Water Vapour Transmission Rate of Ethylene Vinyl Acetate (EVA) Encapsulant with different Curing Levels

Jiang Zhu*, Christina Ng, Daniel Montiel-Chicharro, Thomas R. Betts, Ralph Gottschalg

Centre for Renewable Energy Systems Technology (CREST), Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, United Kingdom, * Corresponding Author <u>J.Zhu@lboro.ac.uk</u>, +44 (0)1509 635313

Abstract

Water vapour transmission rate of EVA sheets with different curing levels is investigated under a various temperature and relative humidity levels. The gravimetric cup method is used to measure the transmission rate. EVA samples' thermal and structural properties are measured and results confirm that the curing level does not affect material VAc contents or crystallinity, though their degrees of crosslinking are significantly different. For the EVA studied in this work, lower degrees of crosslinking (gel content <60%) show water transmission rate at about 35 g/m²/day under 23°C and 1 bar. The transmission rate reduces with the increasing crosslinking degree and reaches about 10 g/m²/day for samples of gel content >80%. Results also show the water transmission is able to be accelerated by temperature with an activation energy of about 7.5kJ/mol.

Introduction

Photovoltaic (PV) modules consist of a series of interconnected solar cells sandwiched between two layers of encapsulants, a layer of front glass, and a back sheet. The lifetime of PV modules is expected to be 25 years or more, which is also the duration most manufacturers guarantee. The prediction of lifetime in dependence of operating environments, however, has not been established as correlations of failure modes, degradation mechanisms and environmental stresses are not yet fully understood.

Moisture ingress related degradation leads to corrosion, delamination, yellowing etc. In order to investigate the effect of moisture ingress into PV module in a realistic period of time, normally modules are subjected to accelerated testing at elevated humidity and temperature levels, which assume the rate of moisture transmitted through the encapsulant is accelerated and significantly higher. However, questions have been raised regarding the relevance and equivalence of accelerated tests to real outdoor conditions [1]. The overall process of degradation mechanism can be regarded as a chain of sub-processes. Each sub-process may lead to a different failure mode under a particular condition. The aim of this work is to bring insight for understanding the sub-processes, which can then be demonstrated to serve as a foundation in

translating accelerated testing conditions to realistic outdoor conditions.

PV modules rely on encapsulation materials to minimise the effect of moisture ingress. Typical wafer based PV modules use ethylene vinyl acetate (EVA) as encapsulant. EVA is a copolymer of ethylene and vinyl acetate (VA) with VA groups randomly distributed along the backbone. Important properties influencing the EVA's resistance to water ingress are material crystallinity, percentage of VAc contents and degree of crosslinking.

This work investigates the water vapour transmission rate (WVTR) of EVA with different curing levels. During PV module operation, water permeates into module and slowly vapour accumulates. It also reacts with EVA and generates acetate acid. The latter may chemically interact with the active element that causes degradation. The speed of this process is, based on past work, expected to depend on the degree of EVA crosslinking [2]. In order to understand the potential mechanisms and model the sub-process of moisture ingress into module, the first step is to measure the rate of water vapour transmitted through EVA, which is carried out in the paper under a various temperature and humidity levels for EVA samples of different curing levels.

Methodology and Mathematical Model

The water vapour transmission rate is measured according to the standard ASTM E96 [3], which uses a gravimetric cup filled with either 25g of desiccant or 30g water, as shown in Fig 1. This is then sealed with the test sample, i.e. cured EVA sheets, and placed in an environmental chamber. The weight change of the gravimetric cup is monitored during the course of water vapour transmitting through the EVA sheet. It can be expressed as a function of time. The WVTR is calculated from the steady-state region.

Mathematically, the primary mechanism of water vapour permeated through EVA, can be expressed as an activated diffusion. This means that the permeant of water vapour dissolves in the film matrix at the higher concentration side and diffuses through the film and evaporates from the other surface. This is driven by concentration gradients. The diffusion is the key step and the rate depends on size, shape of the penetrating molecule of the permeant, which in this work is the water vapour. It also depends on the thermal and structural properties of the EVA film, which will be investigated in this paper.

The water vapour diffusion through EVA can be described by the Henry and Fick's law, which relates the permeation rate with the area and thickness of the film as given below:

$$J = -P\left(\frac{p_1 - p_2}{l}\right) \tag{1}$$

where *J* is the diffusion flux, *P* is the permeation coefficient reflecting the speed at which the permeant diffuses through the EVA, p_1 and p_2 are the water vapour partial pressures at both surfaces of the EVA film and *I* is the EVA film thickness.



