min is due to EVA viscous properties at low curing level. This should be avoided as the melting can cause cell moving, cracking and breakage.

Samples cured at 145°C – 5 min have similar problems with those produced at 125°C – 10 min but with a smaller degradation rate. Samples cured at this condition have gel content around 80% which is better than 125°C – 10 min but lower than the other conditions. The pressure maintaining time is much lower than the other conditions. This means the effectiveness of the pressure on the spatial structure improvement at this condition are less than the other conditions. Due to the short dwell time, adhesion at the encapsulant-backsheet is lower than the other conditions. The low curing, short pressure maintaining time and bad backsheet-encapsulant adhesion lead to an unstable encapsulation system.
Results at 145°C – 20 min show that curing for too long does not increase stability but have adverse effects. Although it has the highest gel content and strongest backsheet-encapsulant adhesion which results in a high chemically stable material, it shows the largest YI increase, large transmittance reduction, and the largest adhesion reduction under thermal cycling. Too quick and too high curing will result in higher residual thermal stresses and the generation of more volatiles during lamination leading to an encapsulation system with imperfect surfaces and the EVA prone to become yellow.

150°C – 10 min represents another over-cooking condition with too high temperature. Samples cured at this condition did not go through detailed characterisation as the backsheet does not quite adhere to the encapsulant.

Samples laminated at 145°C – 10 min have a gel content of 90%, and show least moisture ingress, least EVA hydrolysis and least transmittance reduction. They also have strong adhesion at both the GEI and the EBI. Samples cured at 135°C – 10 min and 145°C – 10 min are comparable except the adhesion strength at EBI which is lower for 135°C – 10 min than that at 145°C – 10 min.

A correlation between the curing level of EVA and the quality of the lamination can be seen. The chemical and optical stability increases with the increasing curing level. The curing level also influences the adhesion strength between encapsulant and backsheet which increases with the increasing curing level. For the adhesion strength between glass and encapsulant, the curing level does not show obvious influences on adhesion formation but more on the long-term performance. The wettability of EVA reduces with increasing crosslinking. If curing occurs too quickly in vacuum process before EVA is sufficiently melted, it can result in imperfect interfaces between EVA and glass. Besides, residual thermal stresses within the laminates built up during lamination also depend on
crosslinking degree. The higher the crosslinking, the more residual stresses are built up within the structure during lamination which will be released as deformation during outdoor operation. This can accelerate de-bonding and cracking. On the other hand, the CTE of the material reduces with increasing crosslinking degree, which means the generated residual stresses due to mismatched CTEs are reduced with the increasing crosslinking degree.

Table 5.2 Performance summaries of the laminates cured at different conditions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Gel content (%)</th>
<th>Chemical Stability</th>
<th>Optical Stability</th>
<th>Adhesion (N/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O-H peak area after 1000h exposure</td>
<td>C=O peak area decreasing after 1000h exposure</td>
<td>T% Losses</td>
<td>Max % Losses</td>
</tr>
<tr>
<td>145°C-20min</td>
<td>92</td>
<td>4</td>
<td>13%</td>
<td>5%</td>
</tr>
<tr>
<td>145°C-10min</td>
<td>90</td>
<td>4</td>
<td>11%</td>
<td>2%</td>
</tr>
<tr>
<td>135°C-10min</td>
<td>84</td>
<td>4</td>
<td>10%</td>
<td>4%</td>
</tr>
<tr>
<td>145°C-5min</td>
<td>80</td>
<td>8</td>
<td>19%</td>
<td>6%</td>
</tr>
<tr>
<td>125°C-10min</td>
<td>68</td>
<td>10</td>
<td>19%</td>
<td>13%</td>
</tr>
<tr>
<td>150°C-10min</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Besides gel content, pressure maintaining time is also important for the lamination quality. Suitable curing duration is required. Too short a pressure maintaining time has a risk of insufficient curing, loose material structure and weak adhesion at encapsulant-backsheet interface. Too long a pressure maintaining time can cause too high curing level and generating samples with unstable optical stability.

It is difficult to define an optimum lamination condition as there are so many properties to be considered. Looking at the chemical stability, lamination conditions resulting in higher gel content are preferred. From an optical
perspective, lamination conditions with gel content higher than 80% but lower than 90% show better stability. Too long curing and too high temperature has a risk of generating more chromophores. If focusing on the adhesion stability between glass and encapsulant, curing condition generating samples of gel content around 70% is better than higher gel content conditions. Regarding the adhesion between backsheet and encapsulant, the higher the curing temperature and the longer the curing time, the stronger the adhesion. In general, lamination conditions generating EVA with gel content lower than 70% shows high risk of moisture ingress, transmittance reduction, weak backsheet-encapsulant adhesion and high risk of EVA flowing. According to the testing results from PI Berlin that is presented in section 2.4.1, 35% of the modules in the market are not well cured. However, this does not mean conditions resulting in the highest curing level are better. Results show that conditions generating gel content higher than 92% will cause samples of unstable optical properties. Too high temperature and too long curing will destroy adhesion with the creation of imperfect interfaces and bubbles. These high conditions should be avoided during lamination. It is also found that conditions resulting in gel content in the range of 85% to 90% produce encapsulation system with comparable stability. Therefore, it is not necessary to pursue gel content higher than 85% to achieve the optimum stability.

5.5 Conclusions

The lamination process is one of the most important factors influencing the reliability of the encapsulation system and thus the durability of PV modules. A process which requires lower energy and shorter time are financially preferred. The influence of different curing temperature and time on the long-term performance of the encapsulation system of PV modules has been investigated from the perspectives of gel content, the optical stability and the chemical
stability of EVA as well as the adhesion strength at glass-EVA and EVA-backsheet interfaces.

Several different degradation phenomena of the encapsulation system are identified. Moisture can penetrate into the encapsulant material inducing subsequent material degradation such as hydrolysis, oxidation, and deacetylation. Transmittance reduction is detected with accompanied yellowing. Adhesion between the glass and encapsulant declines during damp-heat and thermal cycling tests. Among these observed degradations, adhesion reduction is the most obvious one with the quickest and the largest degradation. A stabilised level of adhesion strength is achieved within around 300h under the damp-heat condition of 85 °C / 85% RH. This damp-heat condition is aggressive for the adhesion testing.

