Article

A Study of the Moisture Absorption Characteristics of Vinyl Ester Polymer and Unidirectional Glass Fibre Vinyl Ester Laminates

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Abstract: Vinyl esters are increasingly being used as the matrix polymer in fibre-reinforced composites for demanding large applications which experience long-term exposure to moist and wet conditions. This paper presents the results of a study of ageing due to moisture absorption in vinyl ester polymer and glass fibre–vinyl ester laminates. The moisture uptake kinetics of the two neat VE polymers, cured at different conditions, and their glass-reinforced composites has been characterised by gravimetric methods. These studies have been carried out using submersion in water at 23 °C and 50 °C and exposure to high relative humidity moisture conditions at room temperature. A dynamic mechanical analysis characterisation of the glass transition temperatures of both the aged matrix and the composite is also presented.

Keywords: vinyl ester; glass fibre; composite; hydrothermal ageing; moisture absorption; glass transition temperature

1. Introduction

The wide and expanding range of applications in which composite materials are employed ensures an almost inevitable contact with water liquid and vapour, which can affect both the immediate and the long-term performance of the material. The mechanisms of water absorption, the plasticizing effect of absorbed moisture and the lowering of the glass transition temperature are well-known processes which have been widely studied in polymeric materials [1–16]. To a lesser extent, water absorption has also been studied in composite materials, and it has been shown that, in general, the mechanisms of moisture penetration are much more complex than in the case of the unreinforced matrix [7–16].

Thermoset polymers and composites exposed to humid environments will generally experience weight gain over time as a result of moisture sorption. Moisture-induced degradation is a common cause of failure for many polymeric materials and can be present from the manufacturing stage of the material to its end of life. Moisture sorption can result in both reversible and irreversible changes in the properties and performance of polymers and composites [10]. The severity of the effect depends on the amount of moisture absorbed by the material, but even small amounts can have a negative effect on performance [11]. It has been established that moisture uptake is often accelerated by combined degradation agents, such as thermal degradation and external loading, which may lead to irreversible changes in the material structure and performance [11–14]. Moisture penetrates the structure of polymeric materials following a diffusion-controlled process. In the case of composites, moisture uptake by capillary action is also common, particularly in regions of air entrapment such as voids, cracks and delaminated regions. Moreover, a small amount of moisture may be located in the fibre/matrix interface. However, the majority of moisture absorbed by glass fibre (GF)-reinforced composites is usually concentrated in the polymer matrix. This imbalance in moisture sorption can lead to induced localised stress and strain fields in the composite, which may accelerate failure [10,13,15–17].

Vinyl ester (VE) resins are increasingly being used as the matrix polymer in fibre-reinforced composites for demanding large applications in the marine, offshore, and civil infrastructure sectors. VE formulations are low-viscosity at room temperature and are highly suitable for infusion of reinforcing fabric preforms to make large parts such as windmill blades. VE systems exhibit short fabrication cycles and ease of processability as well as relatively low cost, high environmental durability and adequate level of cured polymer performance in comparison to more expensive epoxies [1,10,18]. A recent review of hydrothermal ageing of glass fibre-reinforced vinyl ester composites [18] concluded that the growing demand for composite materials in infrastructure applications, where exposure to environmental conditions is inevitable, makes ageing studies a necessity. However, given the high costs and time-consuming processes involved with the in-service examination of large composite structures, laboratory-based accelerated ageing studies are of increasing interest in this field.

This paper presents the results of a study of ageing due to moisture absorption in VE polymer and GF–VE laminates. The moisture uptake kinetics of a range of VE-based materials have been investigated. This included two neat VE polymers, one a standard commercial bisphenol-epoxy VE, and the second a developmental VE primarily based on methyl methacrylate. The effect of the curing conditions of the VE polymer samples was also included in this study. Furthermore, unidirectional glass reinforced laminates were prepared with these two VE resins using two commercially available continuous glass-fibre rovings. Ageing characteristics of these materials have been investigated using dynamic mechanical analysis and gravimetric analysis methods under various moisture and temperature environments.

2. Materials and Methods

2.1. Materials

Two types of unidirectional (UD) glass fibre/vinyl ester composite laminate based on two VE resins and two glass fibre rovings were used in this investigation. The glass fibres supplied by 3B Fibreglass (Battice, Begium) were SE3030, a 1200 tex continuous roving containing 17 μm Advantex$^\circledR$ fibres (boron-free E-glass), and W3030, a 2400 tex continuous roving containing 17 μm HiPer-tex$^\circledR$ fibres (produced from a CaO-Al$_2$O$_3$-SiO$_2$ R-glass composition [19,20]). The VE resins (DION$^\circledR$ 1260 and DION$^\circledR$ 1273) were supplied by Polynt Composites (Gamle Fredrikstad, Norway). DION 1260 is a commercial bisphenol-epoxy vinyl ester with a styrene content of 48–52% by weight. DION 1273 is a developmental resin which is a pre-accelerated, modified vinyl ester resin, primarily based on methyl methacrylate (MMA) and styrene (<20% by weight). Material specifications and cure conditions for the laminates are included in Table 1. The SE 3030/1260 laminate was considered a baseline material since it consisted of commercially available matrix and reinforcement. The W 3030/1273 laminate was a developmental composite consisting of the DION 1273 experimental matrix and the W 3030 fibre. Composite laminates were supplied by Polynt as 800 × 800 × 3.9 mm panels with a glass weight fraction of 71.3 ± 0.2%. These laminates were measured as void-free within the experimental error of the standard density method [21]. These were cut to appropriate specimen sizes by water-jet cutting. Prior to ageing, the laminate specimen edges were sealed by using Araldite Epoxy, a 2-part high-viscosity, hydrophobic adhesive. Two thin layers of coating were applied in succession to ensure thorough sealing.

Neat resin specimens were also employed for a better understanding of the hydrothermal response of the matrix material on a bulk scale. Plates of DION 1260 and DION 1273 polymer cured in a closed mould were supplied by Polynt. Plates of DION 1260 polymer were also prepared at the University of Strathclyde using open silicone rubber moulds [21]. Cure conditions for polymer and composite samples are given in Table 1.

Table 1. Polymer matrix and laminate description and cure conditions.

Designation	VE Resin	Glass Fibre	Cure 24 h at RT	Post-Cure (PC)	Max. PC Temp (°C)
AF1260	DION 1260	SE3030		Sealed Mould	60
WF1273	DION 1273	W3030		Sealed Mould	60
1260, SM60	DION 1260	-		Sealed Mould	60
1273, SM60	DION 1273	-		Sealed Mould	60
1260, SM100	DION 1260	-		Sealed Mould	100
1260, OM100	DION 1260	-	Air	Air	100

2.2. Ageing Conditions

Plates of $80 \times 80 \times 3.9$ mm of all laminate and cured polymer specimens were aged, for up to 530 days, by full immersion in deionised (DI) water at 23 °C and 50 °C and in a humid environment of 100% RH at room temperature (20 ± 2 °C). These are referred to as "23 °C", "50 °C" and "100% RH" throughout this manuscript. The selection of immersion in water was used to simulate accelerated degradation mechanisms which may be acting through rainwater in large infrastructure applications. However, since the chemistry of rainwater is variable, DI water was selected in order to simplify the nature of the degradation reactions. The temperature of 50 °C was used as a means of ageing acceleration and to create an ageing environment, similar to ones present in hot and wet climates. The increased humidity environment was chosen to replicate degradation conditions acting in highly humid climates. All specimens were dried for at least 24 h under vacuum prior to ageing to obtain the starting weight W_0 of the dry sample. Samples were systematically removed from the conditioning container at various ageing times (t) to measure their weight $W(t)$, which was determined after any surface moisture was removed using a dry tissue. The time-dependent increase in the weight of the sample $M(t)$ was calculated as $W(t) - W_0$. Four water baths were employed for the DI water ageing, while sealed desiccators were used for the controlled humidity conditions. The 100% RH humidity level was achieved by placing DI water at the bottom of a desiccator and was checked by a digital hygrometer. These ageing conditions are consistent with the previously published study on microscale specimens [22]. 1260-OM100 specimens were only aged at 23 °C and 50 °C.

