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Long-term water immersion ageing characteristics of GFRP composites

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Abstract This paper evaluates the water absorption characteristics of glass fibre reinforced polymers after long-term exposure to a hygrothermal environment. In particular, three types of laminates, fabricated using woven and non-crimp triaxial glass fabric with a polyester matrix, were immersed in deionised water baths for 2.5 years (30 months) at temperatures of 43, 65 and 93 °C. In order to assess the effects of through-thickness delaminations on the water absorption characteristics, a series of specimens were impacted prior water immersion with low-velocity impact using three energy levels of 2.5, 5 and 10 J. The changes in the thermo-mechanical properties of laminates after water immersion were examined using the dynamic mechanical thermal analysis (DMTA) technique. The results revealed that the long-term water uptake profiles had no similarities to the classical Fickian absorption behaviour and they were markedly different for each water immersion temperature. At higher temperatures a multi-stage diffusion was observed, which was attributed to the microporosity of the laminates as well as to the osmotically enhanced uptake through the interfaces, with the peak values showing dependency on the type of material system. The impact damage on laminates immersed in water did not cause any marked change in the maximum water absorption level or at the absorption rate compared to the undamaged specimens. DMTA have shown matrix plasticizing effects at 43 °C and some post-curing effects at 65 and 93 °C while the effect of the time of immersion at all temperatures tested resulted in a decrease of the value of storage modulus.

Introduction

Glass fibre composites with either polyester or vinylester resins have been used extensively in marine structural applications because of their strength to weight characteristics and absence of any corrosion-related problems. Even though the glass fibre composites have good short-term moisture resistance, their stability under long-term exposure is a source of great concern. The expression of these concerns is mainly due to the lack of confidence in predicting the changes caused by the environmental exposure. Changes caused by the environment can be explained and attributed to physically plausible mechanisms that are usually revealed after the long-term usage.

In particular, the effects of aqueous immersion on composites, although studied extensively [1–3], are still a subject of immense practical interest that cannot be classified as resolved. The two main macroscopic effects that are caused by water absorption are the weight increase and the changes in mechanical properties. Under some circumstances these changes are partially or completely reversible. The reversibility of the effects, for a given composite system, depends primarily upon the temperature of water immersion and secondly on the length of time of the immersion. While plasticisation and swelling are reversible processes for example, hydrolysis and microcracking cause irreversible changes in the composite [1]. Immersion in water may also result in significant debonding of the fibre/matrix interface, which allows water to

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penetrate the material via capillary action. Water ingression causes weight gain; however, weight loss can also occur due to leaching of constituents of the fibres and matrix into the water [4]. All these changes that influence the material due to environmental exposure affect as a consequence the mechanical properties.

For the determination of the residual properties of composites, the typical approach for assessment of any changes, due to water immersion of the material itself, is by extensive experimentation. Due to slow rates of change associated with typical low service temperatures, accelerating factors are applied to reduce the observation time of the experiments to practical levels. An increase in the test temperature is the most used accelerating factor. If the degradation mechanism does not change, new degradation mechanisms are not triggered and the rate of degradation changes as a function of temperature, then an Arrhenius type relation can be used to "predict" the behaviour within a range of service temperatures. If the exposure temperature is too high, usually meaning at or above the glass transition temperature T_g of the matrix, degradation mechanisms, not observed at lower temperatures, could be activated. In such cases, the overall process becomes atypical to ambient temperature conditioning and the results obtained can serve as worst-case scenario at given length of time.

The overall aim of the entire project, of which this work is a part, is to enable prediction of the durability of composites in hygrothermal environments. In particular, this paper presents the effects of long-term water immersion ageing at elevated temperatures on the glass fibre reinforced polyester composite laminates and possible explanations of the phenomena that occur are given. It is believed that the complexity of these phenomena make necessary the publication of the experimental data for broader discussion prior to challenging any predictions for the long-term exposure. Results on water absorption after immersion of undamaged and impact damaged specimens in water for periods of up to two and a half years (~30 months) are reported. Three material systems are investigated and three impact energy levels are used in order to assess the effect of delamination on moisture absorption. The changes in the thermo-mechanical properties after water immersion are examined using the dynamic mechanical thermal analysis (DMTA) technique and the results are discussed.

Experimental procedures

Materials

Three E-glass/polyester panels were manufactured by the vacuum assisted resin transfer moulding (VARTM) technique, each measuring 1300 × 1000 mm^2. For all three panels, the isopthalic polyester resin Crystic 489 PA (Scott Bader) was used. One balanced plain woven glass, for material marked A, and two non-crimped fabric (NCF) types for materials type B and D were used for the plates. The lay-up of the three material types along with details of the fabric types is shown in Table 1.

The glass fibre volume fraction of the materials under study has been determined by the resin burn-off technique, as per ASTM D2583 shown in Table 2. For the plain woven mat, of material type A, good compaction was obtained that consequently allowed high volume fraction to be achieved. The stacking sequence of material type D with the three different directions of fibre tows did not allow for close packing so lower volume fraction was achieved compared to material type A.

In addition, neat resin samples have been manufactured in a mould in order to create 3-mm-thick plates for the water absorption experiments. In total, three specimens from neat resin and three specimens from each composite plate type were cut at 4 × 45 mm^2 for the water absorption tests. All the specimens have been post-cured for 3 h at 80 °C. The edges of the specimens have been covered with Hysol XEA 9359.3 QT epoxy adhesive to minimise diffusion through the specimen cut sides.