A correlation between the curing level of the EVA and the reliability of the lamination has been demonstrated. The chemical stability, optical stability and the adhesion strength between encapsulant and backsheet increases with the increasing curing level. The adhesion strength between glass and encapsulant is also influenced by curing level due to viscoelastic properties, thermal stresses and expansion coefficients. Curing level lower than 70% can result in unstable materials. The problems of too high curing are also demonstrated and it is also pointed out that too high curing should be avoided.

A critical temperature range exists for each type of EVA. Lower than this temperature will result in weak adhesion between EVA and backsheet because of insufficient molecular diffusion between the EVA and the EVA compatible materials at the inner side of the backsheet. Temperatures which are too low will also result in a lower curing level generating samples of unstable chemical and optical properties. Temperatures higher than the nominal range of temperature have a high risk of over-cooking. Besides, although higher curing temperature
often result in higher curing state, at the same time increases material thermal stresses which can accelerate interfacial de-bonding. A reasonable curing time is also needed, too short a curing time may cause adhesion failures, insufficient curing and loose EVA structure. However, this does not mean the longer curing time, the better. Too long a curing will also lead to bubble formation and quicker delamination. Overcooking can result from too high temperatures or too long a curing time, both are detrimental to the stability of the encapsulation system.

The reliability of the encapsulation system of PV modules are influenced by both production and operating environment. This chapter presents how different lamination conditions influence the reliability of the encapsulation systems. Correlations between the crosslinking degree of EVA and the stability levels are demonstrated. However, the degradation rates of these identified failures also depend on different stress levels. The influence of different stress levels on the reliability of the encapsulation systems of PV modules are investigated in the next chapter. As is shown in this chapter, adhesion strength has the most obvious degradation and is thus the focusing point in the next chapter.
6. Degradation of Interfacial Adhesion Strength within PV Modules during Damp-Heat Exposure

6.1 Introduction

As is shown in Chapter 5, adhesion decreases during stress testing and the degradation rate is quicker than that of the bulk encapsulant materials. The loss of adhesion strength is expected to vary with the operating environment, depending on factors of temperature, humidity, and irradiance, including UV. Among these, moisture is considered to cause the greatest problems in terms of adhesive joint stability. The effects of moisture on adhesion strength have been discussed in section 3.2. These effects are accelerated by temperature.

There are a number of published studies of adhesion strength degradation for PV modules. But they are normally based on progressive uncontroll ed ageing or carried out at a single controlled operating condition. Jorgensen and McMahon [128] measured the peel strength of different interfaces within thin film PV modules of various technologies and structures before and after damp heat conditioning, and under UV light. Non-uniform adhesion strength reduction was observed at different interfaces and they suggested that tests at higher temperature and relative humidity levels were preferred to screen modules. Pern and Jorgensen [118] investigated the adhesion strength between glass and EVA and its resistance to damp heat exposure by developing different primer formulations for EVA. Enhanced adhesion strength was observed for laminates with EVA having high density siloxane primers. Jorgense and the co-workers [14] tested the durability of the adhesion strength between glass and EVA for laminates with different kinds of backsheets under damp-heat condition at 85°C / 85% RH. It was found that no samples tested were able to maintain adhesion after 100 h of exposure. Although increasing concern is given to adhesion issues,
there have been few reliability tests and quantitative degradation studies. The degradation pattern of adhesion strength is not established and the numerical correlation to environmental stresses such as temperature and humidity levels is currently largely being postulated.

The aim of this chapter is to establish a method that allows a comparison of the ageing behaviour of the adhesion strength of PV modules operating at different humidity and temperature conditions. The objective is to understand the effects of sustained steady state stresses of humidity and temperature on the backsheet adhesion. In standard qualification testing, this is carried out through damp-heat test, where modules are exposed to a relative humidity of 85% at a temperature of 85°C [121,129]. The aim of this chapter is achieved by exposing PV modules under different damp-heat conditions and investigating the acceleration rates of different stress levels on the loss of adhesion strength between backsheet and encapsulant of PV modules due to moisture ingress. The measured peel strength at different damp-heat conditions are presented in section 6.4. Then, the degradation is investigated in dependence of stresses which is discussed in section 6.4.

6.2 Experimental Design

Figure 6.1 presents the testing flow chart for the experiments. Experiments in this chapter require exposure of samples to different temperature and humidity levels as well as the measurement of the adhesion strength between backsheet and encapsulant at selected time intervals. A visual inspection is also carried out after removal of the modules from the environmental chambers, prior to the peel test. To minimise sample-to-sample variations, PV modules produced by a single manufacturer are used.
6.2.1 Samples

The samples used in this chapter are commercial frameless small area laminates with polycrystalline silicon solar cells inside (Figure 6.2). These laminates have no edge seal which accelerates the overall humidity ingress compared with laminates protected by edge seal. The length and width of the mini-module is 140 mm and 100 mm, respectively. The encapsulant material is a conventional cured EVA and the backsheets are a double layer of PET. The curing agent of the EVA used in the commercial mini-modules are different from that used in the laminates in Chapter 5. The thicknesses of the EVA layer and backsheets are approximately 400 µm and 250 µm, respectively, which are measured by microscope. At the back side of the module, there is a narrow opening where the positive and negative contact tabs are fed through to the active region of the module. This imperfect sealing also accelerates moisture ingress.
6.2.2 Peel Test

The adhesion strength between the backsheet and encapsulant is measured by a 90° peel test. Laser cutting system is used with a cutting speed of 762 mm/s with a power of 32 W and 10 passes. The cutting is conducted along the short edge of the module and ten strips are formed for each module. Each of the peel strips is 10 mm in width and 100 mm in length. 20-30 strips from two to three different modules are examined at each testing point.