2.3. Diffusivity Analysis

The use of flat plate samples with a length and width to thickness ratio greater than 20 allowed the use of the classical 1-D Fickian diffusion approach for the analysis of the weight increase with time of the ageing samples. The background to Fickian diffusion is well-documented and will not be reproduced here. The time-dependent weight increase $M(t)$, as a fraction of the final equilibrium value of M_e, in an infinite parallel-sided slab of thickness (h) made of a polymer with diffusion coefficient (D) is given by Equation (1) [23]:

$$\frac{M(t)}{M_e} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 (D\pi^2 t/h^2)\right] \qquad (1)$$

The diffusion coefficient is often obtained in this type of experiment by using the initial slope obtained from a graph of $M(t)/M_e$ versus $t^{\frac{1}{2}}$. However, in this work, the full curve has been fitted to Equation (1) to obtain D. For the laminate samples, the effect of the fibres on the directional diffusion in the material must be considered. There are a number of phenomena which can affect the weight increase in ageing composite materials [8,12,13,24]. However, for a thin plate of unidirectionally reinforced laminate, Shen and Springer [25] have proposed that the through-the-thickness diffusion coefficient (D_c) can be estimated as follows:

$$D_c = \left(1 - 2\sqrt{\frac{v_f}{\pi}}\right) D_m \qquad (2)$$

where D_m is the diffusion coefficient of the polymer matrix and v_f is the fibre volume fraction. Equation (2) was used for the prediction of composite laminate diffusivities for the AF1260 and WF1273, which had measured fibre weight fractions (w_f), measured from ashing experiments, of 71.5% and 71.1%, respectively [21]. These values converted to volume fraction values of 51.9% and 51.4%, respectively. It was assumed that the glass fibres contributed a negligible amount to the weight gain of the ageing laminates, and so an estimation of the expected equilibrium moisture gain of the composite laminates was obtained by using the weight fraction of the matrix multiplied by the moisture gain of the neat polymer at equilibrium.

2.4. Dynamic Mechanical Analysis

Dry and aged laminate and neat polymer specimens were tested by DMA in a 3-point bending configuration using a Q800 Dynamic Mechanical Analyser (TA Instruments, New Castle, DE, USA) and according to ASTM D5023-15 [26]. The input test parameters were frequency of 1 Hz, amplitude of 50 μm, pre-load force of 0.1 N and a force track of 120%. The specimen dimensions were 64 × 13 × 3.9 mm. All specimens were equilibrated at 25 °C for 5 min, then ramped at 2 °C/min up to 150 °C. The glass transition temperature (Tg) assignment was conducted in agreement with ASTM D7028—07 [27].

3. Results and Discussion
3.1. Neat Polymer Moisture Uptake
3.1.1. DION 1260 Polymer

A weight gain vs. exposure time plot of the DION 1260 SM60 polymer for three different conditions is shown in Figure 1. Diffusivity values calculated using these data and assuming 1-D Fickian diffusion for all specimens and the maximum weight gain and diffusivity values (calculated using Equation (1)) for the three differently cured DION 1260 polymer under the three exposure conditions are summarised in Table 2. In some cases, it was unclear if equilibrium was reached and maximum weight gain values were estimated from the curves obtained. These standard cure (SM60) samples exhibited a similar Fickian-type moisture uptake behaviour when immersed at 23 °C in DI water and when conditioned at 100% RH and room temperature. In both cases, an initial Fickian-like weight gain was observed until around 66 days ($\approx 40 \sqrt{h}$), at which point weight gain began to stabilise at an equilibrium value, but there then followed a slow and gradual increase for the remaining ageing period.

This further weight increase observed upon the samples reaching their Fickian equilibrium moisture content is indicative of a two-stage diffusion phenomenon which has been widely observed in polymers and their composites [12,24]. It is normally attributed to the coupling of diffusion with a viscoelastic response. More specifically, the combined effect of coupling between diffusion and polymeric relaxation is governed by two distinct yet interrelated phenomena: diffusion across the thickness of an area of a polymeric material and time-dependent relaxation of the polymeric chains. For instance, moisture diffusion until saturation in a film will occur rapidly, due to its reduced thickness. Therefore, the establishment of a uniform distribution across the film thickness will take place before the relaxation process starts taking place. In this case, moisture ingress is governed by the diffusivity of an unrelaxed polymer. On the other hand, moisture diffusion in a thick slab of a polymer will occur more slowly than relaxation, and therefore the diffusion will be governed by the diffusivity of fully relaxed polymeric chains. However, for intermediate slabs, the phenomena of diffusion and relaxation will occur in combination [12].

The resultant moisture-induced plasticisation of the matrix can be marked by a Tg decrease as a function of moisture content [28]. At equilibrium and as presented in Table 2, the weight gain in both conditions was found to be similar. The time to equilibrium was between 85 ($\approx 45 \sqrt{h}$) and 110 days ($\approx 50 \sqrt{h}$) under both conditions. Diffusivity values under all ageing conditions were of the same order of magnitude as values reported in the literature [29]. Generally, the comparison of the two ageing conditions provides evidence

that exposure to a highly moist environment and direct immersion in an aqueous medium have a similar effect on vinyl ester polymer, although the moisture gain at 100% RH was slightly lower than in water at 23 °C.
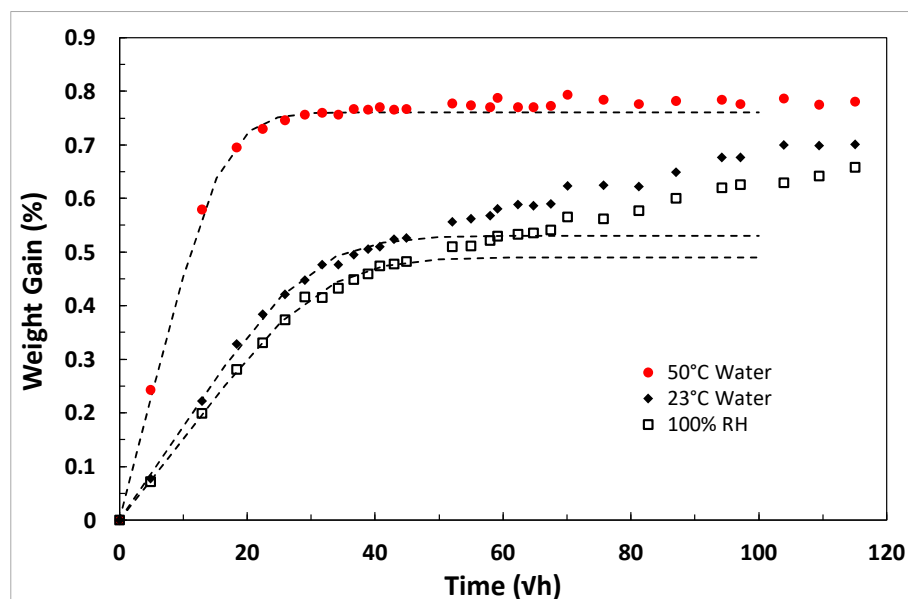

Figure 1. Weight gain vs. ageing time for DION 1260 SM60 polymer under different ageing conditions (dotted lines show fitting of Equation (1)).