Water immersion

Thermostatically controlled water baths manufactured by Grant were used to perform the water immersion experiments in deionised water. The baths were stainless steel lined and had stainless steel lids. The temperature controller was capable of ±0.1 °C. The neat resin specimens were positioned in 1 L sealed glass containers spaced so that the specimens did not touch each other and they were

Table 1 The laminate architecture designated according to the fabric reinforcement

Material name	Fabric type	Lay-up
A	Chomarat 600T	$(0°, 90°)_6$
B	Cotech EBX-602	$(\pm45°)_6$
D	Cotech EBX-602 Cotech ETLX-1169	$((\pm45°, 0°), (\pm45°)_2, (0°, \pm45°))$

Table 2 The density, volume fraction and void content results for all laminate materials

Material type	ρ_c	V_f (%)	V_v (%)	Average thickness
A	1.85	49.57	0.27	3.00
B	1.73	42.07	0.32	3.50
D	1.70	38.52	0.33	3.88

immersed in the baths. The composite plates were immersed in the water using stainless steel racks at (a) low temperature (43 °C), which would be well below the T_g of the resin (given by the manufacturer as 77 °C) and accepted as continuous use temperature for a composite made from this resin; (b) medium temperature (65 °C), close but below the T_g of the resin where short-term use of a composite would not be detrimental, but where on the other hand the exposure acceleration would be significant; and (c) a realistically high temperature (93 °C) for specimens to be immersed in water above the T_g of the resin, where the water degradation accelerating effect would be nearly at its maximum, for water in liquid form at ambient pressure. Specimens immersed at 43 °C are designated with ‘L’, at 65 °C with ‘M’ and at 93 °C with ‘H’, respectively thereon. Also, plates containing impact damage, as described in the section “Impact damage”, were immersed in the water baths in order to assess the effect of an induced delamination on the water absorption under different impact levels.

Water uptake measurements

An Ohaus Explorer, temperature compensating digital scales with accuracy of ±0.0001 g was used for weight uptake measurements. Specimens were taken out of the baths and their surface was dried of the excess water with paper towels before placing on the weighing pan. Specimens taken out from the baths were weighed as fast as possible, because the scales reading did not reach a stable level as there was continuous evaporation of the water. The weight change was calculated as:

$$M = 100\frac{(M_w - M_d)}{M_d} \qquad (1)$$

where M is the percent weight change, M_w is the wet specimen weight after time t, and M_d is the initial dry specimen weight.

Impact damage

Impact damage was introduced for some of the plates before water immersion. A range of three levels of impact energy have been used, namely 2.5, 5 and 10 J. These impact levels are designated with roman numerals I, II and III, respectively. Four specimens were impacted at each impact energy level. The minimum impact energy level was selected so that the force registered would be above the Delamination Threshold Load [5] for all three types of material available. This was expected to be a cause of subsequent reduction in the in-plane mechanical properties. The maximum impact energy level was chosen so as not to cause penetration damage.

The specimens were pneumatically clamped with a pressure of 7 bars between a pair of steel plates. These plates had a 40-mm-diameter window on their centres and the striker was of hemispherical shape with a 10-mm radius. Thickness variations between different specimens of the same material types were not compensated with different height or weight adjustments of the striker. The drop height and therefore the terminal velocity were kept constant at 2.83 m/s and weights were added to the striker sleigh to increase the initial impact energy.

Dynamic mechanical thermal analysis

DMTA tests were performed for some specimens to assess any thermo-mechanical changes caused by the environmental exposure to the laminates. A Polymer Laboratories DMTA instrument was used for this work. The DMTA instrument utilizes the three-point bending test fixture. A sinusoidal stress is applied with frequency ω. The stress can be represented as:

$$\sigma(t) = \sigma_{\max}\sin(\omega t + \delta) \qquad (2)$$

where $\sigma_{\max}$ is the maximum applied stress, and the stress proceeds the strain ε by a phase angle δ. Stress and strain are related as:

$$\sigma(t) = E^*(\omega)\cdot\varepsilon(t) \qquad (3)$$

where $E^*(\omega)$ is the dynamic modulus.

$$E^*(\omega) = E'(\omega) + iE''(\omega) \qquad (4)$$

For a viscoelastic polymer, E' characterizes the ability of the polymer to store energy in an elastic manner and E'' the tendency of the material to dissipate energy in a viscous manner. The phase angle is calculated as the ratio of:

$$\tan\delta = \frac{E''}{E'} \qquad (5)$$

The force exerted by the three-point bending clamps on the specimen is crucial and needs to be consistent [6]. To increase consistency, the bolts holding the clamps on the samples were done using a torque screwdriver set at 20 Nm.

Specimens were cut using a water-cooled diamond-tipped microtome. The dimensions of the cut specimens were such that the width of the specimen was twice the thickness of the specimen. The dimensions were measured with a micrometer with resolution of 0.01 mm and a digital caliper with resolution of 0.01 mm. Specimens type D were only used for these tests. Samples were cut horizontally from specimen plates such that the 0° fibres were in the short width direction. Since no long fibres were along the length direction, results more relevant to the state of the resin and the interface were obtained.

Results

Water absorption

In Fig. 1a, the results from water uptake measurements of all material types at 43 °C are presented. There is relatively large scatter in the measurements taken. This can mainly be attributed to the water droplets left on the plates during the weighing that could artificially create a fluctuation in the measurements. The Fickian diffusion process exhibited typically at such temperature by other material systems is not totally followed here, and the explanation can be possibly given by a relaxation process taking place which alters the saturation boundary [2]. Assumptions cannot be made as to whether saturation has been reached, at least within the study time of 30 months.