6.2.3 Environmental Stressing

The different stress levels are achieved by multiple environmental chambers operating at five different combinations of temperature and relative humidity as listed in Table 6.1. It includes three different levels of relative humidity (85%, 65%, and 45%) at a temperature of 85°C as well as another two temperatures (95°C and 65°C) with relative humidity of 85%. The testing time and number of modules at each condition are shown in Figure 6.1.

<table>
<thead>
<tr>
<th>T</th>
<th>RH</th>
<th>85%</th>
<th>65%</th>
<th>45%</th>
</tr>
</thead>
<tbody>
<tr>
<td>95°C</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>85°C</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>65°C</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1 Testing conditions for PV modules
The stress levels chosen here are based on the IEC qualification test standard IEC 6125 where the damp-heat test is conducted at 85°C / 85% RH. Varying temperature and humidity levels are selected based on this condition to give an indication of the acceleration rates of different humidity and temperature levels. Because the environmental chambers are limited to 90% RH, no humidity levels beyond 85% are chosen. Two lower relative humidity levels, i.e. 65% RH and 45% RH are selected. Another two temperature levels, with one of the temperature higher than 85°C and the other one lower than 85°C, are selected to accelerate moisture ingress at different rates. An elevated temperature of 95°C is selected to accelerate moisture ingress with the hope not to trigger new degradation mechanisms.

Before the experiment, trial tests are performed at 85°C / 85% RH to roughly qualify the modules and the test points are chosen according to the data collected there. It is found that the adhesion strength degrades to 2-3 N/cm after only 100 h exposure at this stress condition. Therefore, in general, daily measurements are carried out.

### 6.3 Results of Adhesion Strength during Damp-Heat Exposure

#### 6.3.1 Visual Inspection

Several types of visual defects are observed during damp-heat exposure. Some of the more severe ones are depicted in Figure 6.3. Delamination is seen, mostly at corners and edges of the mini-module. The lack of an edge seal left the edge directly open to environment where stronger influences are experienced compared with those devices with an effective moisture barrier. Imperfect
lamination may also contribute to the developing fault. Moisture penetration is also identified. Some bubbles appear during degradation and most of them are at the backsheet/EVA interface causing backsheet delamination. After 24 h stress exposure at 95°C / 85% RH, a large bubble around the electrodes is observed. This is due to the poor protection around the external contacts where an access cut in the backsheet is not well sealed, allowing water vapour ingress. The majority of the modules have passed visual inspection.

Figure 6.3 Defects observed after damp heat testing: edge/corner delamination (a), moisture ingress (b) and bubble near electrode exit (c)

6.3.2 Failure Locus

The fracture during peel test can happen either at an interface or in the bulk of a material (cohesive failure) if the structural integrity is weaker than the bonding strength at the interface. The failure interface during the peel test is checked visually as well as by taking microscopic photos at the surface of the inner side of backsheet. An example is shown in Figure 6.4 which presents the microscopic image of the surface of one of the peeled backsheet strips after 48 hours degradation at 85°C / 85% RH. No EVA is identified attached on this surface which indicates that the failure locus is interfacial rather than cohesive and the measured peel strength is that of the interface between backsheet and encapsulant.
6.3.3 Degradation of Adhesion Strength with Time

Adhesion strengths are plotted against time of stress exposure in Figure 6.5 for all the conditions listed in Table 6.1. The adhesion strength under different conditions shows a similar degradation pattern in the form of a stretched exponential decay. The adhesion strength decreases quickly at the beginning and then tends to slow down after a certain time. The largest degradation occurs at 95°C / 85% RH which has lost over 90% of the adhesion after 48 h exposure. This is followed by the stress condition of 85°C / 85% RH, 85°C / 65% RH and then 85°C / 45% RH. The smallest reduction of adhesion is seen at the stress condition with the lowest temperature of 65°C / 85% RH. Increased humidity accelerates the loss of adhesion. Temperature further enhances the effect of humidity at a faster rate. Besides 65°C / 85% RH, modules under all the other conditions degrade to a level of around 3 N/cm within 200 h. In general, the reduction of the adhesion strength is rather quick, but this can be attributed to the high stress levels and the absence of an edge seal in these particular samples. The small sample size of 0.012 m² which is about 1-2% of a normal commercial module further increases humidity uptake. All of these factors increases
acceleration in the tests; however, the principles of degradation remains unchanged.

Figure 6.5 Reduction of peel strength in dependence of applied stresses and time

The adhesion strength with degradation time under different conditions can be fitted by the following equation:

\[ S_t = S_0 e^{-\left(\frac{t}{t_{\text{del}}}\right)^\beta} \]  

(6.1)

where \( t \) is the stress exposure time, \( S_0 \) is the adhesion strength before stress exposure (i.e. at \( t=0 \)), \( S_t \) is the adhesion strength at time \( t \), \( \beta \) and \( t_{\text{del}} \) are two parameters controlling the slope and tail of the degradation curves. The parameter \( t_{\text{del}} \) primarily determines the slope of the degradation and \( \beta \) represents the magnitude of the influence of \( t_{\text{del}} \). The overall behaviour of the degradation depends on the combination of \( t_{\text{del}} \) and \( \beta \). The fitted values of \( t_{\text{del}} \) and \( \beta \) for each condition are documented in Table 6.2. Different stress conditions have different values of \( t_{\text{del}} \) and \( \beta \). Therefore, the prediction of adhesion strength reduction with time based on Eq 6.1 requires additional modelling of the dependence of \( t_{\text{del}} \) and \( \beta \) on stress levels and duration. An alternative simplified
solution would be to develop a parameter that enables the modelling of adhesion degradation with this single variable. This will be discussed later in section 6.4.