Table 2. Weight gain and diffusivity of DION 1260 polymers under different ageing conditions.

DION 1260	Ageing Condition	Equilibrium Weight Gain (%)	Diffusivity $\times 10^{-6}$ (mm²/s)	Max. Ageing Period (Days)	Max. Weight Gain (%)	Re-Dried Weight Loss (%)
SM60	100% RH	0.49	0.80	530	0.67	−0.23
	23 °C DI	0.53	0.90	530	0.70	−0.24
	50 °C DI	0.76	3.00	530	0.78	−0.27
SM100	100% RH	0.57	0.90	175	0.60	−0.27
	23 °C DI	0.59	1.00	175	0.60	
	50 °C DI	0.68	4.00	175	0.74	
OM100	23 °C DI	0.95	0.52	658	1.37	−0.18
	50 °C DI	1.39	2.00	389	2.60	−0.61

The samples submersed in water at 50 °C also exhibited Fickian-like behaviour but with a significantly higher weight gain and a higher diffusivity level. The time to obtain the higher equilibrium weight increase (35 days $\approx 28\ \sqrt{h}$) was significantly shorter when compared to 23 °C and 100% RH. Although matrix relaxation was apparent at room-temperature ageing and is nevertheless more likely to take place in higher temperatures [30], only a very small post-equilibrium increase ($\approx 0.02\%$) in sample weight could be observed in the data in Figure 1. One possible explanation for this is that the higher water temperature induces a much more rapid relaxation in the polymer, which means that the associated increased moisture uptake takes place during the initial Fickian period and is essential over by the time that Fickian equilibrium is reached.

Another possibility is that ageing at elevated temperatures induced anti-plasticisation effects, i.e., a combination of leaching and secondary cross-linking, instead of plasticisation. Han and Drzal [31] have proposed the presence of two types of bound water in thermoset networks; type I, which is associated with a reduction in Tg and polymer plasticisation, and Type II, bound water which is responsible for secondary cross-linking and increased Tg. Further claims made by Apicella et al. [32] suggest that high-temperature hydrothermal environments

are associated with Tg increases in thermosets through post-curing, often accompanied by leaching. In addition, they stated that such effects can reduce the degree of plasticisation of the matrix (anti-plasticisation). Leaching and secondary cross-linking effects have been previously observed by Visco et al. [33] for a vinyl ester matrix aged at 60 °C in water. Similar effects have also been observed by Apicella et al. [32] for incompletely polymerised styrene-containing unsaturated polyester. Thomason and Xypolias have observed that microdroplets (approximately 100 µm in diameter) of this same vinyl ester polymer are essentially totally degraded after only 100 h of exposure to water at 50 °C [22].

Despite the observation of Fickian-like plots, irreversible weight loss was confirmed for all specimens. All specimens were re-dried upon the completion of ageing after 530 days ($\approx$120 $\sqrt{h}$). Re-drying was conducted at 45 °C for 72 h, following storage in a dry desiccator at room temperature for a minimum of 24 h. Weight losses of 0.24%, 0.27% and 0.23% were observed for the conditions of 23 °C, 50 °C and 100% RH, respectively. Polymer matrix ageing has been associated both with matrix leaching (matrix decomposition)—hydrolysis, and (or) leaching polymer unreacted oligomers—not an indication of hydrolysis. A common indicator for hydrolysis is the change in matrix colour after ageing. In this case, a mild change in colour in the matrix was observed at 23 °C and 100% RH, whereas a more profound discolouration was featured at 50 °C (see Figure 2). The latter observation confirms matrix hydrolysis at 50 °C, while the former is an indication that hydrolytic effects had only started to take place at room-temperature ageing. DMA measurements were carried out to further elucidate any effects on the polymer Tg.

Figure 2. DION 1260 SM60 polymer colour changes under different ageing conditions.

Post-curing the DION 1260 matrix at a higher temperature of 100 °C did not have a great effect on moisture uptake kinetics, as shown in Figure 3. Despite the ageing period of the DION 1260 SM100 specimens being shorter than that of the SM60 samples, similar equilibrium water uptake values were obtained. while the moisture gain values and diffusivities were also found to be within the same range, as shown in Table 2.

A notably different ageing behaviour was observed for the specimens cured in an open mould for the first part of the cure, which allowed oxygen interaction with the curing specimen. The average water uptake trends for specimens submerged at 23 °C and 50 °C are shown in Figure 4. Specimens aged at 23 °C also initially followed a Fickian-like behaviour, reaching equilibrium after approximately 100 days ($\approx$50 $\sqrt{h}$) and absorbing approximately 0.9% of water. Subsequently a further weight increase, which was approximately linear with time (again indicative of matrix relaxation and swelling), took place, but at a much greater rate than shown by samples SM60 and SM100 in Figures 1 and 3. The samples aged

at 50 °C also initially exhibited Fickian-like behaviour, reaching an apparent equilibrium weight increase earlier and at a higher level compared to the sample aged at 23 °C. Perhaps more notable from the results shown in Table 2 is that the equilibrium water absorption levels of the open-mould samples (OM100) were approximately double that of the sealed-mould prepared samples (SM60, SM100). This significant increase in weight gain of the open-mould specimens, when compared to standard sealed-mould cure, could be caused by the interaction of oxygen with the curing polymer, as well as probable styrene evaporation due to a difference in polymer (surface) structure [34–36]. It is noteworthy that pronounced styrene evaporation, which was apparent in this case, can significantly decrease the hydrophobicity of the matrix [37,38]. A parallel study on the effect of oxygen on the curing of these two VE resins concluded that oxidation and styrene loss effects were significantly reduced by the use of sealed-mould curing conditions [39].
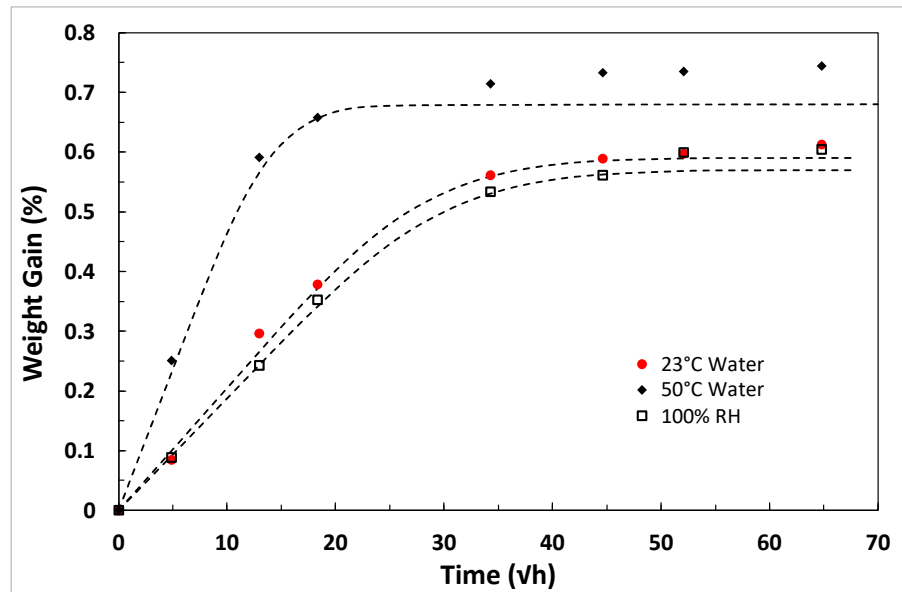

