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

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A B S T R A C T

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.

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^{-1} and 3700 cm^{-1} 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. Badiee 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 session 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 Lusanne (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 μm 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 Calorimetic (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.

2.2. Kinetics of degradation

The rate of material conversion $(d\alpha/dt)$ of a solid state process has the following general form

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the conversion degree or fractional weight change, t is the reaction time, k is a rate constant which depends on the temperature (T) and $f(\alpha)$ is a kinetic model function which is a first order reaction in this case [31,32]. In this study the conversion degree is defined as,

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{2}$$

where m_0, m_t and m_∞ are initial sample mass, sample mass at time t and sample mass at the end of the reaction, respectively. As the reactions to be considered here are related to thermal processes, $k(T)$ is assumed to be of an Arrhenius form, such that Eq. (1) becomes,

$$\frac{d\alpha}{dt} = Ae^{\left(\frac{-E}{RT}\right)}f(\alpha) \tag{3}$$

where A is a pre-exponential (frequency) factor, E is the activation energy and R is the universal gas constant. For non-isothermal experiments carried out with constant heating rates, $\beta = dT/dt$, it is possible to arrive at,

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{\left(\frac{-E}{RT}\right)}f(\alpha) \tag{4}$$

The activation energy can be obtained from non-isothermal data without choosing the reaction model. The generalised Kissinger's method is an established technique to calculate the activation energy. Kissinger's method is derived by taking the time derivative of Eq. (3), and noting that at the maximum degradation rate, $d^2\alpha/dt^2 = 0$. This allows for the calculation of E at the maximum rate of degradation when the heating rate is constant, and the time and temperature derivatives of weight loss are linearly related. Therefore, data can be plotted as a function of time or temperature and analysed by Kissinger's method.

$$\ln\frac{\beta}{T_p^2} = \ln\left[\frac{A.R}{E}\right] - \frac{E}{R.T_p} \tag{5}$$

where T_p is temperature at the maximum degradation rate and β is the heating rate. It is possible, therefore, to plot $(\ln\beta/T_p^2)$ vs. $1/T_p$ and obtain the activation energy and pre-exponential factor from the slope and intercept respectively. This method allows the activation energy to be obtained independently of the kinetic model [33].

3. Results and discussion

3.1. Thermogravimetric Analysis (TGA)

Fig. 1 shows TGA curves corresponding to dynamic experiments carried out at a range of heating rates. The results show evidence of a two-step thermal degradation process. The first stage, completed at around 370 °C, suggests a deacetylation process in the vinyl acetate fraction. The second stage has previously been identified as complete chain scission of the residual main chain (within the interval of 380–480 °C). As should be expected, the temperature at which the reaction is complete rises as the heating rate increases. Since the maximum temperature that photovoltaic systems operate is around 85 °C, chain scission is not considered as significant; therefore, the focus in this work is on the deacetylation of EVA.
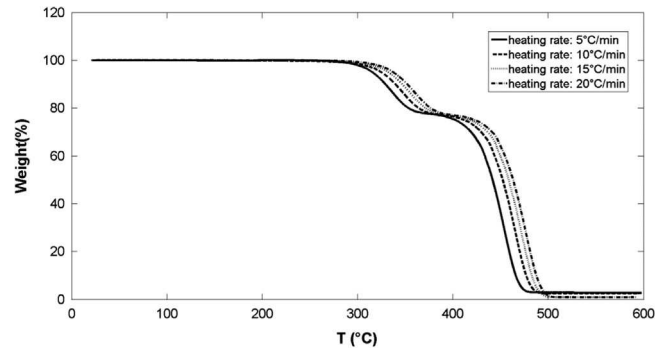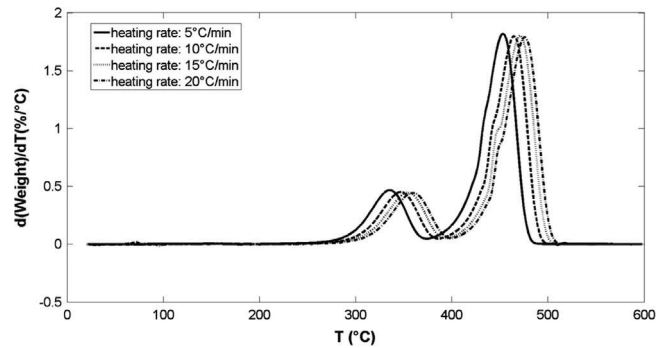

Fig. 1. TGA thermogram of at various heating rates.