Table 6.2 Parameters for the adhesion strength degradation

<table>
<thead>
<tr>
<th>Conditions</th>
<th>t_{del}</th>
<th>B</th>
<th>Experiment R_D</th>
<th>Acceleration Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>65°C - 85% RH</td>
<td>230</td>
<td>0.74</td>
<td>11%</td>
<td>1</td>
</tr>
<tr>
<td>85°C - 85% RH</td>
<td>53</td>
<td>1.03</td>
<td>26%</td>
<td>2.3</td>
</tr>
<tr>
<td>95°C - 85% RH</td>
<td>14</td>
<td>0.687</td>
<td>56%</td>
<td>5.1</td>
</tr>
<tr>
<td>85°C - 65% RH</td>
<td>81</td>
<td>0.9</td>
<td>21%</td>
<td>1.9</td>
</tr>
<tr>
<td>85°C - 45% RH</td>
<td>118</td>
<td>0.86</td>
<td>14%</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Also listed in Table 6.2 are the degradation rates (R_D) calculated from experimental data (average R_D for each condition) and the corresponding acceleration rates (AR). The degradation rate is defined as the percentage adhesion strength decline over time:

\[ R_D = \frac{s_t-s_t^0}{t} \times 100\% \]  

(6.2)

The degradation rate at 65°C / 85% RH is the lowest with an average decline of 11% while that at 95°C / 85% RH is the highest with average value of 56%. If taking the lowest degradation at 65°C / 85% RH as baseline, 1-5 times acceleration rates (the ratio of the degradation rates at different conditions) are observed for the other four conditions. Lower stress levels (lower temperature, lower humidity) cause lower degradation and higher stress levels (higher temperature, higher humidity) lead to higher degradation. However, this correlation is suitable to certain stress ranges. Once the applied ambient humidity is low enough, the direction of moisture flow will change from ingress into PV modules to drying out of the module. When the temperature is too high, thermal mechanical degradation will be dominant. These conditions are likely to trigger different degradation effects and thus it is not possible to extrapolate the adhesion degradation behaviour observed in this chapter to very low humidity or extreme high temperature conditions.
The adhesion strength shown in Figure 6.5 is the average values for the entire module (i.e. the averaged measurements from the full lengths of all peel strips) at each testing point. They do not give any indication of variations across the module. An impression of this variation can be obtained by aligning all peel tests for one module side-by-side to create a contour plot. This kind of spatial profile can give an insight of how the adhesion strength varies over the surface of a module and how it changes over time under stress. Figure 6.6 is the contour plots showing the development of adhesion strength at each of the damp-heat conditions at different exposure times. One sample is randomly selected at each exposure time. The x-axis represents the strip number with each strip in 10 mm width and the y-axis is the distance from the peeling end in mm, i.e. the length of strips. The colour scale demonstrates the adhesion strength in N/cm and the blank areas at corners and edges indicate null data where the strips snapped during the peel.
Figure 6.6 Contour plots of the measured adhesion strength over the module surface (the scale bar represent the peel strength in N/cm)

As shown in Figure 6.6, the peeling of all strips starts close to the distance of 85 mm and ends at the 0 mm point. The first 15 mm is peeled off before the actual test to create the peeling tab for the machine to seize. In general, the adhesion
strength reduces as the modules degrade. Several peaks in adhesion strength exist at different locations before degradation but gradually disappear during exposure and become more evenly distributed. The degradation trends are consistent with that shown in Figure 6.5.

Although from the contour map it is not easy to define a precise degradation pattern, it presents the spatial distribution of adhesion strength across the surface of the whole module which could be helpful for the identification of the weakest spots in a production batch. This would be useful in module production for quality control and diagnosing manufacturing faults. For this module, it can be observed that large spikes often exist near 10 mm because that is where the silicon cells end and although it is checked that the peeling still progress over the EVA-backsheet interface, the sudden change of the substrate results in higher adhesion values. It is also noticed that before degradation, the edges of the modules has lower adhesion strength than the centres. Possible explanations are poor quality lamination at the edge, or the open edge of the modules being more influenced by the environment so that some degradation has occurred.

In order to see the chemical changes of the backsheet during degradation, FTIR-ATR spectroscopy tests are conducted at the inner side of the backsheet. An example of the results is shown in Figure 6.7 by presenting the normalised ATR spectrum of the samples shown in Figure 6.6 that degrade at 65°C / 85% RH for 0 h, 72 h and 192 h within the spectral range of 600 cm\(^{-1}\) to 2000 cm\(^{-1}\). Some of the main absorption bands observed are listed in Figure 6.7 [130-132]. Absorption at 1410 cm\(^{-1}\) is associated with the aromatic skeletal stretching and is used as reference. Peaks at 1710 cm\(^{-1}\), 1242 cm\(^{-1}\), 1096 cm\(^{-1}\) are attributed to ester C=O stretching which will decrease if hydrolysis occurs. Bands at 723 cm\(^{-1}\), 870 cm\(^{-1}\) and 1017 cm\(^{-1}\) correspond to the benzene vibration. Absorption at 1340 cm\(^{-1}\) and 1370 cm\(^{-1}\) are CH\(_2\) wagging which represent the trans and gauche conformation respectively and can be used as an indicator of PET crystallinity.
To examine the chemical changes of the backsheet in details, the normalised band area at $1710 \text{ cm}^{-1}$ (C=O band of ester) and $1340 \text{ cm}^{-1}$ (crystallinity band) are calculated using average values of all the ten strips for each of the three samples with the results shown in Figure 6.8. No obvious changes of the ester and crystallinity groups are observed, indicating that the backsheet have not experienced too much chemical degradation, although its adhesion strength with EVA has degraded by around 58%. Therefore the interface between the EVA and backsheet is much more affected than the bulk material.
Figure 6.8 Normalised absorption of inner backsheet during degradation at 65°C / 85% RH: band at 1710 cm⁻¹ represents the C=O stretching of ester, band at 1340 cm⁻¹ shows the evolution of crystallinity of PET and band at 1410 cm⁻¹ is used as reference.

6.4 Degradation of Adhesion Strength in Dependence of Humidity and Temperature

In this part, the degradation of adhesion strength is investigated by correlating the degradation rates with environmental stresses aiming to compare the backsheet adhesion degradation of PV modules operating at different environmental conditions.

