NON-LINEAR RESPONSE OF ENVIRONMENTALLY AGED POLYMER COMPOSITES: A PHYSICOCHEMICAL AND MECHANICAL STUDY

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Abstract
In this paper, the anomalous behaviour of polymer composites subjected to hygrothermal aging is discussed in reference to the results of a characterization study on polyester matrix fibre reinforced polymer (FRP) composites. Hygrothermal aging, the combination of moisture and elevated temperatures, has been proven to affect the durability of FRPs. Significant structural degradation can be expected as a consequence of hygrothermal aging, however it has been shown that some material properties exhibit a strong non-linear and even beneficial behaviour as a consequence of hygrothermal exposure, indicating the presence of different competing mechanisms. To study these different mechanisms which control the structural performance of an exposed material, FRP samples were exposed to short-term hygrothermal aging for 112 days. Moisture absorption characteristics and mechanical performance were assessed at prescribed time frames throughout aging. With a view to examining any induced intrinsic and surface characteristics, Computed Tomography scan (CT-scan) and Scanning Electron Microscopy (SEM) were also employed. Lastly, impedance spectroscopy was used as an innovative tool to efficiently follow moisture absorption during aging.

1. Introduction

The construction industry has been taking advantage of Fiber Reinforced Polymer (FRPs) composites since the 1960s. FRPs are being increasingly employed as structural and non-structural elements in the civil engineering sector. FRPs are being used in a wide range of applications starting from window and door frames to FRP bridges. FRPs are attractive engineering materials due to their increased specific properties and their relatively low cost. This combination renders FRPs key structural materials when pertaining to resilient, adaptable and lightweight infrastructure with low CO_2 impact [1]. Although composite materials are increasingly adopted by construction companies, their acceptance as primary and secondary structural elements is still hampered by their non-linear structural performance in time and their low moisture-tolerance. There is a lack of knowledge of long-term durability which stems from the non-linear response to environmental exposure (moisture ingress, thermal cycling, etc.) and makes performance prediction a real challenge. The latter effectively leads to reduced reliability when it comes to the design of a structure. The durability of polymer composites is highly dependent on the severity of the service environment and the time of exposure. Moisture ingress induces the most severe deterioration of durability amongst others (i.e. thermal cycles, UV, etc.). The degradation rate increases when very high (>40°C) or very low (<0°C) service temperatures occur paving the way for the reduction of the '*designed*' durability and the

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'*expected*' lifetime. Moisture ingress leads to (i) plasticization (lower stiffness) hydrolysis, chain scission and overall decomposition of the polymer matrix, (ii) etching, leaching and embrittlement (lower strength) of the reinforcement as well as (iii) swelling and micro-cracking of the bulk composite. Those result to lower stiffness and strength, lower load bearing capacity, lower ductility etc. [2, 3].

This paper presents a complete characterization study on the response of FRPs to hygrothermal (or hot/wet) aging. The work is part of the EPSRC funded Duracomp project (EP/K026925/1). The analysis of the long-term properties of the FRPs in a reasonable time-frame was achieved by exposing specimens in short-term hot/wet aging for 112 days. The induced degradation was assessed by a complementary study which involved moisture uptake tests, mechanical testing, inherent and micrographic examinations such as Computed Tomography (CT-scanning) and Scanning Electron Microscopy (SEM). Impedance spectroscopy was used as an innovative technique to effciently monitor hygrothermal aging. This work is expected to strengthen the knowledge and overall understanding of the (non-linear) behaviour of FRPs when exposed to extreme service conditions.

The work was conducted on a commercially available pultruded glass FRP (GFRP) flat sheet (FS040.101.096A, Series 1500 (I)) supplied by Creative Pultrusions Inc. (http://www.creativepultrusions.com/). It consists of a 5-layer polyester matrix laminate reinforced by E-glass fibres rendering a nominal thickness of 6.4mm. Fig.1 displays the structure of the material consisting of three Continuous Strand Mat layers (CSM) with a 33.3% volume fraction of fibres and two UniDirectional (UD) layers with an average 54.5% volume fraction of fibres. The outer surfaces of the flat sheet are covered by an additional protecting thin and non-structural polyester veil, which has the dual functions of retarding moisture ingress and protecting the FRP material from UV radiation.

