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# The thermo-mechanical degradation of ethylene vinyl acetate used as a solar panel adhesive and encapsulant

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## ABSTRACT

The thermal ageing of an ethylene-vinyl acetate (EVA) polymer used as an adhesive and encapsulant in a photovoltaic module has been investigated. The EVA is used to bond the silicon solar cells to the front glass and backing sheet and to protect the photovoltaic materials from the environment and mechanical damage. Using a range of experimental techniques, including Dynamic Mechanical Analysis, Differential Scanning Calorimetry and Thermo-gravimetric Analysis, it was possible to show a link between changes in mechanical properties with both the transient temperature and the degree of long-time thermal ageing. Importantly, it was possible to show that the ageing related property changes were likely due to long term structural changes rather than any modification of the chemistry of the material.

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## 1. Introduction

In order to support the continuing and growing consumer demand for energy, there is an expanding need for sustainable energy sources [1]. Solar energy harvesting methods, such as those employing photovoltaic (PV) modules, are a step towards achieving this goal. Currently, however, PV module take-up and installation is dependent upon government subsidy, owing to the marginal economic benefit to the user as a consequence of the high capital cost and relatively low lifetime [2,3].

The lifetime of a PV module is generally limited by the degradation of the constituent parts, leading to a decrease in efficiency and eventual failure [4–7]. One part that is particularly susceptible to degradation is the adhesive encapsulant. The encapsulant is used to bond the silicon cell to the front glass and backing sheet in a lamination process into a weatherproof structure, called a PV module or a solar panel. The encapsulant is also essential for mechanical protection and electrical insulation and is expected to protect the solar cells from environmental damage, including rain, snow, dust, thermal and mechanical stresses. Degradation of this layer can lead to optical decoupling owing to discolouration, with subsequent power loss, loss in adhesion strength, delamination and corrosion in metallic parts due to acetic acid production [8].

Currently, the most common encapsulant material for PV modules is ethylene-vinyl acetate (EVA), which is a copolymer of ethylene and vinyl acetate [9]. It is popular in the PV industry

owing to its low cost, high adhesion strength and high transparency, with glass like transmission properties in the range of 400 nm to 1100 nm [8,10,11]. In addition to this, EVA has high electrical resistivity, a low polymerisation temperature and a relatively low water absorption ratio, all of which points to it being a good, cost effective, choice for a PV module encapsulant [12]. A typical EVA co-polymer formulation for PV modules is 28–33% by weight vinyl acetate, compounded with additives such as curing agents, ultra violet (UV) absorbers, photo antioxidants and thermo antioxidants. Despite this, EVA undergoes chemical degradation when it is exposed to the environmental conditions seen in service, especially heat, humidity and UV irradiance, leading to material ageing and the possibility of a complex interaction of several different ageing mechanisms.

Determining the effect of environmental stresses and artificial ageing on polymeric materials is of concern in many engineering applications and has been the subject of significant research [13–17]. A number of authors have considered the effect of laminating conditions and ageing processes on EVA in PV devices [18–20]. Wu and colleagues [21] reported that humidity was the main cause of the reduction in adhesion strength in PV modules on ageing and that temperature determined the speed of degradation, with the loss of adhesion due to humidity ingress demonstrating an exponential relationship. Rashtchi et al. [22] studied moisture absorption in EVA and showed that the spectral region between 3400 cm<sup>-1</sup> and 3700 cm<sup>-1</sup> is the best indicator of moisture presence. They also showed that double-bonded water is initially absorbed in the EVA matrix, followed by single-bonded water, the latter being lost first on drying. Iwamoto et al. [23] Investigated

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the presence of free and bonded water in EVA with different vinyl acetate content. Their FTIR results showed that one- and two-bonded water coexist in the copolymer and increasing the vinyl acetate content also increased the proportion of two-bonded water. In the case of two-bonded water every OH is hydrogen bonded to a C=O. In one-bonded water, an OH is bonded to C=O of ester group and another OH is free. Two-bonded water is initially absorbed in the EVA matrix, followed by one-bonded water. However, one-bonded water is lost first by increasing temperature, followed by the two-bonded water. Badiée et al [24] investigated the effect of UV ageing on the chemical degradation of EVA. Their results indicated significant chemical changes, including the formation of carboxylic acid, lactone and unsaturated groups, which caused discolouration in EVA. Their results also illustrated the dominant degrading influence of UV compared to other degradation factors. The influence of the degree of ageing on the thermal stability of EVA has been investigated by placing EVA granules in a laboratory oven at 85 °C, in air and measuring the material properties at different times up to 30 weeks [25]. The results showed that EVA undergoes a two-step degradation, where the first stage is acetic acid evolution and the second involves main chain degradation. Both of these degradation steps shift to lower temperature as a consequence of oxidation and chain scission as ageing proceeds, therefore, the degradation accelerates following ageing. Significant work has been performed to understand the chemical processes involved in degradation. It has been reported that the initial product of EVA degradation is exclusively acetic acid [26]. The effect of degradation on the physical properties of EVA, for example, glass transition temperature, has been reported [27]. Buch et al. [28,29] studied the behaviour of epoxy resin at elevated temperatures, its thermal degradation and thermo-oxidation. They showed that the degradation of epoxy resin is a two stage process where the second stage occurs only in the presence of oxygen and leads to material loss whereas in the case of EVA chain scission happens even in the absence of oxygen. In their paper the activation energy of thermal degradation was calculated using different methods and no significant difference was found between them.