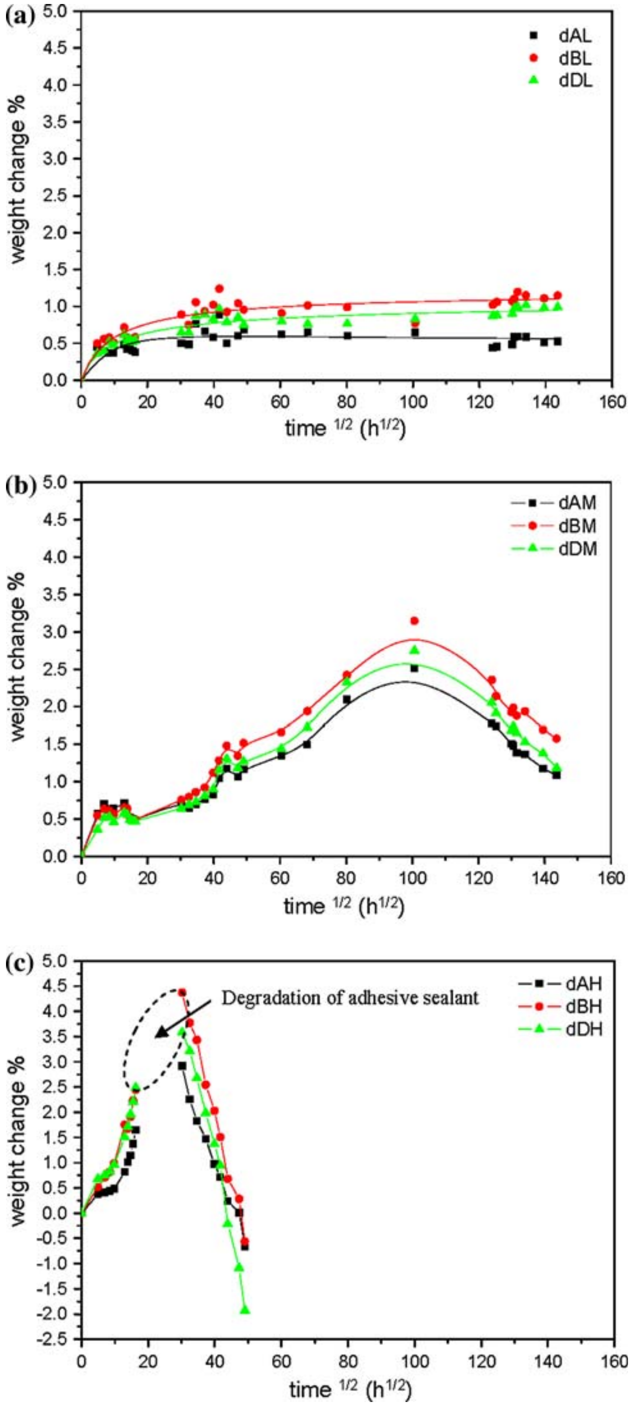


Fig. 1 The weight change versus time results for low (43 °C), medium (65 °C) and high (93 °C) water immersion temperatures designated with L, M, and H, respectively, for material types A, B, and D

Increasing the temperature of water immersion caused an increase of the level of peak water absorption as shown in Fig. 1b and c from the results obtained at 65 and 93 °C, respectively. A reduction in weight for all specimen types is observed after about $t = 100\ \mathrm{h}^{1/2}$ (~14 months) at 65 °C and after $t = 30\ \mathrm{h}^{1/2}$ (~1 month) at 93 °C, respectively. The adhesive sealant at 65 °C for all specimens was intact, although visible changes from its original vivid green colour to dark green were evident. For both 65 and 93 °C, no saturation plateau was found; instead a steady weight reduction was recorded most probably due to the dissolution of the polymer matrix. Such behaviour is also reported elsewhere [7].

However, for specimens kept at the 93 °C bath, the experiment was stopped early, at $t = 17\ \mathrm{h}^{1/2}$ (~12 days), as the epoxy adhesive degraded and started flaking-off, thus not allowing for direct comparison with other cases to take place. The relative level of contribution for the water uptake and weight loss of the adhesive is therefore unclear. The part of the curve after the brake in Fig. 1c refers to measurements taken after the remaining of the epoxy adhesive was totally removed manually. The fact that measurements continued below the 0% level prove that some of the original material was being dissolved. The peak of weight change appears to be at between $t = 20\ \mathrm{h}^{1/2}$ (~16 days) and $t = 30\ \mathrm{h}^{1/2}$ (~1 month), although the absolute value remains unknown at present.

To further investigate the problems faced with the use of the epoxy sealant for water absorption experiments at 93 °C, some additional tests were performed. A parallel experiment was conducted at 93 °C to assess the behaviour of neat resin plates and plates with same dimension as before but with no sealing at the edges involved, for a short period of time. As shown in Fig. 2, the behaviour in terms of water uptake clearly changes at about $t = 12\ \mathrm{h}^{1/2}$ (~6 days). The period between $t = 5\ \mathrm{h}^{1/2}$ and $t = 12\ \mathrm{h}^{1/2}$ can be seen as a first saturation limit, signifying a multistage diffusion process. A number of visible to the naked eye cracks and blisters started forming on the neat resin plates from the third day. The samples gradually started becoming less translucent and the density of cracks increased. The general trend that neat resin has higher diffusion rate from reinforced plates is affirmed here.

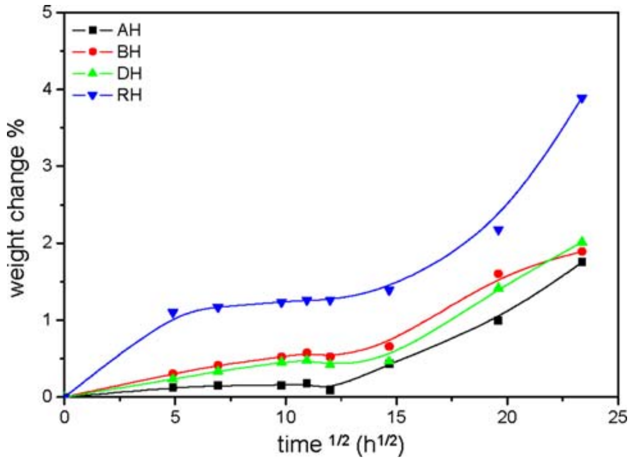


Fig. 2 Water uptake results at high temperature H (93 °C) for small specimens of materials A, B, and D with the edges not sealed. The R designates the neat resin specimens

Consequently, the glass fibres reduce the quantity of water absorbing material and thus the water absorption of the composite materials is less compared to that of the polymer matrix.

As in the case of specimens immersed in water at 43 °C, the weight change plots for all materials under study at the higher temperatures indicate no similarity to the classical Fickian absorption behaviour. In particular, as seen from Figs. 1b, c and 2, uptake was dominated initially by water diffusion through the matrix of the GFRP. After an initial slow increase, a steeper slope increase in water gain is also seen, indicating that a multistage diffusion takes place. This divergence suggests uptake, possibly related to the voids/microporosity as well as interfaces. It has been proposed that osmosis at the interface takes place by alkali metal oxides leaching from E-glass in the presence of moisture to form concentrated salt solutions [8]. This drives supplementary diffusion of water toward the interface. Debonding resulting from osmotic pressure from this process would further assist water transport along interfaces. Such osmotically enhanced uptake may have occurred at $t = 50\ \mathrm{h}^{1/2}$ to $t = 75\ \mathrm{h}^{1/2}$ (~3–8 months) at 65 °C in the uptake history and $t = 13\ \mathrm{h}^{1/2}$ (~1 week) at 93 °C, consistent with the behaviour seen in Figs. 1 and 2. Similar situations of water diffusion have been modelled either by the Langmuir type model [9] or with moving boundaries type model [2, 10]. Experimentally, this type of two-stage initial diffusion behaviour followed by weight reduction has also been presented and described in other studies [10, 11].