Fig. 2. Derivative of weight loss as a function of temperature for unaged EVA at various heating rates.

Table 1

Temperature of peak degradation rate for aged and unaged EVA samples at different heating rates.

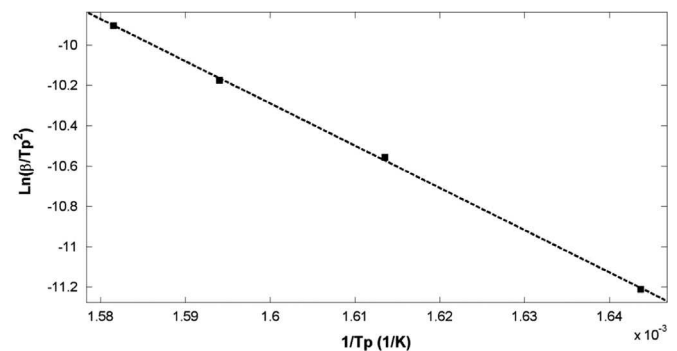| Heating rate (°C/min)	Temperature of peak degradation rate T_P (°C)			
	Unaged	Aged for 40 days	Aged for 60 days	Aged for 80 days
5	335.2	336.5	336.6	336.5
10	346.6	348.8	348.6	348.7
15	354.2	355.4	365.0	356.3
20	359.2	361.8	362.2	362.0

Fig. 3. Plot of $\ln(\beta/T_p^2)$ versus $1/(T_p)$ for unaged EVA.

In order to calculate the activation energy based on the generalised Kissinger's method the temperature of the peak degradation rate (T_p) is required. Fig. 2 shows the derivative of weight loss with respect to temperature, which yields T_p, as presented in Table 1. Fig. 3 shows the relationship between $\ln\left(\beta/T_p^2\right)$ and $1/T_p$ for one heating rate, from which the activation energy and pre-
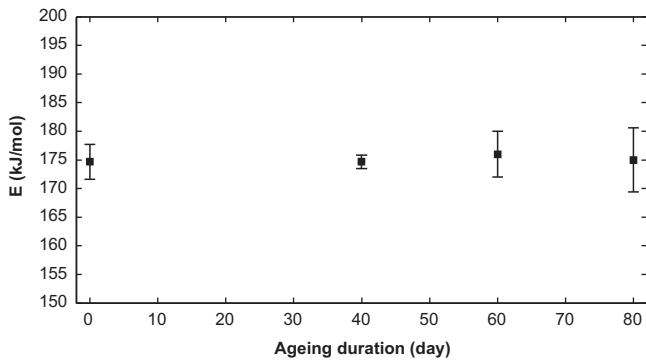
Fig. 4. Calculated activation energies for unaged and aged EVA.

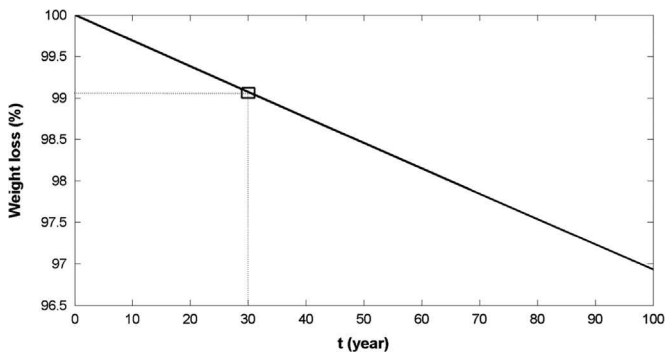**Fig. 6.** Storage modulus vs temperature for aged and unaged EVA.

Fig. 5. Predicted thermally induced weight loss of EVA over one hundred years from Eq. (3), illustrating the predicted weight loss after thirty years (desirable lifetime of a PV module).

exponential factor can be obtained. This approach shows the best agreement around the peak degradation rate temperature, by definition, but beyond this point systematic differences are observed, which could in part be attributable to other processes occurring, such as dehydration. In the case of unaged EVA the calculated values for the activation energy and pre-exponential factor were $E=174$ (kJ/mol) and $A=2.46 \times 10^{14}$ (min^{-1}) respectively. The generalised Kissinger method was also applied to thermally aged EVA. Fig. 4 shows the calculated activation energy for unaged and aged EVA and indicates that there is no clear effect of ageing on the activation energy.