These previous studies have illustrated the main mechanisms through which thermal degradation of EVA occurs. However, the influence of thermal ageing on the mechanical properties and structure of EVA, which directly affect its encapsulant capabilities, has not been thoroughly investigated and there is a missing link between the ageing process and consequences of that ageing within the context of mechanical behaviour. This paper seeks to address the need to understand the changes in mechanical properties on thermal ageing of EVA by examining the link between the chemistry, the structure and the mechanical behaviour. In this paper the samples are tested dry and without UV exposure to isolate the thermal degradation affects.

## 2. Methodology

The approach taken in this paper was to determine the reaction kinetics of thermal degradation of the EVA and then to relate the state of degradation to the physical and mechanical properties. This should, in theory, enable the properties of EVA, which are critical to its role as an adhesive encapsulant, to be predicted from its thermal history. This methodology was achieved by the use of a number of experimental thermal analysis methods, as described below.

### 2.1. Experimental techniques to characterize the encapsulant material

The characterisation of EVA was separated into two parts. First, the mechanical properties as a function of temperature and thermal ageing were determined. Secondly, the degradation rate of the material was determined as a function of temperature. Three experimental techniques were used to achieve this. Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA) and Dynamic Mechanical Analysis (DMA). These techniques enable the investigation of structure and state of the material as the temperature is changed (DSC), the evolution of degradation products from a sample exposed to changes in temperature and thus, the reaction rates (TGA) and the viscoelastic mechanical properties of the material and their relation with the thermal conditions (DMA). The base material was a cured EVA copolymer with 33% vinyl acetate and gel content of 80%, which was supplied in 0.5 mm thick sheets (provided by Ecole Polytechnique Fédérale de Lausanne (EPFL)). The curing process is fully described in [30]. The EVA sheets were aged in a dark laboratory oven at 85 °C for up to 80 days.

#### 2.1.1. Dynamic Mechanical Analysis (DMA)

DMA was used to investigate the temperature dependant viscoelastic properties of the EVA. Samples were loaded in tension with a cyclic strain of 15  $\mu\text{m}$  at a frequency of 1 Hz. The storage modulus, loss modulus and phase angle (i.e., the lag between stress and strain) were then calculated. The temperature was ramped from  $-70$  °C to 100 °C with a heating rate of 5 °C/min in air to determine the relationship between mechanical properties and temperature.

#### 2.1.2. Differential Scanning Calorimetric (DSC)

DSC is a calorimetry method which measures heat flow as a function of temperature. This heat flow can vary due to thermally active transitions such as the glass transition in polymers and melting, but can also indicate other structural changes that are driven by thermal processes. In this study all DSC experiments were conducted in an inert atmosphere with a nitrogen atmosphere (50 ml/min) using a TA instrument (TA-Q10). The DSC program used to evaluate the behaviour of the previously cured EVA samples was a heat-cool-heat cycle based on ASTM-D 3418-08. The first heating was done at 10 °C/min from  $-75$  °C to 200 °C. The temperature was held at 200 °C for 5 min and then cooled down at  $-10$  °C/min to  $-75$  °C and held at this temperature for 5 min. This cycle was then repeated for a second time. Samples were cut into circular disc shapes weighing approximately 8 mg for this test and experiments were carried out in hermetic Al pans.

#### 2.1.3. Thermo-gravimetric Analysis (TGA)

Thermo-gravimetric Analysis (TGA) is a thermal analysis technique which measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. TGA measurements are particularly powerful when coupled with knowledge of the chemistry of the sample, as one can then correlate changes in the weight of the subject with its chemical state. All experiments in this study were conducted in an inert atmosphere with a nitrogen atmosphere (100 ml/min) with a TA instruments TA-SDT 600 and heating rates of 5, 10, 15 and 20 °C/min; recording mass loss and the rate of mass loss as a function of temperature. Samples were cut into circular disc shapes weighing approximately 15 mg and experiments were carried out in platinum pans.

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