The material most resistant to water absorption was the woven glass reinforced type A, which was also found to have the highest reinforcement volume fraction V_f. The two NCF reinforced material types B and D have shown higher levels of water absorption which can be linked to their lower V_f compared to material type A. Well-impregnated composites have theoretically lower water absorption than poorly impregnated composites, i.e. higher microporosity/voids that could increase water absorption. Absorption enhancement due to void content has been described elsewhere for a range of glass/epoxy composites exposed to 100% humidity where a direct linear proportionality was reported between void level and the rate of uptake [12]. The voids may act as a moisture sink through osmosis promoted by soluble salts (remaining from the polyester resin synthesis) which continue drawing in water after the polymer is semi-saturated. These voids usually result from water in the liquid resin as supplied and that generated during the condensation polymerisation.

The water immersion was seen to heavily damage all the laminated plates irrespective of material type, especially at 65 and 93 °C. Initially, the weight gain was accompanied by colour changing and reduced translucency of the specimens judged from visual inspection. The dry composite was turquoise while for 2–6 months of conditioning at 65 °C and 0.5 months for 93 °C this turned to yellow. After month 12 for 65 °C and 4 months all the materials became dark yellow followed by a decrease in weight due to material loss. Matrix cracks and interface damage between the matrix and the fibres are shown in Fig. 3. Fibre tows and stitching in the surface plies became exposed on the front face from pitting and erosion. Evidently, the severity of these mechanisms as the time progressed for the 65 and 93 °C suggests that polymer hydrolysis had occurred.

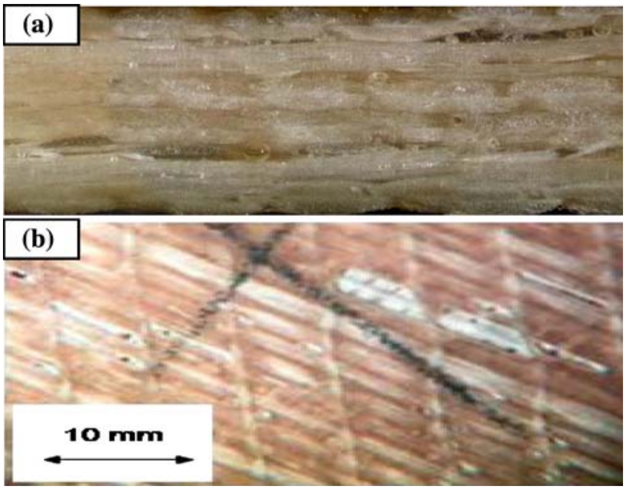


Fig. 3 Degradation of material type D after immersion in water at 65 °C for 24 months revealing **a** side view with extensive cracks and fibre/matrix interfacial damage, and **b** front face view with surface matrix degradation and exposure of first ply fibres and stitching

Effect of impact damage on water absorption

A series of water immersion tests were performed to evaluate the effect of existing impact damage upon the rate and the peak level of water uptake. Specimens with dimensions of 55 × 89 mm^2 were used whose edges were not sealed. Along with these specimens some resin plates of the same dimensions were manufactured and tested for comparison. The sets of specimens were impacted at 2.5, 5 and 10 J before immersion. Based on the assumption that the relative ranking in terms of water uptake would agree with the results obtained from the smaller specimens, presented in the previous section, not all materials in all temperatures were tested.

Damage caused by low-velocity impact was in the form of delaminations, matrix cracks, fibre debonding and breakage. This was thought that could lead to higher absorption rate and possibly higher saturation level, as more paths were available for diffusion. The damage size for the dry impacted specimens and for impacted specimens after prolonged water immersion was recorded using water-coupled ultrasonic testing. As shown in Fig. 4, the immersion of glass reinforced composite material in water at the elevated temperatures resulted in partial or complete loss of translucency. The impact damage played a significant role as the cracks provide a path for further diffusion apart from water diffusion through the matrix and penetration through capillary action. It is believed that the larger the area of damage, the more water was accumulated in the specimens. The effect relevant to water-coupled ultrasonic system was water penetration inside the specimens that acted as coupling medium reducing the signal loss that would normally be associated with the damaged material [13]. The end result was reduced efficiency of the water coupled C-scan and practically indistinguishable delaminations areas as illustrated in Fig. 5.

Figure 6a shows the results obtained at 43 °C. The resin specimens clearly reach a higher saturation level within the test time. The impact damage seems to have an effect on the saturation level as well at this temperature as specimens impacted at 5 and 10 J group separately from the specimens with no damage or impact at 2.5 J. The small size of damage caused by the 2.5 J impact does not allow for large discrepancies from the undamaged specimen. At 65 °C, Fig. 6b, the role of damage caused by impact seems to be reduced, with only the heavily damaged BIIIM specimens showing trends of higher absorption compared to the rest. This could signify that the swelling caused by water absorption is fast enough to act as an effective crack closure method. A similar case has also been reported elsewhere [14]. For the neat resin specimens the curve is different. At this temperature the resin is susceptible to microcracking, as shown in Fig. 7. Small cracks have been observed to form near the surface and inside the material. The density of cracks increased with time, reaching a level where light transmission was not effective for observation. The rate of formation of these cracks could allow for the explanation of both the sudden increase in water uptake, when compared to reinforced specimens, and the abrupt weight loss. It also seems that an incubation time exists between the formation and the activation of the cracks.