The determination of the activation energy and the pre-exponential factor allows predictions to be made about the thermal degradation and associated weight loss over the lifetime of a module. Assuming that the material was at a module operating temperature of 85 °C (which is the temperature of the material near to the cells as they generate heat during the conversion of photons to electronic potential), the determined activation energies and pre-exponential factors were used to determine the conversion of material as a function of time through the solution of Eq. (3). The key point from this figure is the weight loss predicted after the typical lifetime of a module (usually considered around 30 years). Fig. 5 shows that this is predicted to be around 1%, which is likely to have little impact on the module performance.

3.2. Dynamic Mechanical Analysis (DMA)

Fig. 6 shows the storage modulus (E') determined as a function of temperature at a frequency of 1 Hz. As the temperature increases the curves show the characteristic glassy, rubbery and viscous regions of a viscoelastic material. Significant changes are seen in the storage modulus over the observed temperature range, with 4 decades difference between the moduli at −75 °C and
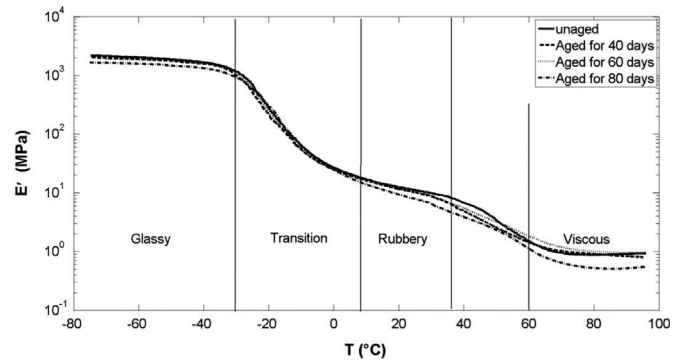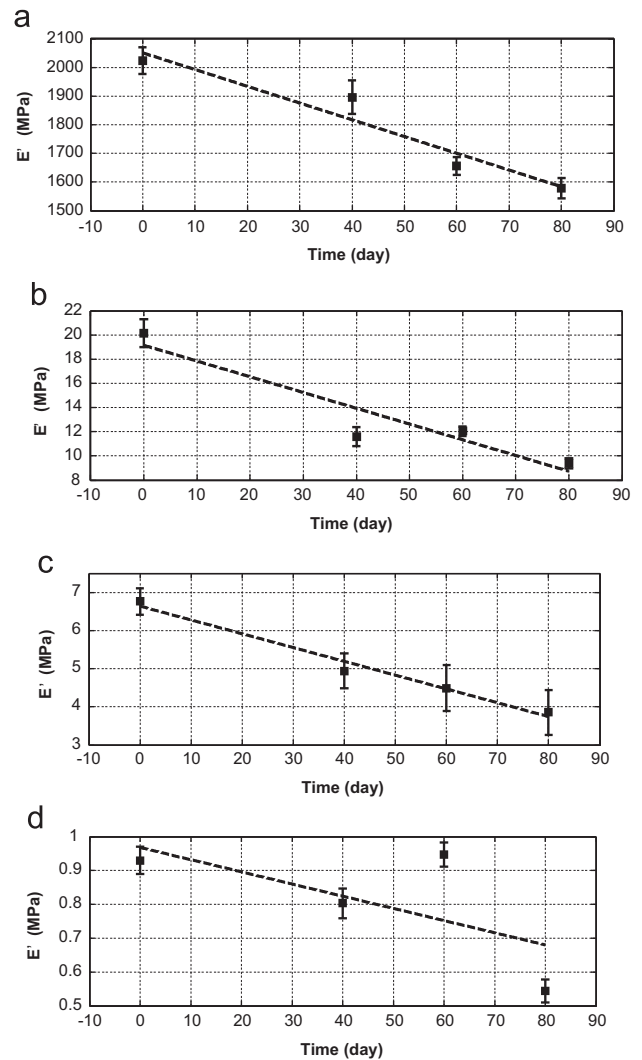

Fig. 7. Storage modulus measured at (a) −60 °C, (b) 20 °C (c), 40 °C (d) 95 °C as a function of ageing time at 85 °C.

95 °C. There is a sharp decrease at around −30 °C, which can be attributed to the glass transition and then another stepped decrease between 40 °C and 65 °C, perhaps indicating some crystal melting.