Figure 3. Weight gain vs. ageing time for DION 1260 SM100 post-cured polymer under different ageing conditions (dotted lines show fitting of Equation (1)).
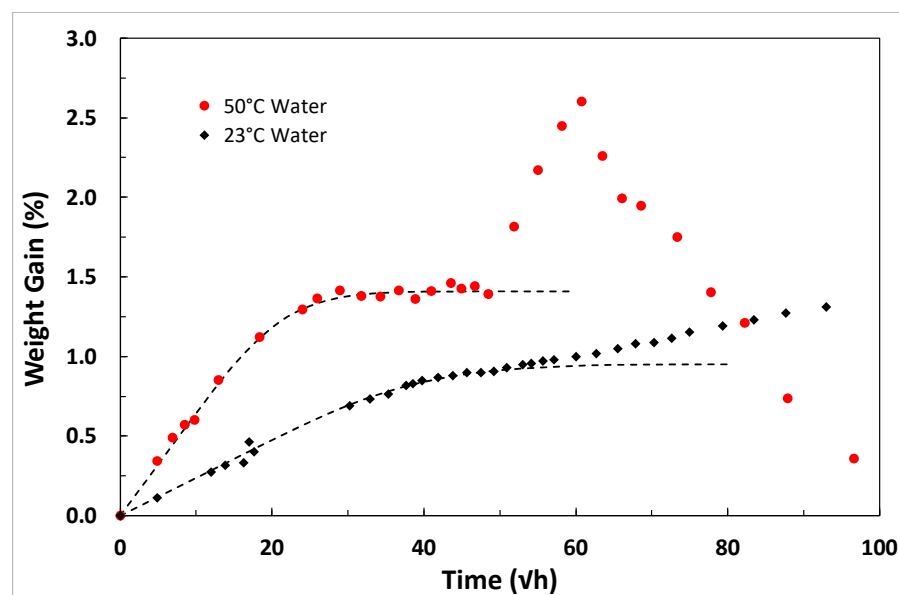

Figure 4. Weight gain vs. ageing time for DION 1260 OM100 polymer at 23 °C and 50 °C (dotted lines show fitting of Equation (1)).

An interesting and very different response to hydrothermal ageing was exhibited by the specimens exposed at 50 °C when the water submersion experiment was continued for longer times. The data featured in Figure 4 are averages of three specimens, which all noted a similar behaviour with each other, with only slightly varying moisture gain. The samples initially reached weight stabilisation after 30 days ($\approx$27 $\sqrt{h}$) of exposure at around +1.4%, indicative of the Fickian equilibrium. However, an unexpectedly abrupt increase in weight was observed at around 100 days ($\approx$50 $\sqrt{h}$). The slope of this post-equilibrium weight increase was very significantly greater than that observed with the sample aged at room temperature. This increase can be attributed to probable more significant plasticisation and matrix relaxation of a more hydrophilic polymer. Nonetheless, leaching became apparent and dominated sorption after an average maximum weight gain of 2.6% was obtained, resulting in a pronounced weight loss.

At the end of the water absorption measurements, the aged specimens were thoroughly dried and weighed in order to examine probable leaching effects. Samples aged at 23 °C were found to have lost approximately 0.18% after 658 days of ageing ($\approx$125 $\sqrt{h}$), whereas the samples aged at 50 °C had lost 0.6% of their weight after just 389 days ($\approx$97 $\sqrt{h}$) of exposure. These data would seem to confirm the possibility that leaching of some vinyl ester polymer components had occurred during the extended water aging experiments. Difficulty in extracting absorbed moisture was noted with both SM and OM specimens. Re-drying open-mould specimens was particularly challenging, and rigorous drying schedules were employed for most specimens. A decaying weight loss was recorded for all specimens, upon heating in an air circulation oven (at 45 °C—below the polymer Tg) and placement in a dry desiccator. Thus, it is challenging to provide definitive answers on weight loss. The difficulty of re-drying the matrix was a possible indication of water molecules trapped within micro-cavities and capillaries found in the thermoset polymer network making it susceptible to hydrolysis. This effect has been previously studied by Han and Drzal [31] and has been shown to be an indication of chemical ageing.

3.1.2. DION 1273 Polymer

The weight gain behaviour and diffusivity values of the DION 1273 SM60 polymer were found to be relatively close to those of DION 1260, although the former absorbed more moisture at equilibrium. Weight gain vs. time plots for DION 1273 SM60 polymer are presented in Figure 5, while the derived diffusivity and moisture gain values are contained in Table 3. The weight gain behaviour and diffusivity values recorded for DION 1273 at 23 °C and 100% RH were similar to each other, confirming the similarity of the two conditions also observed with the DION 1260 polymers. The DION 1273 samples also exhibited a two-stage moisture absorption process indicative of an initial Fickian absorption behaviour later overlaid by an approximately linear (with $\sqrt{time}$) slow weight increase due to polymer relaxation and swelling. Due to an increasing weight gain in all cases, equilibrium was assumed when the weight gain reached a temporary plateau—at the "flattest" point of the curve. The initial Fickian equilibrium levels were attained between 63 ($\approx$38 $\sqrt{h}$) and 69 days ($\approx$40 $\sqrt{h}$), significantly earlier than observed with DION 1260, which reached equilibrium between 85 ($\approx$45 $\sqrt{h}$) and 110 days ($\approx$50 $\sqrt{h}$). The moisture gain at this point was also significantly higher than for DION 1260 under both conditions. Namely, 0.76% was recorded at 23 °C, as opposed to 0.53% found for DION 1260, and 0.67% at 100% RH, compared to 0.49% noted for DION 1260. The post-equilibrium continuous weight increase is indicative of matrix relaxation and swelling.