6.4.1 Stress Model Development

6.4.1.1 Micro Climate

In order to quantify the stresses acting on the modules over a certain period of time, the ambient macro climate, i.e. the ambient temperature and the relative humidity measured at ambient temperature, must be translated to module micro
climate, i.e. module temperature and the relative humidity at the surface of the backsheet at the module temperature. In field deployment under irradiation, PV module operating temperature is higher than ambient air temperature. The higher module temperature means that the relative humidity experienced by the device is lower than the ambient. There are different published models in literature that can be used to predict module temperature from ambient temperature [133,134]. The damp-heat tests in environmental chambers, as presented here, are different to realistic operation because the device temperature is equal to ambient temperature, i.e. module temperature ($T_m$) is identical to chamber air temperature ($T_a$). This difference needs to be considered when attempting to predict a service life-time for an outdoor installation.

Relative humidity is defined as the ratio of the partial pressure of water vapour to the saturated pressure of water at the given temperature [135]. The ambient relative humidity ($RH_a$) can be described as following equation:

$$RH_a = \frac{P_w}{P_s(T_a)}$$  \hspace{1cm} (6.3)

where $P_w$ is the partial water vapour pressure of the atmosphere, $P_s(T_a)$ is the saturated pressure of water vapour at ambient temperature ($T_a$). The microclimatic relative surface humidity at the backsheet of PV modules for outdoor exposure can be calculated as shown in Eq 6.4 using the model proposed by Koehl et al [136]:

$$RH_m = \frac{P_w}{P_s(T_m)} = \frac{RH_a \cdot P_s(T_a)}{P_s(T_m)}$$ \hspace{1cm} (6.4)

where $RH_m$ is the relative humidity at the surface of the backsheet, $P_w$ is the partial water vapour pressure of the atmosphere, $P_s(T_m)$ are saturated water vapour pressure at module temperature ($T_m$). This model is adopted from the definition of relative humidity with the consideration of the module temperature. There are some assumptions of this model that the surface of the backsheet is in thermodynamic equilibrium with the atmosphere and the temperature is uniform across the module. The calculations of saturated and absolute water
vapour pressure of the atmosphere are made according to the standard BS 1339-1:2002 [135]:

\[ P_s = f \cdot P_s' \]  \hspace{1cm} (6.5)  
\[ P_w = \text{RH} \cdot P_s = \text{RH} \cdot f \cdot P_s' \]  \hspace{1cm} (6.6)  

where \( P_s' \) is the pure saturation vapour pressure at a given temperature, \( P_s \) is the saturated vapour pressure in the air, \( f \) is an enhancement factor to transfer \( P_s' \) to \( P_s \), and \( P_w \) is the partial pressure of water vapour in the air. \( P_s' \) is influenced by temperature and can be calculated as a function of absolute temperature \( T \):

\[
\ln P_s' = -\frac{6096.93}{T} + 21.2409642 - 2.711193 \cdot 10^{-2} \cdot T + 1.673952 \cdot 10^{-5} \cdot T^2 + 2.433502 \cdot \ln T \]  \hspace{1cm} (6.7)  

The enhancement factor \( f \) can be approximated from different models in literature. For a simplification, it can be obtained from the following equation:

\[
f = 1.0016 + 3.15 \cdot 10^{-8} P - 74 P^{-1} \]  \hspace{1cm} (6.8)  

where \( P \) is the total pressure in air. The value is 1.00406 at the standard atmosphere pressure.

For the calculations of \( P_s' \) and \( f \), except Eq 6.7 and Eq 6.8 that are listed here, there are also many other models and simplification forms available from literature with different levels of uncertainty. But all of the forms are functions of temperature. As both \( P_s' \) and \( f \) are functions of temperature, \( P_s \) and \( P_w \) are also dependent on temperature. Figure 6.9 shows the actual water vapour pressure (\( P_w \)) curve versus temperature at different relative humidity levels from 45% to 95% calculated based on Eq 6.5 – Eq 6.8. An exponential relationship between water vapour pressure and temperature is evident. For example, an outdoor environment condition of 45% RH and 35\(^\circ\)C will result in an ambient water vapour pressure of 2.5 KPa. But at the same relative humidity level with a higher temperature of 85\(^\circ\)C used in this study, the water vapour pressure will increase to 26 KPa which is almost 10 times that of the outdoor condition. Similarly, if assuming the module temperature of an outdoor installed PV module can reach
85°C, the saturated water vapour pressure at the surface of backsheet can be much higher than that at ambient temperature. Therefore, the differences between ambient relative humidity and module surface relative humidity induced by differences between $T_a$ and $T_m$ need to be considered when describing the stresses experienced by the module.

![Figure 6.9 Actual water vapour pressure versus temperature](image)

Substituting Eq 6.5 and Eq 6.6 into Eq 6.4, the relative humidity at the surface of the backsheet can be written as:

$$ RH_m = \frac{P_w}{P_{s}'(T_m)} = \frac{RH_a\times f(T_a)\times P_{s}'(T_a)}{f(T_m)\times P_{s}'(T_m)} $$

(6.9)

where $P_{s}'(T_a)$ and $P_{s}'(T_m)$ are saturated water vapour pressure of pure water at ambient temperature $T_a$ and module temperature $T_m$, $f(T_a)$ and $f(T_m)$ are relative enhancement factor at $T_a$ and $T_m$. For outdoor exposure, module temperature is often different from ambient temperate due to irradiance, wind speed, installation method, heat exchange with the environment and the condition of the sky etc. Therefore, $RH_m$ is different from $RH_a$. In contrast, in laboratory-based damp-heat tests, as stated above, $T_a$ equals $T_m$, thus the relative surface humidity of backsheet simply becomes ambient relative humidity:
\[ RH_m = RH_a \]  \hspace{1cm} (6.10)