(a) (b) Fig 1: Illustration of the gravimetric cup method a) with water, and b) with desiccant.



Fig 2: A typical WVTR measurement showing a transient phase at beginning.

In the experiment, the pressure difference $\Delta p = p_1 - p_2$ ($p_1 > p_2$) is constant as the water vapour partial pressures on both sides of the EVA film are assumed to be constant within the testing period. The diffusion flux *J* representing the total mass of

transmitted water per unit area per day (g m⁻² day⁻¹) can be measured by the weight change of the gravimetric cup:

$$T = \frac{\Delta G}{tA} \tag{2}$$

where ΔG is the weight change during the time *t*, and *A* is the testing area of EVA film. As the thickness of film varies, the water vapour transmission rate (WVTR) is normalised to film thickness *I* to obtain the specific rate:

$$VVTR = J \cdot l = \frac{\Delta G}{tA} l = -P \cdot \Delta p \tag{3}$$

where in this work all EVA sheets tested are corrected to the thickness of 0.42mm. Therefore, the WVTR is a function of permeation coefficient and the water vapour pressure difference between the two surfaces of EVA.

A typical measurement of WVTR is demonstrated in Fig 2. It shows that the transmission of water vapour was slower in the first five days and accelerated afterwards. Therefore the WVTR should be determined from the data points without the first data during the transient phase.

Experimental

1 EVA samples of different curing levels

Samples of single layer EVA sheets laminated under a fixed time of 10 minutes, but different temperatures between 125°C and 150°C (L125 – L150) were produced in order to investigate the effect of curing level on WVTR.

The degree of EVA crosslinking was measured for samples of L125, L135, L145 and L150 by the standard method of Soxhlet–type extraction process [4]. Up to five samples were measured for each lamination condition.

2 Thermal gravimetric analysis (TGA)

Small EVA samples extracted from EVA sheets L125, L135, L145 and L150 were subject to TGA measurement to calculate the VAc contents. Samples were heated up from 30°C to 600°C at the rate of 10°C per minute. Three samples of about 5mg were measured for each laminating condition.

The VAc contents of EVA is related to the first weight loss between 280-380°C and calculated as below [5]:

$$VAc\% = weight \ loss \times \frac{M_{VA}}{M_{HAc}} \tag{4}$$

where M_{VAc} is the atomic mass of VAc and M_{HAc} is the atomic mass of HAc.

3 Differential Scanning Calorimetry (DSC)

Small EVA samples extracted from ÉVA sheets L125, L135, L145 and L150 were also tested with DSC for two heating and cooling cycles between -25°C and 225°C at the rate of 10°C per minute to evaluate the EVA crystallinity. The first cycle is to remove the volatile impurities and erase the former thermal history [6]. The crystallinity, X_c , can be calculated from the second cooling cycle according to the equation below:

		Sample lamination temperature						
		L125	L128	L135	L140	L1	45	L150
Testing emperature	23°C	W, 30%	W, 30%	W, 30%	W, 30%	W, 3	30%	W, 30%
	33°C	W, 30%	W, 30%	W, 30%	W, 30%	W, 3	30%	W, 30%
	60°C					D, 60%	D, 85%	
	70°C					D, 60%	D, 85%	
	80°C					D, 60%	D, 85%	
t	85°C					D, 60%	D, 85%	

Table I: WVTR testing condition (W: water, D: desiccant, 30% - 85%: testing relative humidity).

$$X_c = \frac{\Delta H_f}{\Delta H_f^*} \times 100\%$$
 (5)

where ΔH_f^* is the enthalpy of fusion of a perfect polyethylene crystal (which is 277.1J/g [7]), and ΔH_f is the enthalpy of fusion of the EVA sample. Three samples of about 6mg were measured for each lamination condition.

4 WVTR at different temperature and humidity levels

The test units of WVTR, as shown in Fig 1, were placed in environmental chambers. The chambers were set to a number of combinations of temperature and relative humidity levels as shown in Table I. For low temperatures, water was put in gravimetric cups, while desiccant was used when testing at high temperature levels. Each condition has tested two to four samples to ensure good repeatability. Tests at 23°C and 33°C were used to investigate the correlation of curing level and transmission rate. Tests at higher temperatures were used to evaluate the thermal activation effect.

Results and Discussions

1 Gel content

Fig 3 plots the averaged values of gel contents for EVA samples L125, L135, L145 and L150. The L125 shows gel content less than 60%. Samples of L135, L145 and L150 show a linear increase in gel contents from 73% to 86%. EVA samples with a variety of crosslinking degrees, achieved by different lamination temperature, were used in the work.