DION 1273 attained a similar weight gain pattern at 50 °C compared to 23 °C and 100% RH but absorbed significantly more moisture. The short-term equilibrium was estimated at around 26 days ($\approx$25 $\sqrt{h}$), also somewhat sooner than observed with the DION 1260 polymers. Furthermore, the estimated equilibrium value of 1.09% for DION 1273 polymer was much higher than that for DION 1260 polymers. In addition, for an ageing period of 530 days, the maximum moisture gain obtained by DION 1273 at 50 °C was 1.4%, whereas a significantly lower maximum moisture uptake of 0.78% was attained by DION 1260 (see Tables 2 and 3). In

addition to the overall higher moisture equilibrium values observed with DION 1273 polymer, the slope of the post-equilibrium linear increase in sample weight observed in Figure 5 was significantly higher than that obtained with the DION 1260 samples in Figures 1 and 3. Hence, it seems reasonable to conclude that DION 1260 polymer is more hydrophobic compared to DION 1273 polymer. One possible reason for this is that DION 1260 has a much higher styrene content than DION 1273, and styrene is known to increase the hydrophobicity of vinyl ester polymers [38]. Moreover, the two resins consist of two different primary monomers, methyl-methacrylate (MMA)—DION 1273, and bisphenol-epoxy—DION 1260, which in turn produce a matrix with polymer networks entirely different from each other. N'Diaye et al. [40] have reported that although methyl-methacrylate polymers (PMMA) are hydrophobic, they have been found to absorb up to 2% of water and can undergo swelling and plasticisation, as did DION 1273 under all ageing conditions.
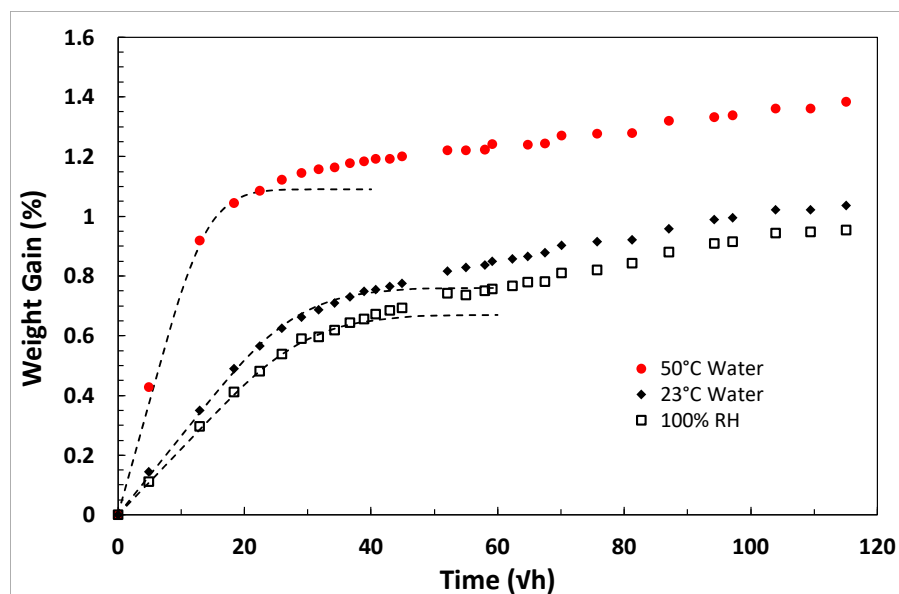

Figure 5. Weight gain vs. ageing time for DION 1273 SM60 polymer under different ageing conditions (dotted lines show fitting of Equation (1)).

Table 3. Weight gain and diffusivity of DION 1273 SM60 polymers under different ageing conditions.

Ageing Condition	Equilibrium Weight Gain (%)	Diffusivity $\times 10^{-6}$ (mm²/s)	Max. Ageing Period (Days)	Max. Weight Gain (%)	Re-Dried Weight Loss (%)
100% RH	0.67	0.9	530	0.97	−0.19
23 °C DI	0.76	1.0	530	1.05	−0.18
50 °C DI	1.10	3.8	530	1.4	−0.42

All aged DION 1273 SM60 polymer samples were re-dried at the termination of the aging experiments to determine any overall weight loss which occurred during their submersion. The drying conditions used were identical to those used for the DION 1260 SM60 samples (see Section 3.1.1). Values are tabulated in Table 3. At 23 °C and 100% RH, the final weight loss of DION 1273 was slightly less than that of DION 1260, despite the former absorbing more moisture. However, at 50 °C, DION 1273 noted a significantly higher weight loss than DION 1260, indicative of the susceptibility of the matrix to hydrothermal attack at elevated temperatures. Pronounced discolouration, indicative of chemical ageing, was also observed for all DION 1273 samples under all ageing conditions (see Figure 6).
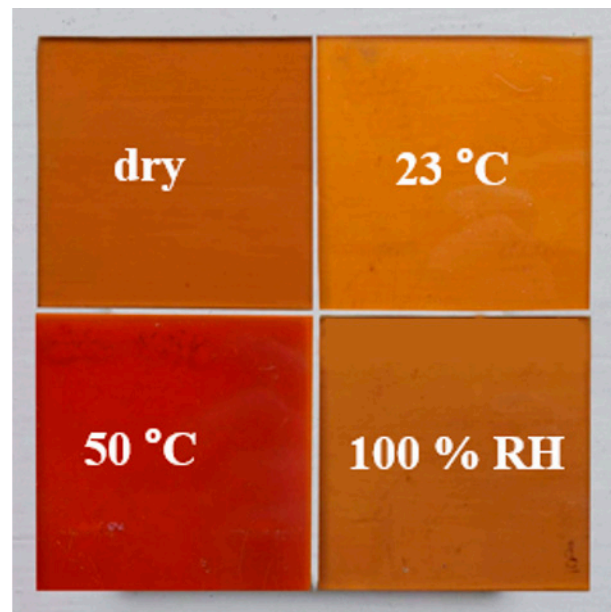
Figure 6. DION 1273 SM60 polymer colour changes under different ageing conditions.

3.2. Laminate Moisture Uptake

Figure 7 presents a weight gain vs. time plot for the AF1260 laminates under different ageing conditions with the dotted lines showing the fitting of the 1-D Fickian diffusion model in Equation (1). The 80 × 80 × 3.9 mm specimen geometry was selected to allow direct comparison with the results for the neat polymer plates presented in the previous section. Similarly, Figure 8 shows the results for the long-term moisture absorption measurements on the WF1273 laminates. In both cases, a similar pattern of weight increase with time can be observed, as seen in the respective polymer matrices. Under all conditions, the composites exhibited an initial Fickian-like weight increase approaching a plateau equilibrium level followed by a further slow linear (with sqrt time) weight increase at longer times. Composite diffusivity and weight gain values obtained experimentally are compared in Table 4 with diffusivity and weight gain values predicted from the neat polymer matrix ageing values. The average matrix weight fraction of 0.29 was used for the evaluation of the predicted equilibrium moisture gain. The same weight fraction was converted to a volume fraction value of 0.52 for use in Equation (2). In all cases, the experimentally obtained diffusivity and weight gain values were higher than the theoretical predictions. In most cases, the measured and predicted Fickian equilibrium weight gain values were relatively close. Given the uncertainty in the measured values generated by the possible overlap of the second, slower, observed moisture absorption phenomenon of weight uptake in the polymers, it seems reasonable to state that the predicted and measured values were equivalent within the experimental error. However, the diffusivity values showed a very different behaviour. In this case, the measured composite diffusion coefficients were significantly greater (approximately ×4) than those predicted by Equation (2).