### 6.4.1.2 Dose Model Development

After obtaining the module micro climate, a humidity dose model can then be established to quantify the effective cumulative stresses imposed on the module within certain time duration that contribute to the degradation. Under the steady state damp-heat stresses, the micro climatic relative surface humidity of the backsheet (\( RH_m \)) is considered as the dominating driving factor while module temperature is assumed as an accelerating factor which can be modelled using an Arrhenius function. The Arrhenius form is a commonly used acceleration model defining the relationship between degradation and temperature when a single mechanism dominates the ageing process [18,81,137,138]. This allows the development of a model to quantify stresses in different operating environments. A cumulative function of time with relative surface humidity of the backsheat and module temperature as weighting factors within a time duration of \( \Delta t \) can be established as follows:

\[ dose = RH_m e^{-\frac{E_a}{RT_m} \Delta t} \]  \hspace{1cm} (6.11)

where \( E_a \) is the activation energy of the degradation process, \( R \) is the gas constant \( (8.314 \, J/(K\cdot mol)) \) or Boltzmann’s constant \( (8.617 \times 10^{-5} \, ev/K) \) depending on the units and \( T_m \) is the absolute module temperature in Kelvin. Considering the postulated \( RH_m \) in Eq 6.9 and Eq 6.10, the humidity dose for the tests in this study can be written as:

\[ dose = RH_m e^{-\frac{E_a}{RT_m} \Delta t} = \frac{RH_m e}{f(T_m) \cdot P_s(T_m)} \cdot e^{-\frac{E_a}{RT_m} \Delta t} = RH_a e^{-\frac{E_a}{RT_m} \Delta t} \]  \hspace{1cm} (6.12)

This model implies that it is not the ambient humidity but the relative surface humidity of the backsheat that is the most important driving factor for moisture ingress. It also considers the influences of module temperature on micro climatic humidity. Temperature contributes to the dose in an exponential form and the magnitude depends on the activation energy. \( E_a \) can normally be extracted by
measuring the degradation rate at multiple temperature conditions. This dose model is only responsible for degradation induced by humidity and may only apply to limited temperature and humidity levels. The key descriptor required for the prediction of ageing is the activation energy which is determined in the next section.

### 6.4.2 Degradation of Adhesion Strength and Humidity Dose

It is believed that the degradation of adhesion strength increases with increasing humidity dose, but whether its form is linear, exponential, power or logarithmic is unknown. The correlation between adhesion strength degradation and humidity dose are investigated. Two approaches, i.e. the conventional linear relationship and exponential degradation model are studied. For each approach, the activation energy is calculated and the relationship between adhesion degradation and humidity dose is discussed.

#### 6.4.2.1 Linear Model

The linear model is the simplest degradation model which assumes the adhesion strength degradation (∆S) to be directly proportional to humidity dose:

$$\Delta S = k \times \text{dose} = kRH_ae^{-\frac{E_a}{RT_m}}$$  \hspace{1cm} (6.13)

By dividing time duration (∆t) at both sides of Eq 6.13, the degradation rate (R_D) is obtained and the equation can be restructured as follows:

$$R_D = \frac{\Delta S}{\Delta t} = kRH_ae^{-\frac{E_a}{RT_m}}$$  \hspace{1cm} (6.14)

This enables the extraction of E_a by taking the natural logarithm of both sides of Eq 6.14, which will generate an Arrhenius plot:

$$\ln \frac{\Delta S}{\Delta t} = -\frac{E_a}{R \cdot T_m} + \ln(kRH_a)$$  \hspace{1cm} (6.15)

By plotting the natural logarithm of R_D and the reciprocal of T_m, linear lines are obtained. The slope of the generated linear correlations is -E_a/R while the intercept is ln(kRH_a). At conditions of constant relative humidity but varying
temperature, one linear curve will be generated while with both different relative humidity and different temperature conditions, parallel linear curves are generated with different intercepts.

Figure 6.10 shows the Arrhenius plot results for this study at constant RH\textsubscript{a} of 85% but varying T\textsubscript{m} of 95°C, 85°C and 65°C. The degradation rates used to obtain the plot are the average R\textsubscript{0} at each of the three testing conditions which are listed in Table 6.2. Seen from Figure 6.10, a linear relationship is observable and its slope allows the determination of E\textsubscript{a} to be approximately 54 kJ/mol:

\[
\text{slope} = -\frac{E_a}{R} = -6466
\]

\[E_a \cong 54 \text{ kJ/mol} = 0.56 \text{ eV} \quad (6.17)\]

Figure 6.10 Arrhenius plot between natural logarithm of degradation rates and the inverse of absolute module temperature

With the activation energy calculated, the proposed humidity dose in Eq 6.12 can be computed for all the five humidity and temperature conditions listed in Table 6.1. The adhesion strength degradation shown in Figure 6.5 can then be re-investigated as dependent on the humidity dose and the results are plotted as scattered points in Figure 6.11. It can be seen that with the increasing of dose, the adhesion strength decreases.
According to the defined linear degradation model in Eq 6.13, adhesion strength after a certain degradation time ($S_t$) should be:

$$S_t = S_0 - \Delta S = S_0 - k \cdot \text{dose} \quad (6.18)$$

Theoretically, $S_t$ should decrease linearly with dose. However, as can be seen from Figure 6.11, the adhesion strength does not follow the conventional linear approximation with dose. Most of the points with dose less than $1.4 \times 10^{-6}$ are below the proposed linear model curve. The actual adhesion strength degradation rate is much reduced with dose higher than $1.0 \times 10^{-6}$ and tends to stabilise afterwards. But the linear model describes the decreasing of adhesion strength at the same rate until adhesion is lost completely. It does not allow a stabilisation stage.

Instead of a linear correlation, the data points in Figure 6.11 demonstrate an exponential decay and the fitting is presented in Figure 6.12. This implies that the linear form does not suit the degradation and an exponential model may better represent the degradation. The divergences between the proposed linear model and the experimental data may result from the assumption that constant
degradation exists throughout the whole ageing procedure which in reality is a decelerating process. The use of average $R_D$ values at each condition hid the detailed features of degradation.