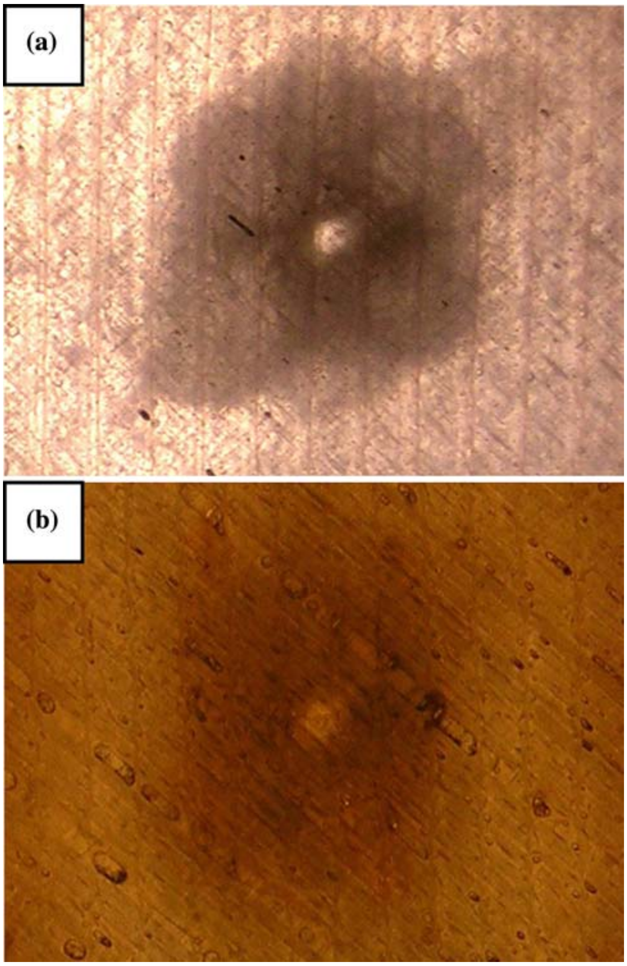
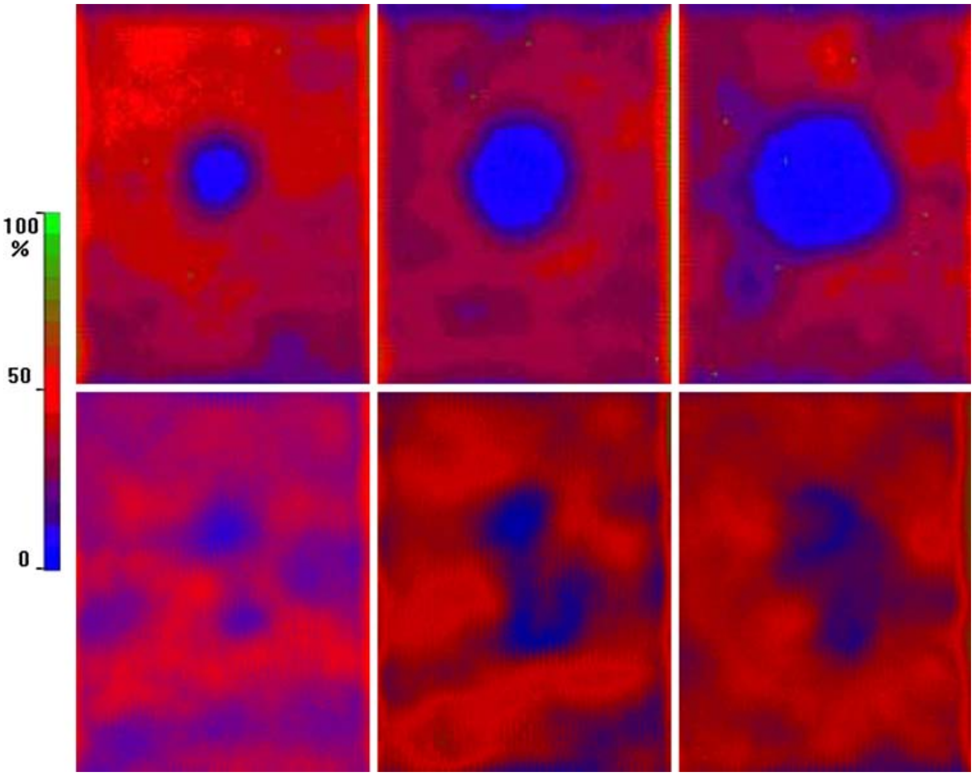


Fig. 4 Close-up photos taken with backlighting showing **a** a specimen not exposed to water with impact damage of 5 J, **b** a specimen immersed in water for 1 week at 93 °C with impact damage 5 J having colour change and loss of translucency

At 93 °C, the results shown in Fig. 6c reveal that the impact damaged specimens do not differentiate considerably in terms of water uptake rate or maximum level. This can again most probably be attributed to the swelling being very fast due to the high temperature. Only the heavily damaged, with 10 J, specimens show slightly higher water uptake than the rest of the specimens and are the first to start losing weight. These also have the highest rate of weight loss. In this set of specimens a maximum point is reached, whereas for the test of small coupons, presented in

Fig. 5 Comparison of C-scans using the water-coupled ultrasonic testing equipment. The top row shows dry specimens impacted with 2.5, 5, and 10 J and the bottom row shows water immersed specimens for 24 months impacted with 2.5, 5, and 10 J prior immersion



the section "Water absorption", this was not possible. This peak though cannot be considered as a saturation level. It is rather the point in time where the hydrolysis mechanism becomes dominant and faster weight loss occurs compared to the water uptake. This trend of abrupt behaviour change confirms partially the results at the same temperature presented above for the smaller specimens. The negative weight change, especially in such a short term, about $t = 25\ \mathrm{h}^{1/2}$ ($\sim$26 days), points out the extremely high rate of degradation at this temperature. If the observed peak at 65 °C is considered analogous to the peak observed at 93 °C, the time required for the former was found to be after $t = 100\ \mathrm{h}^{1/2}$ ($\sim$14 months) of water immersion. At 43 °C, no such peak point was found within the experimental observation limits. It remains uncertain if such a peak would be found at this temperature.