Three possible reasons for such deviations have been suggested by Karbhari and Zhang [41]. These include relaxation of elastic forces induced by the cross-linked network after the initial weight-gain plateau, and (or) wicking at the interface, and (or) the presence of manufacturing voids and the likelihood of them being increased by ageing. Furthermore, the degradation of the edge sealant during ageing is a common issue in the ageing of composites. According to the literature, simplistic 1-D diffusion models can lead to erroneous results, especially when removal of the sealant occurs. More complex diffusion models may thus be employed to understand the full effect of ageing when changing specimen geometry [24].
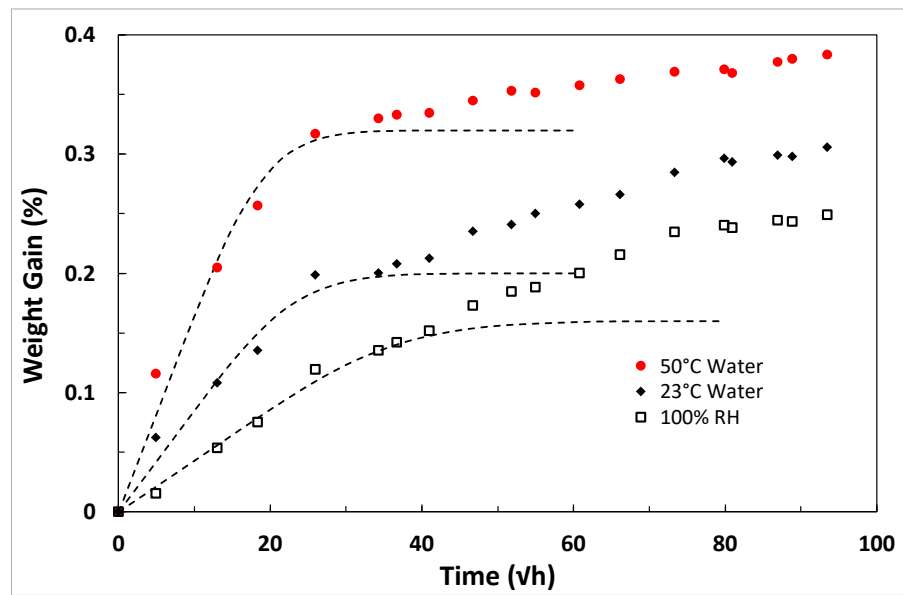
Figure 7. Weight gain vs. ageing time plot for AF1260 composite specimens under different ageing conditions (dotted lines show fitting of Equation (1)).
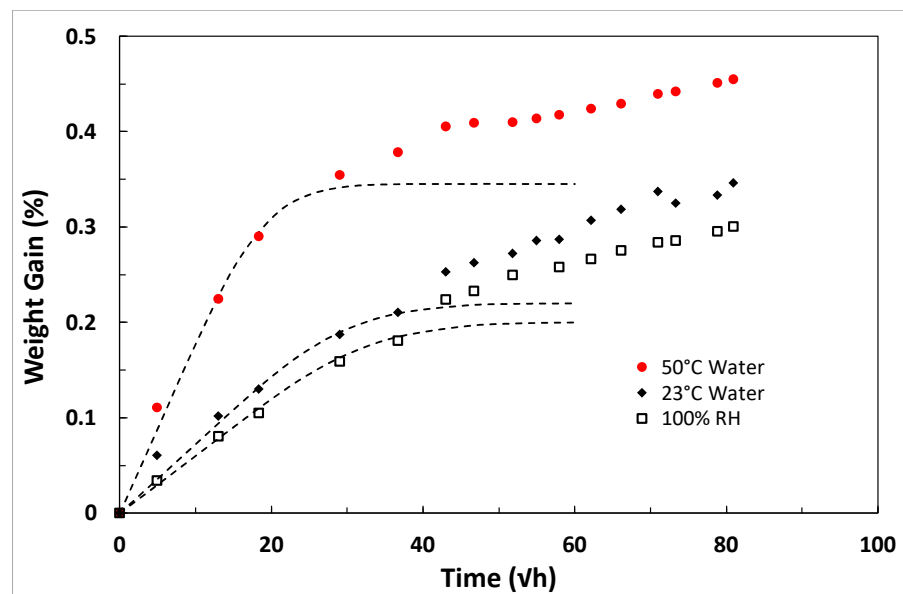

Figure 8. Weight gain vs. ageing time plot for WF1273 composite specimens under different ageing conditions (dotted lines show fitting of Equation (1)).

Table 4. Experimental vs. predicted composite diffusivity and weight gain values.

Composite Reference	Ageing Condition	Equilibrium Prediction (%)	Measured Equilibrium (%)	Diffusivity Prediction (10^{-6} mm^2/s)	Measured Diffusivity (10^{-6} mm^2/s)
AF1260	100% RH	0.14	0.16	0.16	0.60
	23 °C DI	0.15	0.20	0.17	1.50
	50 °C DI	0.22	0.32	0.57	2.20
WF1273	100% RH	0.19	0.20	0.17	0.75
	23 °C DI	0.22	0.22	0.19	0.90
	50 °C DI	0.32	0.35	0.75	2.20

3.3. Dynamic Mechanical Analysis

3.3.1. DMA of the VE Polymer Matrices

The DMA results for the storage and loss moduli of SM60 vinyl ester polymers of DION 1260 and DION 1273 are compared in Figure 9. Both polymers exhibited a single glass transition in the temperature range studied. The glass transition temperature (as characterised by the peak in the loss modulus curve) was found to be 101 °C for DION 1260 compared to a much lower value of 77 °C for DION 1273. The Tg values for all polymer and composite samples after aging are summarised in Table 5. DION 1260 SM60 and SM100 polymers exhibited an approximate 10 °C Tg reduction for all aging times and conditions listed in Table 2. Figure 10 compares the DMA loss modulus curves for DION1260 SM60 polymer after 180 days of aging under the three different conditions used in this study. The Tg depression due to the exposure to, and absorption of, moisture for these polymers can clearly be observed by the peak in loss modulus shifting to lower temperature. It is interesting to note in Figure 11 that the reduction in Tg exhibited by these samples appears to be fully reversible upon re-drying the aged samples.
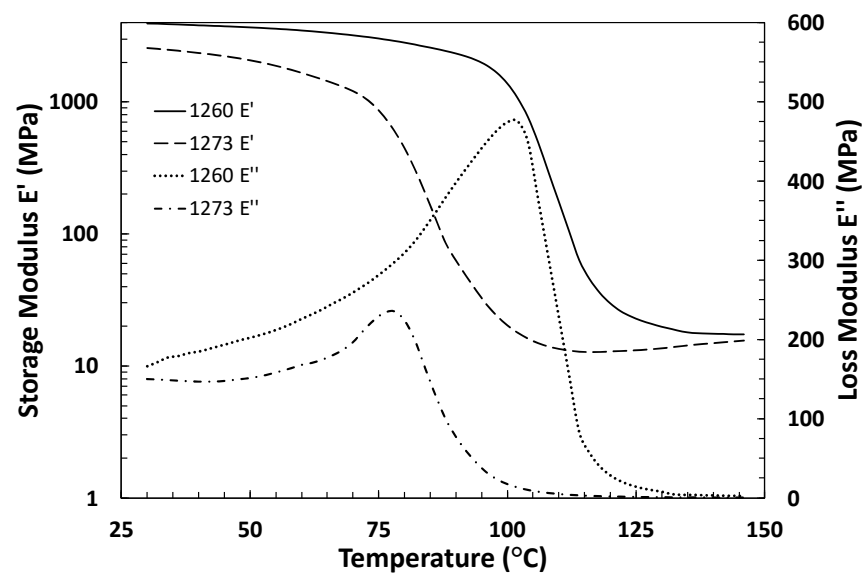

Figure 9. DMA results for un-aged DION 1260 and DION 1273 polymers.

Table 5. DMA-determined (loss modulus peak) Tg of polymers and composites.