![Figure 6.12 Fitting of adhesion strength using exponential function](image)

### 6.4.2.2 Exponential Model

Analysing Figure 6.12, an exponential model is established to describe the correlation between adhesion strength and humidity dose during degradation:

$$S_t = S_0 e^{-k\cdot dose} = S_0 e^{-k\cdot (R_H a \cdot e^{-\frac{E_a}{R T_m} \cdot \Delta t})}$$

(6.19)

Eq 6.19 can be restructured by moving $S_0$ to the left side of the equation and taking the natural logarithm of both sides twice:

$$\ln \left(- \ln \left( \frac{S_t}{S_0} \right) \right) = - \frac{E_a}{R T_m} + \ln \left( k \cdot R_H a \cdot \Delta t \right)$$

(6.20)

By plotting $-\ln(S_t/S_0)$ vs. $1/T_m$, straight lines can be obtained whereby $E_a/R$ determines the slope of the curve and the combined parameter of ($k\cdot R_H a \cdot \Delta t$) determines the intercept. In principle, at constant $R_H a$ but varying $T_m$, parallel lines with the same slope and different intercepts can be obtained at different
degradation times. Figure 6.13 shows such curves at a constant RH of 85% but varying temperatures of 95°C, 85°C and 65°C at degradation times of 24 h, 48 h and 72 h respectively. As there are three degradation times, three data sets are generated which can all be fitted with straight lines. Among the three data sets, two of them at degradation times of 24 h and 48 h show some divergence from the linear approximations while 72 h demonstrates good linear fitting. This may be because at the beginning of ageing, degradation is a bit faster than the proposed exponential decay model. Another important source of divergence is the variation resulting from the experiment, especially for the peel tests which are destructive. This can be seen from Figure 6.5 where the standard variation at 24h and 48h is much higher than that at 72h for the three different temperature conditions. The reason why we choose data at these three time slots is because it approaches the lowest detectable threshold of the adhesion strength for the stress condition of 95°C / 85% RH and degradation results at longer exposure time is meaningless at this condition. The 95°C / 85% RH is one of the three temperature regimes used to calculate the Ea. The fitted three lines are almost parallel with each other, indicating a similar slope. Taking the average slope of the three fitted curves gives an activation energy with the value around 63 kJ/mol (0.65 eV).
Figure 6.13 Plot of $\ln(-\ln(S/S_0))$ against inverse of absolute module temperature at degradation times of 24 h, 48 h and 72 h for exposures at 95°C / 85% RH, 85°C/ 85% RH, 65°C / 85% RH

Similar to the linear model, with the new calculated activation energy, the humidity dose for all five conditions listed in Table 6.1 are computed. The adhesion strength vs. humidity dose is also investigated for the exponential model with the results shown in Figure 6.14. It is observed that the five curves in Figure 6.5 have been normalised by dose and a strong exponential agreement between adhesion strength and humidity dose is evident which can be approximated as:

$$S_t = S_0 e^{-3.28 \times 10^7 \cdot \text{dose}}$$

(6.21)

The fitted coefficient of determination is over 0.92 which means it is highly correlated. This verifies the suitability of exponential model to describe the correlation between adhesion strength and humidity dose. With increasing humidity dose, adhesion strength decreases. According to the exponential model, 90% degradation occurs within a dose level of $8 \times 10^{-8}$ and the degradation rate greatly reduces thereafter and is infinitely close to zero.
Figure 6.14 Degradation of adhesion strength versus humidity dose with activation energy calculated from exponential model

The degradation of adhesion strength may be caused by multiple mechanisms. In this experiment, there will at least be moisture effects and thermal effects but it is assumed that humidity effects dominate the degradation which is thermally enhanced. Eq 6.12 and Eq 6.21 are only responsible for humidity induced degradation and thus the adhesion strength may follow Eq 6.12 and Eq 6.21 over only limited temperature and humidity ranges. In Figure 6.14, data at 95°C / 85% RH show some divergence from the fitted curve which indicates that some other unaccounted-for degradation mechanisms may have been triggered or are becoming increasingly important at this temperature. However, the data at 95°C / 85% RH in Figure 6.14 are not so far away from the model, which suggests that the primary degradation mechanism is still humidity even at this high temperature condition.
6.5 Conclusions

A methodology is established in this chapter that can be used to model the adhesion strength degradation due to moisture ingress of the encapsulation materials of PV modules operating at different humidity and temperature conditions. This is achieved by exposing the devices under different humidity levels at different temperatures and then investigating the correlation between the degradation and the cumulative stresses imposed on the devices that contribute to the degradation.

Results show that the loss of adhesion follows an exponential decay with exposure time but it varies significantly under different stress conditions. This makes the comparison of adhesion performance complex under different stress levels. A simple method linking different operating environments is achieved by developing a stress dose model to describe the cumulative stresses imposed on the device. In this research, a humidity dose is defined by assuming the relative surface humidity at the backsheet as the main driving factor and module temperature as the accelerant with an Arrhenius influence of the degradation process. The calculation of relative surface humidity of the backsheet transfers the environmental humidity to module surface humidity and considers the influence of module temperature on the effective humidity at the surface of backsheet. Great differences between the atmospherical environment and the module environment have been demonstrated. Care needs to be paid when assessing the stress levels for outdoor operation where atmospheric environment needs to be transferred into module micro-climates.

The establishment of the stress dose model enables the modelling of the loss of adhesion with the dose. Results show that the adhesion strength decreases with the increasing humidity dose and demonstrates a strong exponential correlation. The conventional linear model fails to describe this relationship.
The premise of the dose model and degradation model developed in this chapter is that the degradation is mainly induced by humidity, i.e. humidity is the primary driver of the reduction of adhesion strength and temperature determines the speed of degradation and it needs to be under steady state stresses. In outdoor operation, steady state stresses are impossible and modules will experience cyclic humidity and cyclic temperature. There will also be other stress factors such as irradiance and pollutants that contribute to the adhesion degradation. These different stress factors and the cyclic changes of environmental conditions will trigger different mechanisms with different activation energy and generating different degradation behaviours. Adhesion performance under each of these contributions should be investigated separately before a full model is established for outdoor prediction.
7. Conclusions

The reliability of the encapsulation system of PV modules is not well understood but absolutely crucial for the performance of PV modules. This includes in particular the influence of different lamination conditions as well as different stress levels on the long-term reliability of the encapsulation system. This thesis has improved the understanding of these issues by investigating the correlation of different curing temperature and curing time with the reliability of the encapsulation system and the degradation of adhesion strength under variable damp-heat conditions.