2 VAc contents

The TGA measurements of EVA samples L125, L135, L145 and L150 are plotted in Fig 4. It clearly shows all the measured curves are the same, which means the VAc contents are the same for the samples though their degrees of crosslinking are significantly different. The calculated VAc contents are around 32% for these EVA samples.

3 Crystallinity

Crystallinity of EVA can be calculated according to Eq (5) from the peaks of DSC curves shown in Fig 5. The calculated crystallinity values are around 6% for all the samples, though there are minor shifts in the heat flow curves. This means the degree of crystallinity of EVA after different levels of crosslinking remains unchanged. VAc contents of EVA correlate with the crystallinity is reported in [8] as well.



Fig 3: Averaged gel content of EVA versus lamination temperature.



Fig 4: TGA curves of cross linked EVA cured at different temperature.



Fig 5: DSC curves of cross linked EVA cured at different temperature.

4 WVTR and crosslinking degree of EVA

Thermal and structural properties of EVA material have been examined for all samples, which show no changes in VAc contents and crystallinity. Thus, influences from these two factors can be excluded.



Fig 6: Actual water vapour pressure at different temperature and relative humidity.



Fig 7: Normalised WVTR at 23°C and 33°C.



Fig 8: Arrhenius plot of normalised WVTR.

According to Eq (3), the WVTR is related to the pressure difference, Δp , between the two surfaces of EVA. The actual water vapour partial pressure varies at different temperature and relative humidity levels, which is estimated in [9] and plotted in Fig 6. The measured WVTR at different conditions for different samples needs to be corrected for the pressure difference. In this work, all results are normalised to pressure difference of 1 bar and reported as gram per square meter per day (g/m²/day) as shown in Fig 7. L125 samples, which are the low cross linked ones, have the largest transmission rate of about 35 g/m²/day at 23°C. As the degree of crosslinking increases, the WVTR decreases from 35 to 10-15 g/m²/day. At 33°C, the WVTR is generally higher due to thermal acceleration. Its dependency on crosslinking degree follows the similar trend as that at 23°C.

The transmission rate at different temperatures is found to be well described by the Arrhenius relation [10]. Fig 8 plots the measured WVTR at different conditions normalised to 1 bar against testing temperature. With result of L145 samples, the activation energy can be estimated, which is 7.5kJ/mol. The results of L125, L135 and L150 samples so far exhibit similar activation energies.

Conclusions

DSC and TGA measurements show no changes in VAc contents and crystallinity for EVA after curing to different degrees, which excludes the influences from these two factors. A clear correlation between EVA crosslinking degree and WVTR is observed. Less cross linked EVA samples exhibit significant higher transmission rate. This can be explained by the relative high existing free volume within the polymer and thus the mobility of water vapour is relatively easier. The WVTR is thermal activated and the rate is accelerated with an activation energy of 7.5kJ/mol for the EVA material investigated.

References

[1] S. Kurtz, et al, A framework for a comparative accelerated testing standard for PV modules, IEEE 39th Photovoltaic Specialists Conference, 2013.

[2] J. Zhu, et al, The role of EVA encapsulation in the degradation of wafer based PV modules, in 12th Photovoltaic Science, Application and Technology Conference, 2016, Liverpool.

[3] ASTM E96/E96M-16 Standard Test Methods for Water Vapor Transmission of Materials, ASTM International, West Conshohocken, 2016.

[4] American Society for Testing and Materials, Standard Test Methods for Determination of Gel Content and Swell Ratio of Crosslinked Ethylene Plastics, ASTM D2765–11, 2006.

[5] X.E. Cai, H. Shen, Apparent activation energies of the non-isothermal degradation of EVA copolymer, *Therm. Anal. Calorim.*, vol. 55, no. 1, pp. 67–76, 1999.

[6] L.M. Huang, et al, The Evaluations of Physical Properties and Lamination Process Parameters of EVA Encapsulant by Thermal Analysis, in 24th European Photovoltaic Solar Energy Conference, Hamburg, Germany, 2009.

[7] J. Brandrup, et al, Polymer handbook. Wiley-Interscience, New York, 1999.

[8] X.M. Shi, et al, Non-isothermal crystallization and melting of ethylene-vinyl acetate copolymers with different vinyl acetate contents, eXPRESS Polymer Letters Vol.2, No.9, 2008, pp. 623–629.

[9] A. Wexler, Vapor pressure formulation for water in range 0 to 100°C. A revision. J. Res. Natl. Bur. Stand. 80A, 1976, pp. 775-285.

[10] J.R. Welty, et al, *Fundamentals of Momentum, Heat, and Mass Transfer.* Wiley, 2001.