DMTA results

Results obtained from samples after water immersion for various time lengths are presented later. Tests were performed at three frequencies at 1, 10 and 100 Hz in order to examine the effect of strain rate on the specimens as well. The tests at the three frequencies work sequentially and so it is not possible to obtain at exactly the same temperature reading for all frequencies. The test method applied is that of a thermal scan. The temperature cycle applied was set between 35 and 140 °C with a rate of 0.5 °C per minute. The upper temperature was chosen as not to allow for burning or charring of the resin in the test fixture.

The changes of the value of peak tan δ, shown with vertical lines, from which the glass transition temperature (T_g) is obtained, with respect to different water immersion times and immersion temperatures are presented in Fig. 8a and b. Compared to the curve of the reference sample DREF, long-term immersion in water at 65 and 93 °C brings an increase of the peak value of tan δ of the samples. The value of T_g is found as the peak of the curve of tan δ with respect to temperature. The T_g of the specimens increases with increasing exposure to the medium and high temperatures. The exception is the sample exposed for 2 months at 65 °C for which the T_g is slightly lower from the reference sample but the peak value of tan δ is increased. The sample that has been immersed at 43 °C shows a reduction of the T_g. This behaviour can be justified from plasticization of the matrix due to the water uptake but this is not counter-balanced by any serious post-curing effect due to the low water immersion temperature.

The effects of the different test frequencies on the measured values of peak tan δ and T_g are shown in Figs. 9 and 10, respectively. The value of the peak tan δ seems to linearly increase with time of water immersion. The higher the test frequency, the higher levels of peak tan δ are recorded. A shift of the T_g towards higher value as the

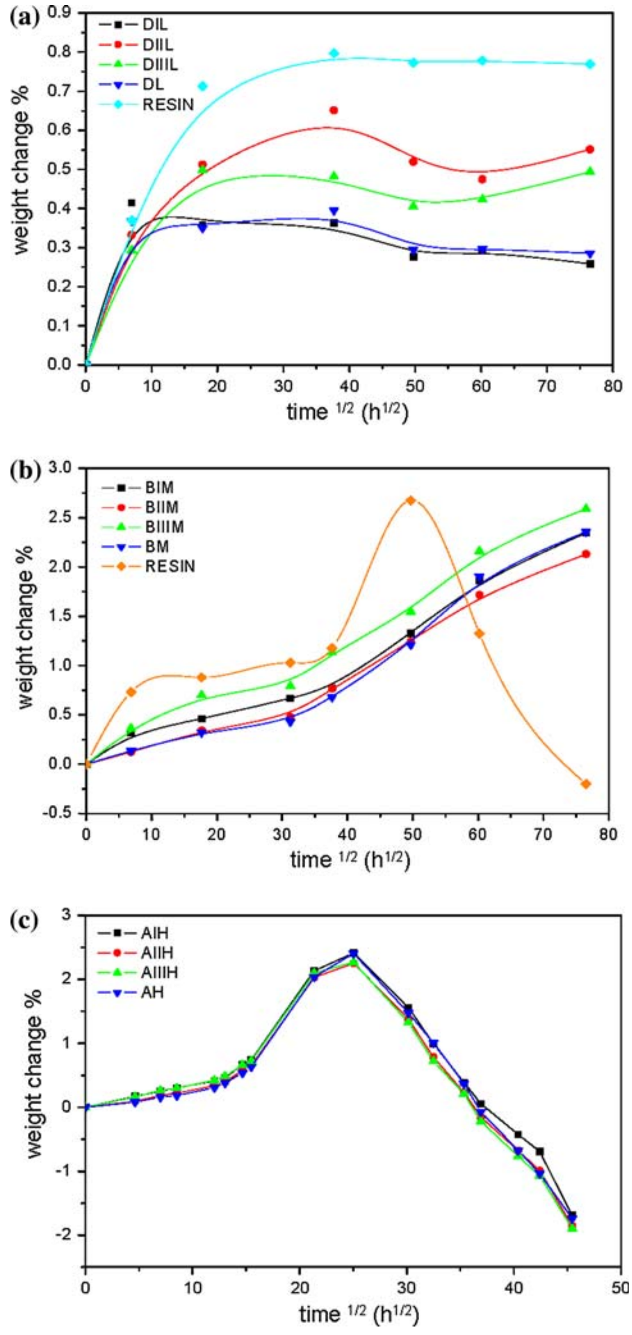


Fig. 6 Weight change after immersion in water for materials A, B, and D at **a** 43 °C (L), **b** 65 °C (M) and **c** 93 °C (H), respectively. The roman numerals I, II and III refer to impact prior to immersion at 2.5, 5 and 10 J, respectively

frequency of testing increases is also notable. Given the viscoelastic nature of polymer composites this behaviour is normal.

The change in the storage modulus E' maxima at different test frequencies with respect to time of water immersion at 65 °C is presented in Fig. 11. An exponential decrease of the storage modulus E' with respect to the