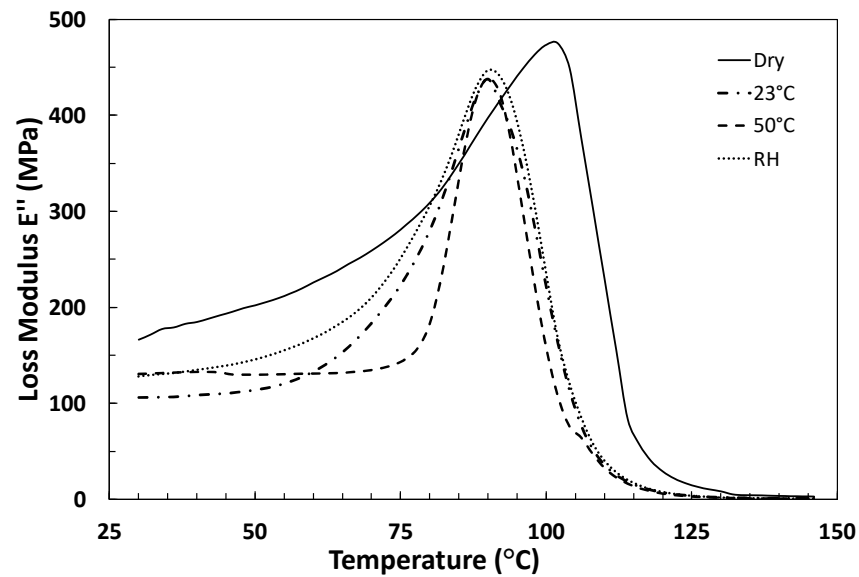| Sample	Glass Transition Temperature (°C)					
	0 Days (=0 $\sqrt{h}$)	30 Days ($\approx$27 $\sqrt{h}$)	90 Days ($\approx$46 $\sqrt{h}$)	180 Days ($\approx$66 $\sqrt{h}$)	270 Days ($\approx$80 $\sqrt{h}$)	Re-Dried ($\approx$112 $\sqrt{h}$)
1260 SC RH		92		90		101
1260 SC 23	101	92	90	89.5		101
1260 SC 50		90	90.5	90		102
1260 PC RH		94		93		
1260 PC 23	99	94		93		
1260 PC 50		93	92	93		
1273 SC RH						83
1273 SC 23	77					82
1273 SC 50						88
AF1260 RH	107		102	100.5		
AF1260 23			102	100		
AF1260 50			98	98		
WF1273 RH	89		82	80	79	
WF1273 23			81	79	78	
WF1273 50			77	77	77.5	

Figure 10. DMA loss modulus curve for DION 1260 polymer aged for 180 days under different conditions.
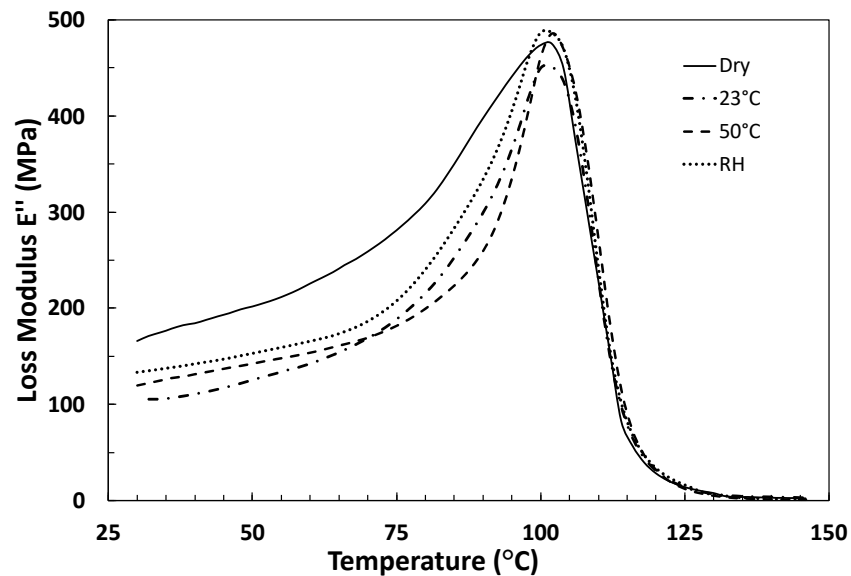

Figure 11. DMA loss modulus curves for aged and re-dried neat DION 1260 polymer specimens.

This implies that the majority of the Tg reduction can be attributed to plasticisation—reversible degradation [11,28,31], especially for specimens aged at 23 °C and 100% RH. This is in correlation with the moisture sorption behaviour of the specimens, which exhibited a continuously increasing weight pattern, indicative of matrix relaxation through plasticisation. However, narrowing of the loss modulus peak upon ageing under either of the three ageing conditions may be a hint of secondary cross-linking. In particular, as shown in Figure 10, the narrowing of the loss modulus peak followed the intensity of the ageing conditions. It was the broadest at 100% RH and the narrowest at 50 °C. Such changes may be indicative of anti-plasticisation effects starting to take place after room-temperature ageing, and being more apparent at a higher temperature. Moreover, these were denoted by the weight loss of the samples upon ageing and their discolouration, which was mildest at 23 °C and 100% RH and more amplified at 50 °C, which is in line with the observation regarding anti-plasticisation effects. Any increased cross-linking in these samples did not result in a significant Tg increase, but anti-plasticisation effects may be nonetheless counteracted by subsequent moisture-induced degradation. It is possible that further ageing would have resulted in amplified anti-plasticisation effects and a higher Tg.

Gravimetric and DMA results for DION 1260 SM60 vinyl ester polymer can be summarised as follows. For specimens aged at 23 °C and 100% RH, plasticisation/relaxation was the dominating moisture-induced effect. This was manifested by the continuous increase in the weight of the specimens and was confirmed by a Tg decrease as a function of ageing. The majority of degradation was indeed physical and was confirmed upon re-drying the specimens and measuring their Tg, which remained close to the Tg of the un-aged specimens. However, chemical ageing did take place in the form of leaching. Leaching effects were apparent, as indicated by the discolouration and weight loss of the aged specimens. Leaching seemed to have introduced secondary cross-linking, indicated by the narrowing of the loss modulus curve. The latter effect, along with discolouration, was more pronounced for the specimens aged at 50 °C. The weight uptake vs. ageing behaviour of the plate aged at 50 °C resembled Fickian diffusion, and relaxation effects were not apparent. Despite the attainment of a Fickian curve, DMA results during ageing showed a notable Tg decrease—plasticisation, whereas DMA results after ageing and re-drying indicated a small Tg increase and narrowing of the loss modulus curve, which may imply cross-linking. It can thus be concluded that competing ageing effects took place at 50 °C. Similar degradation did indeed take place under all ageing conditions, but evidently at a slower rate, which is expected considering that 50 °C is an accelerated ageing environment.

The Tg of the un-aged DION 1273 SC60 polymer was measured by DMA to be 77 °C. This was notably lower than that of DION SC60 (101 °C). Due to the developmental nature of the DION 1273 resin, there was insufficient material available to carry out a full DMA ageing study, and so DMA was only carried out on un-aged samples and upon the completion of ageing (530 days) and re-drying. The results for the DMA loss modulus Tg values for these aged and re-dried samples are also presented in Table 5. In all cases, the aged and re-dried specimens exhibited a higher Tg than the un-aged samples. Tg values of 82 and 83 °C were found after ageing at 23 °C and 100% RH, and 88 °C after ageing at 50 °C. This Tg increase upon ageing is a clear indication of moisture-induced cross-linking. Secondary cross-linking has been previously associated with anti-plasticisation effects [29,42,43]. In this case, these were probable, indicated by the pronounced discolouration of the specimens and their weight loss through leaching. Nevertheless, the DION 1273 polymer samples underwent a continuous weight increase during ageing, indicative of relaxation through plasticisation, which is a form of physical ageing. It is thus likely that competing relaxation and secondary cross-linking effects were apparent, whereby relaxation dominated but was reversed upon re-drying the specimens.