In order to investigate the effect of ageing further on the mechanical properties of the EVA, the storage modulus at a given temperature was plotted against the ageing time for the sample.
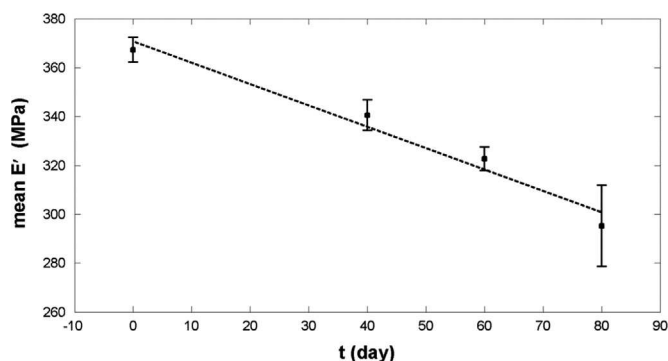
Fig. 8. Mean storage modulus versus ageing time with line fitting ($y = -0.87x + 370.7$), $R^2 = 0.97$.

Table 2
The fitting parameters for storage modulus at different fixed temperatures based on Fig. 8a–d.

Temperature (°C)	Gradient	Intercept	R^2
−60	−5.84	2051	0.93
20	−0.03	5.52	0.93
40	−0.02	2.65	0.85
95	−0.003	0.97	0.44
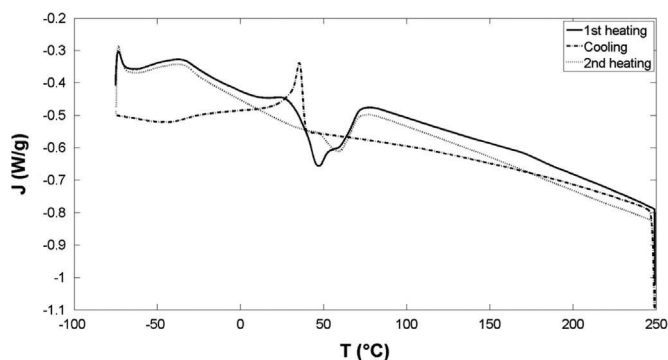
Fig. 9. Typical DSC thermogram during heating, cooling and re-heating.

Fig. 10. DSC first heating thermograms for the unaged and aged EVA.
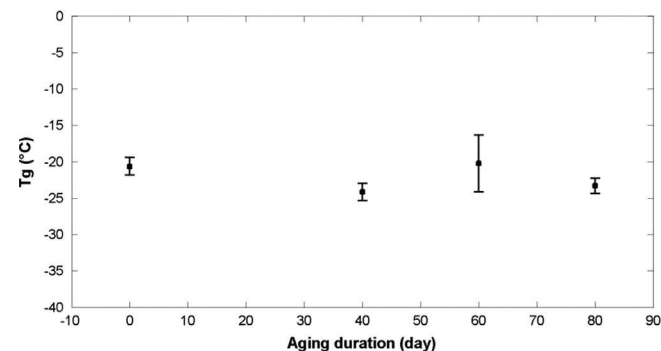
Fig. 11. Glass transition temperature versus ageing time.

Fig. 7(a–d) shows this for four temperatures. One can see that E' reduces with increasing time of ageing, although the confidence in the fit and the calculated gradient decreases with increasing temperature. As a way of approximating the general trend, E' vs temperature for four temperature values was consolidated into one plot as a mean. This is shown in Fig. 8, which shows a monotonically decreasing storage modulus as the material ages. Further, the variation in modulus depends on temperature; as the measurement temperature increases, the dependence on the ageing duration weakens (Table 2). That is to say, the storage modulus reduction rate, when measured at a given temperature, varies more slowly when measured at a higher temperature than a lower temperature. It is worth emphasising that this is for the same ageing condition of 85 °C. It therefore appears that thermal ageing can result in significant changes in the mechanical properties, but considering the very small changes in weight loss, this is unlikely to be associated with chemical changes and any subsequent material volatilisation.