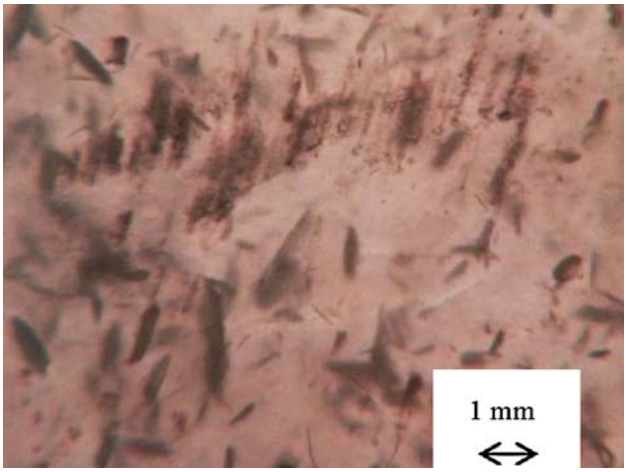


Fig. 7 Neat resin plate microcracking after immersion at 65 °C

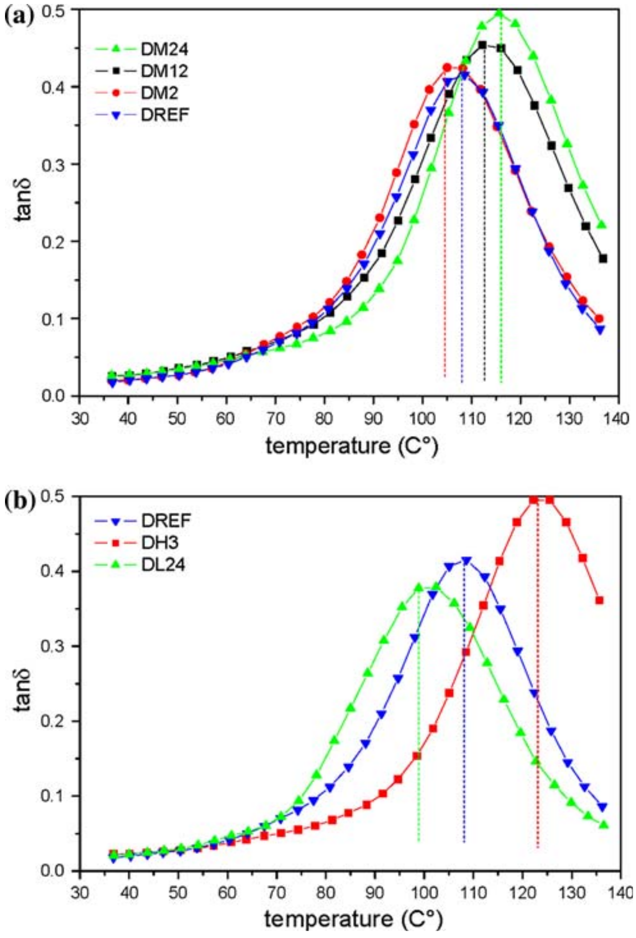


Fig. 8 Results from DMTA at 10 Hz for material type D. REF is sample with no immersion in water. The *vertical lines* show the peak of tan δ where the T_g value is obtained from. Results in **a** are for specimens immersed at 65 °C (M). Results in **b** are for specimens at 43 °C (L) and 93 °C (H). The numbers next to the samples refer to immersion duration in months

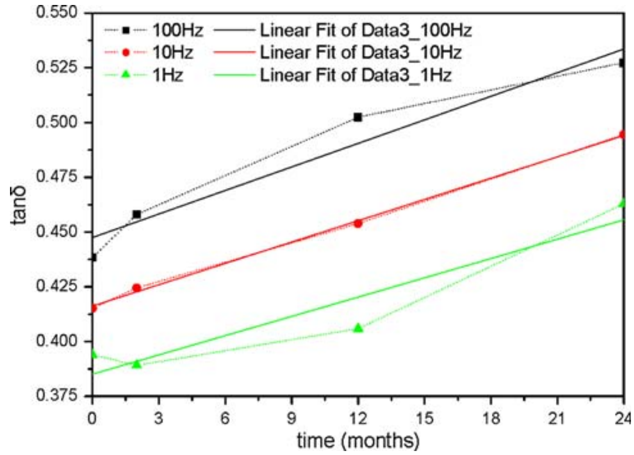


Fig. 9 Frequency dependency of peak tan δ with respect to time for material type D immersed in water at 65 °C

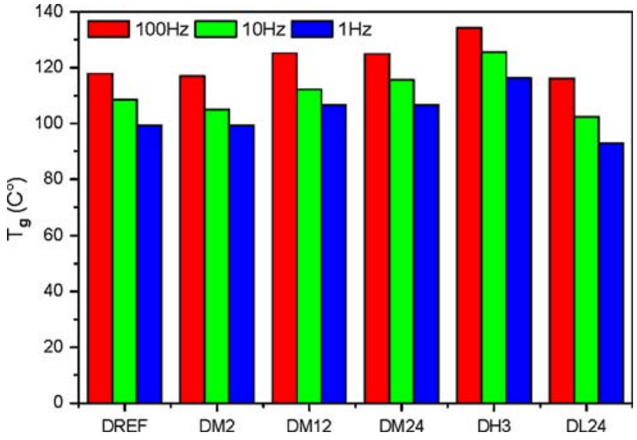


Fig. 10 Test frequency dependency of T_g of specimens from material type D after water immersion at 43 °C (L), 65 °C (M) and 93 °C (H). The numbers next to materials type D signify length of immersion in months and REF designates the reference dry specimen

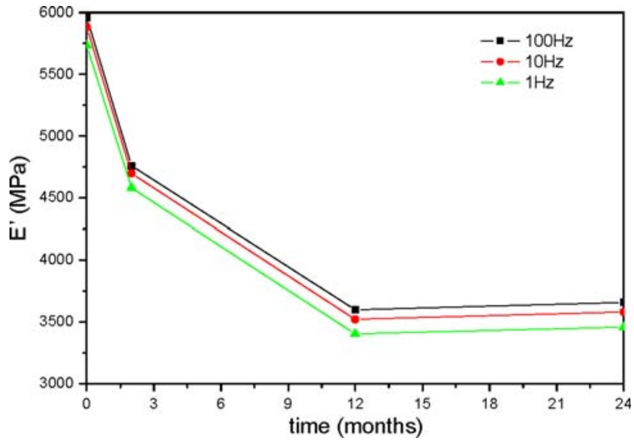


Fig. 11 Variation of E' with respect to time of immersion for specimens of material type D immersed at 65 °C