The investigation of different curing temperature and curing time on the reliability of the encapsulation system has identified several main encapsulation related degradation phenomena under humid environments, i.e. moisture ingress and EVA hydrolysis, formation of chromophores that cause discoloration, depletion of residual crosslinking initiator, and adhesion strength degradation. Among them, adhesion strength demonstrates the greatest and the fastest degradation.

A correlation between the curing level of EVA and the reliability of the lamination has been demonstrated. The chemical stability, optical stability and the adhesion strength between encapsulant and backsheet increases with the increasing curing level. For the adhesion strength between glass and encapsulant, the curing level does not show obvious influences on the adhesion formation but more on the long-term performance as a result of the influence of viscoelastic properties, thermal stresses and expansion coefficients.

Gel content lower than 70% shows high risk of moisture ingress, transmittance reduction and weak backsheet-encapsulant adhesion. However, it demonstrates the best adhesion stability under humid condition which is resulted from EVA
melting. The melting allows the formation of stronger secondary forces but carries the risk of cell movement and cracking and should be avoided during lamination. However, this does not mean high curing level is always good. Too high curing level which can be achieved through high temperature or long curing will cause samples of unstable optical properties. The more severe problem for too high curing is that the adhesion can be destroyed with the creation of imperfect interfaces and bubbles. Even for samples without visible bubbles and strong adhesion strength is formed, higher curing level can accelerate delamination because of the high residual thermal stresses built up during lamination. Results show that too high curing reduces reliability and should be avoided during lamination. It is also found that gel content in the range of 85% to 90% presents comparable chemical and optical stability. From the financial viewpoint, it is not necessary to pursue gel content higher than 85% to achieve the optimum chemical and optical stability.

The reliability of the adhesion is further investigated by studying the degradation of adhesion strength under different damp-heat conditions to see how different stress levels influence the encapsulation reliability. The degradation of adhesion strength with time has been found to follow an exponential format. The correlation between the adhesion degradation and temperature and humidity levels has been established. In order to achieve this, a stress model has been developed which enables quantitative description of the moisture related stresses on PV modules. The stress model demonstrates the great differences between the atmospherical environment and the module environment which needs to be considered for outdoor prediction. Based on the stress model, an exponential correlation has been established between the adhesion strength with different humidity and temperature levels. It is also shown that the conventional linear model is unsuitable for the prediction of the degradation of adhesion strength.
Work of this thesis has provided more information on the influence of lamination conditions and stress levels on the reliability of the encapsulation system of PV modules. Curing level of EVA is checked and is used for quality control. The reason for checking the curing level is mostly for a single purpose of avoiding EVA flowing. Work of this thesis has pointed out the importance of EVA curing level from other perspectives by demonstrating the influences of curing level on other properties of the encapsulation system which was poorly understood before. It also concludes that too high level of curing is adverse to the reliability. This is somewhat different to the current considerations, where the requirements for curing levels are only to have a minimum level and not maximum. Unlike the other reliability studies that only evaluating the long-term performance of the encapsulation system based on single degradation phenomenon, this work has evaluated the reliability from diverse perspectives with the comparison of several different degradation phenomena. It is found that interfacial adhesion strength has the biggest problem under humid environment.

Prior to this work, there are limited understandings on adhesion degradation. This thesis demonstrates experimentally rather than speculatively the degradation behaviour of adhesion strength. Various well-controlled stress levels are investigated rather than single stress condition. The development of the correlation between adhesion performance and environmental conditions is an area with almost blank information in the PV industry. Work in this thesis fills scientific contents in this area by establishing an exponential model to describe the correlation of adhesion and the humidity and temperature levels. The suitability of the model has also been validated using experimental data at steady state. However, this model is only suitable for adhesion degradation induced by humidity at steady state. In realistic outdoor operation, cyclic environmental stresses are experienced and more degradation mechanisms are involved such as cyclic temperature and photochemical reactions. Further steps to quantify additional effects from the other stress factors such as the UV light, cyclic
temperature and cyclic humidity as well as the combination of these factors are required before an outdoor adhesion degradation model can be made. But this can only be achieved on a mechanism-by-mechanism level and built up to an effective overall model. The methodology developed for the adhesion degradation modelling under damp-heat condition can also be applied to the studies under other stress factors and also other degradation phenomena. A full degradation model of the encapsulation system of PV module in different environments appears to be possible based on the methodology developed here.

The importance of the reliability of the encapsulation system is because it influences power performance of PV modules. This thesis only looks at encapsulation relevant issues rather than performance levels. Understanding the reliability of the encapsulation system is a first step of understanding power degradation. Linking the encapsulation material states and the actual device performance requires significant additional amounts of research but the work of this thesis represents a step towards this goal and has opened a lot of possible areas which need to be addressed to achieve this goal.
List of Publications Arising Through This Work

Conference Publications


D. Wu, J. Zhu, T. R Betts, R. Gottschalg, Factors influencing the measured adhesive strength between glass and encapsulant of Photovoltaic modules, 9th


Journal Publications

References


13. BGI Research, Ethylene vinyl acetate (EVA) global market to 2015 - photovoltaic encapsulants to drive EVA demand in the future, 2011.


49. D. Berman, S. Biryukov, and D. Faiman, EVA laminate browning after 5 years in a grid-connected, mirror-assisted, photovoltaic system in the Negev desert:


77. M. D. Kempe, G. Jorgensen, K. Terwilliger, T. Mcmahon, C. E. Kennedy, and T. Borek, Acetic acid production and glass transition concerns with ethylene-


135. BS 1339-1:2002 - Humidity. Terms, definitions and formulae, 0208.


Appendices

Appendix 1 FTIR-ATR Results for Free Stand Cured EVA

[Graph showing FTIR-ATR results with wavenumbers and absorbance values for different temperatures.]

Absorbance
Wavenumber (cm⁻¹)
Appendix 2 Transmittance Results for Free Stand Cured EVA