3.3. Differential Scanning Calorimetry (DSC)

In order to understand the changes in morphological behaviour, DSC was performed with three passages, consisting of a heating, a cooling and final heat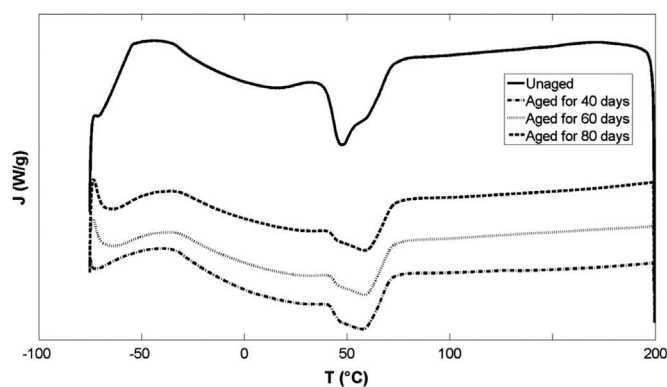ing stage (described in Section 2.1). The results of these experiments are shown in Fig. 9, which shows the DSC thermograms for samples that have been cycled. There are significant changes around 50 °C and the peaks in this region can be associated with internal structural changes or crystallisation transitions. This correlates with the last step in the DMA results which were associated with crystal melting. In the second heating, one can observe that the peaks have largely disappeared, suggesting that in the process of going through the previous cycle the structure has been eliminated and has not reformed during the cooling process. Fig. 10 compares the first heating thermograms of the unaged and aged EVA. The glass transition, determined by a step change in the heat flow typically between −30 °C and 20 °C, was found to be around −25 °C for aged and unaged samples, suggesting ageing has no significant effect on Tg (Fig. 11). The melting transition of the ethylene segment has been accepted as being associated with a peak with a shoulder observed between 40 °C and 70 °C [34,35].

The relative crystallinity, X_c, of the samples was calculated as a function of ageing duration through the following relation,

$$X_C = \frac{\Delta H_f}{\Delta H_f^*} \times 100\% \qquad (6)$$

where ΔH_f^* is the fusion enthalpy of the perfect polyethylene (277.1 J/g) crystal and ΔH_f is the enthalpy of fusion of the EVA samples, respectively [36]. Analysis of the first heating results shows that crystallinity decreases due to ageing, (Fig. 12), which when correlated with the changes in mechanical behaviour, suggests that it is the changes in internal structure that is driving the changes in the storage modulus, E'. It can also be observed that there is no change after second heating. This reversion to a constant crystallisation content points towards a reduction in the structure at higher temperatures, and a consequent reduction in
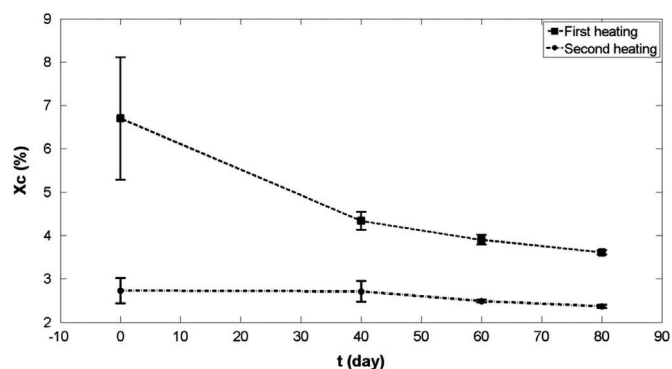
Fig. 12. Crystallinity versus ageing time after first and second heating.

modulus and a weakening in the relationship between ageing driven modulus reduction at higher temperatures.

4. Summary and conclusions

The thermal degradation of EVA, which is an adhesive polymer used as encapsulation material in PV modules, has been studied using techniques that enabled the viscoelastic properties and thermal stability to be measured. Key findings were that the activation energy of the first stage of degradation was unaffected by the ageing process and storage modulus at 1 Hz was significantly reduced with increases in temperature. Ageing was shown to reduce the storage modules monotonically as a function of ageing degree, though this effect was weakened when measuring at elevated temperatures. TGA measurements showed that chemical changes due to thermal activation were insignificant, even over the typical lifetime of the module, but examination of DSC results suggested that property changes could be connected to structural modifications.

It can be concluded that when predicting thermal effects on the mechanical performance of the encapsulant in a PV module the most significant factor is the transient temperature of the EVA, for example Fig. 7 shows that modulus is highly sensitive to temperature over the typical operating range of a module. Thermal cycling or ageing was also seen to bring about a decrease in the crystallinity of the EVA, although an equilibrium was reached after which crystallinity remained constant. There is also a long term progressive degradation in properties due to a thermally activated chemical reaction, however, this is slow enough at module operating temperatures to be considered insignificant compared to the other two thermal effects. Therefore, an efficient method of modelling mechanical performance would be to use the temperature dependent properties after equilibrium crystallinity has been reached. In the field, however, the modules will be subjected to light and humidity as well as elevated temperatures. Any absorbed moisture would be expected to affect the mechanical properties of the EVA in a similar way to increasing temperature and both absorbed moisture and UV would be expected to influence chemical degradation. This is the subject of future work.

Acknowledgements

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