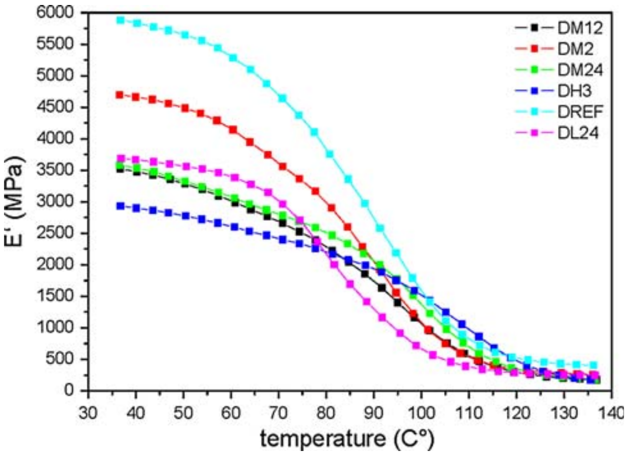


Fig. 12 Storage modulus results from DMTA at 10 Hz for specimens of material type D. REF is sample with no immersion in water. L, M and H refer to temperature of exposure 43, 65 and 93 °C, respectively. The numbers next to the material type D refer to immersion duration in months

length of immersion at 65 °C, where most experiments were performed, is observed. A minimum plateau is also reached at a level of about 0.6 of that of the initial dry reference material. An increase of the absolute values of E' with increasing test frequency is also seen. This trend is in accordance with what was presented previously for the change of the T_g value. The viscoelastic nature of the composite material is sensitive to strain rate effects and an increase in the test frequency leads to an apparent corresponding increase of the value of the storage modulus. The change in storage modulus E', at a constant frequency of 10 Hz, with respect to temperature and length of immersion is presented in Fig. 12. It is seen that the effect of any time of immersion at any temperature tested resulted in a decrease of the value of E'. The starting value of E' at 6 GPa would initially seem low, but as mentioned previously, it becomes reasonable when taking into consideration that there are no fibres running along the length of the specimens which coincides with the 90° direction on the D-type specimens. For the sample exposed to high temperature for 3 months, the modulus is decreased to just half that of the reference, at 35 °C test temperature.

Discussion

The results presented in this study have confirmed that water diffusion in glass reinforced polymers is a temperature controlled process. Both the initial rate of absorption and the apparent maximum level of water uptake were found to be temperature dependant. Common to all accelerated degradation experiments, increasing the test temperature yielded an accepted result in a sense that the degradation rate was found to increase with increasing water temperature. The word degradation at this stage is not directly linked with a marked reduction of the mechanical properties of the given materials but rather with a physical and chemical state deterioration as manifested by specimen weight loss, colour change, surface blistering and micro-cracking.

The common problem to all accelerated degradation experiments is the possibility of activation of side mechanisms not normally present under normal operating conditions. These can cause significant deviation from normally expected behaviour. It has been shown numerous times that glass fibre reinforced polymers immersed in water at ambient temperature should experience a behaviour that can be fitted with a Fickian-type diffusion model [2]. When the immersion temperature is near or above the T_g, significant changes can be expected from the normal behaviour. These changes can be manifested in the form of a multistage diffusion curve, such as in the case of specimens at 65 °C, or sudden weight loss as in the case at 93 °C. Although reasons for these types of behaviour are understood and mechanisms such as hydrolysis, blistering and matrix micro-cracking have been linked as the main causes, there are yet no firm ways to predict at which point of time and to what extent, if at all, they will be activated. This is the main reason why extensive experimental datasets, such as the one produced by this project, are needed.

At the low water immersion temperature of 43 °C data scatter is visible. Since the changes in weight after the initial steady increase are very small, the experimental error involved becomes comparable to magnitude of the difference measured. This error is introduced mainly because of the testing procedure. Specimens as discussed earlier were dried using only paper towels. Variation of results was possible due to non-complete sample surface drying. This is further strengthened by the results presented in Fig. 6a for the resin plates. These specimens are perfectly flat and square so the data recorded show markedly less variation since drying these specimens with paper towels is more effective.

The results obtained by using the DMTA technique yielded information about the complex interaction of processes happening during the water immersion. At 43 °C even in the long term and in the short term for specimens immersed at 65 °C, the T_g drops. This drop can be attributed to matrix plasticization. At 93 °C and for long-term immersion at 65 °C, the T_g increased. This can be attributed primarily to post-curing effects but also to another reason. At the initial stages of immersion, small fragments acting as matrix plasticizers were leached out causing in the long term the main chains to become less mobile. In addition, within the set of specimens tested using DMTA, no increase was found in terms of E' in the through the thickness direction but rather a monotonic reduction which was found to be time and temperature dependant. After 24 months of immersion, the stiffness reduction of specimens immersed at 65 °C was very nearly matched by those immersed at 43 °C.

Another aspect that has been studied here was the effect of pre-existing impact damage on water absorption. It has been found that damage inflicted on composites plates by low-velocity impact before water immersion does not seem to cause significant differences in terms of water absorption. A feasible explanation that has also been reported elsewhere [14] could be that upon immersion in water the matrix is swelling and does not allow more water to be absorbed through the cracks. When the damage is extensive such as in the case of impact with 10 J, only a very little difference is observed against undamaged specimens during immersion. At 93 °C, specimens impacted with 10 J seem to have steeper weight reduction curve compared to the other specimens. This could signify that the effect of pre-existing impact damage only becomes more pronounced later when the material reaches the stage where decomposition starts.

Conclusion

At the set of temperatures investigated, the behavior of the specimens regarding water absorption varied markedly. The laminate with the woven fabric showed the lowest initial rate and absorption level at all temperatures tested. This was related to the lower void content and the highest glass volume fraction compared with the other material systems with the NCF reinforcement. The water immersion did not cause any remarkable differences in terms of water absorption for the impact damaged specimen due to swelling caused by water absorption acting as an effective crack closure method. Only those specimens subjected to higher impact energy of 10 J have shown slightly higher values.

Within the limits of the study time, for all material types a steady weight increase was initially observed at 43 °C which was followed by a much slower increase after prolonged exposure. A drop of the T_g compared to the reference materials was evident as studied using DMTA. At 65 °C, the situation was more complicated for all material types as a multistage diffusion was observed. Initially, a fast water uptake was followed by a first plateau only to have a second stage where diffusion with higher rate was observed. A maximum was reached and then weight loss followed from material dissolution. Continuous post-cure effects were important at this temperature as the T_g of the specimens tested increased with time of immersion. Immersion at 93 °C was seen to cause the most severe degradation in a very short time. The degradation caused by hydrolysis becomes dominant very fast causing the early weight reduction on the specimens. Post-cure effects were quite significant as the T_g of specimens was the highest value measured in the shortest time of only 3 months.

The viscoelastic nature of the composite material was sensitive to strain rate effects and an increase in the test frequency led to an apparent corresponding increase of the value of the storage modulus. The effect of any time of immersion at any temperature tested resulted in a decrease of the value of the storage modulus.

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