3.3.2. DMA of the GF-VE Laminates

The DMA results for the loss moduli glass transition temperatures of AF1260 and WF1273 laminates are summarised in Figure 12 (with values presented in Table 5). Both composite systems exhibited a similar pattern of Tg reduction with moisture ageing, which plateaued out after approximately 90 days ($\approx$46 $\sqrt{h}$). This was after the moisture absorption level attained the Fickian equilibrium level indicated in Figures 7 and 8. For the AF1260 laminate, the Tg was approximately 6 °C higher than that of the neat matrix. However, for the WF1273 laminate, the increase was much greater, at 12 °C. The addition of reinforcements has been frequently observed to result in an increase in the measured polymer matrix Tg [44–47]. This is generally thought to be a reflection of the restriction of motion of the polymer matrix molecules in the vicinity of the fibre surface due to the interfacial interactions between fibre and polymer. A direct measure of the interfacial interaction in these two fibre-matrix systems has been reported. Single-fibre micro-bond testing of the interfacial shear strength of the WF1273 system was reported at 43.5 MPa, which was significantly higher than the 35.3 MPa found for the AF1260 system [21,22].
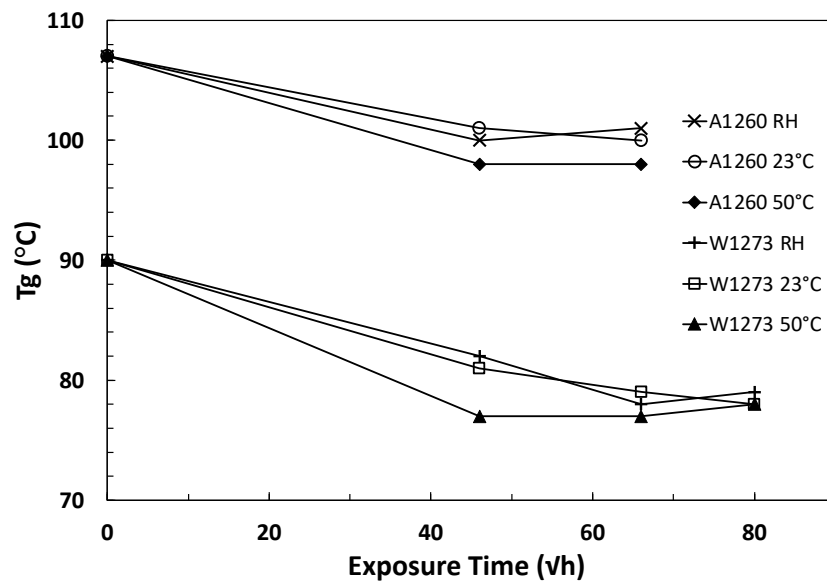
Figure 12. DMA-determined Tg values for laminates aged under different conditions.

Under the range of ageing conditions studied, the Tg change of the AF1260 composite was relatively small, with the greatest effect observed for samples submerged at 50 °C. Moreover, the trends in Tg for the AF1260 composite tracked the changes observed in the 1260 matrix polymer, so presumably the composite changes may also be attributed to moisture-induced plasticisation. The Tg depression upon ageing was slightly greater for WF1273 than that of AF1260. The fact that all of the aged composite samples maintained a significantly higher Tg compared to the unreinforced polymer may be taken as some evidence that the level of interfacial fibre–polymer interaction, which resulted in the higher Tg observed in the composites, was not significantly degraded by the long-term exposure to moisture over the term of these measurements.

4. Conclusions

In conclusion, this study enabled a comparison between two vinyl ester matrices and their composites:

- DION 1260—a baseline VE, and DION 1273—a developmental VE, polymers under long-term wet environments. A comparison between different curing conditions for DION 1260 was also included.
- AF1260—a baseline laminate and WF1273—a developmental laminate.

Generally, the DION 1260 matrix was found to be less hydrophilic than DION 1273. Overall, wet ageing at 23 °C and moisture exposure (100% RH at room temperature) had a similar effect on both matrices and were found to be milder than wet ageing at 50 °C, which was characterised by a higher moisture gain and more pronounced degradation. Submersion in DI water at 50 °C was used as a means of accelerating ageing. However, the degradation mechanisms activated by this elevated temperature in combination with the direct water contact were irreversible in most cases. Chemical degradation in the forms of hydrolysis, leaching and secondary cross-linking was induced by the elevated temperature environment, which was not always apparent in room-temperature conditioning. It is possible that such effects may be evident when ageing composites in humid environments at average normal outdoor temperatures in the long term or in warmer climates. This study further validated that oxygen intrusion in the polymerising vinyl ester medium and styrene loss can alter the chemistry of the polymer. Different uptake kinetics were exhibited by DION 1260 open-mould specimens, which were characterised by a higher moisture gain and a more anomalous water uptake behaviour. On the other hand, the effect of a higher

cure temperature of 100 °C did not have a great effect on the uptake kinetics of the DION 1260, provided it was cured in a sealed mould.

DMA measurements showed Tg depression for both polymers tested in their wet state. However, Tg was fully recovered upon re-drying the specimens, and most of the reduction was attributed to plasticisation. For re-dried specimens, there was a hint suggesting secondary cross-linking, primarily for elevated temperature conditioning. DMA indicated plasticisation of DION 1260 open-mould specimens aged at 23 °C, suggested by broadening of the loss modulus shoulder, which was also shifted at lower temperature values. On the other hand, depression of the loss modulus shoulder was evident in DION 1260 open-mould specimens aged at 50 °C, indicative of secondary cross-linking of the lower-Tg, presumably styrene-rich phase of vinyl ester. Secondary cross-linking was also indicated for re-dried DION 1273 polymer, as denoted by a notable Tg increase.

It was found that the Tg of AF1260 laminate in its un-aged state was 6 °C higher than that of its neat polymer matrix, whereas the Tg of WF1273 was 12 °C higher than that of its neat polymer matrix. Although a definitive answer cannot be provided on what may be causing such a Tg increase when adding glass fibres to the VE polymers, it can be presumed that this is an interfacial effect. It is possible that certain chemical reactions take place between the glass, the sizing and in turn the matrix, which result in an increase in Tg. This has been shown to correlate with a higher measured interfacial strength in the WF1273 system. Under the range of ageing conditions studied, the change in the Tg of the AF1260 composite was relatively small, with the greatest effect observed for samples submerged at 50 °C. Moreover, the trends in Tg for the AF1260 composite tracked the changes observed in the 1260 matrix polymer, which were attributed to moisture-induced plasticisation. The Tg depression upon ageing was slightly greater for WF1273 than that of AF1260. The fact that all of the aged composite samples maintained a significantly higher Tg compared to the unreinforced polymer was taken as some evidence that the level of interfacial fibre–polymer interaction, which resulted in the higher observed Tg in the composites, was not significantly degraded by the long-term exposure to moisture over the term of these measurements.

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