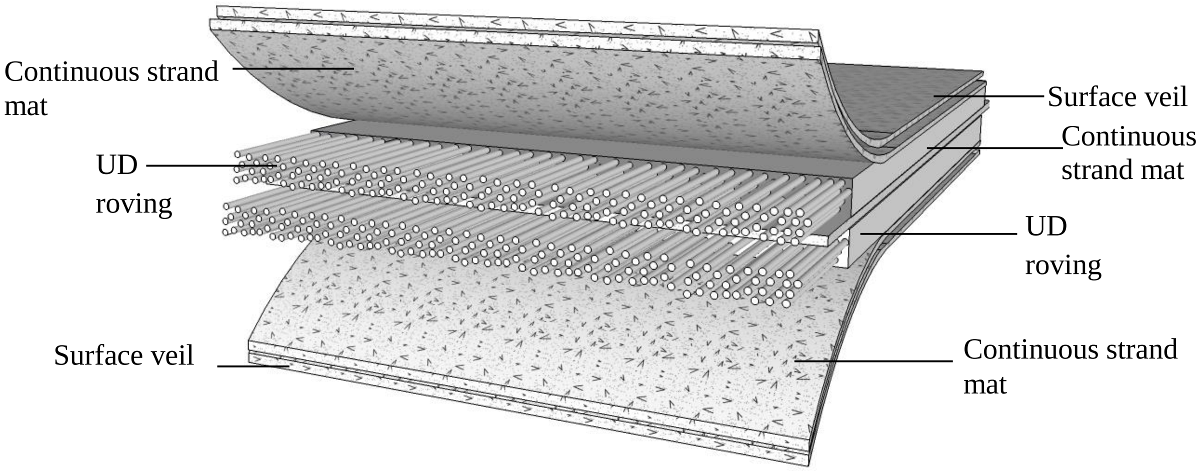

Figure 1. Construction of the five layered pultruded GFRP flat sheet material.

2. Experimental

2.1 Testing methods

2.1.1 Moisture absorption

For each temperature moisture uptake measurements were conducted over a period of 112 days. Square specimens of 40x40mm^2, 60x60mm^2, 80x80mm^2 and 200x200mm^2 were soaked in water and

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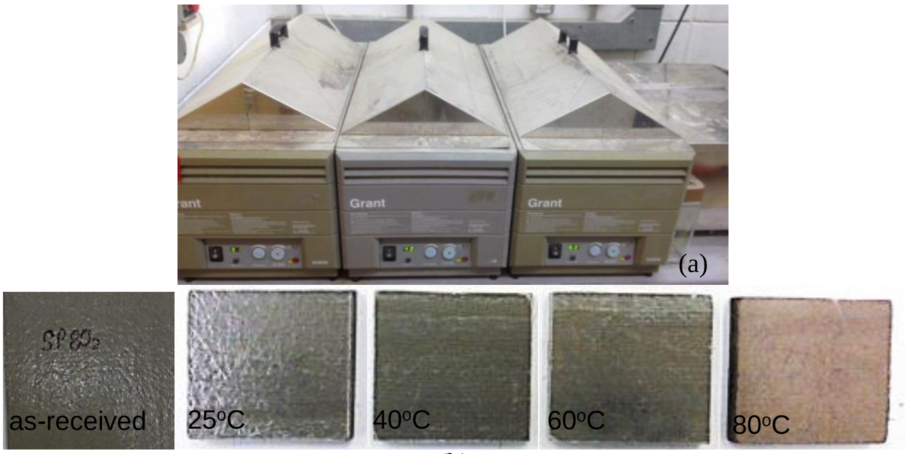
their weight gain was frequently recorded according to ASTM D 5229. The relative moisture change (*M(%)*) for a sample was determined using Equ. 1:

$$M(\%) = \frac{M_t - M_0}{M_0} \times 100\% \quad (1)$$

where M_t is the mass at time t and M_o the dry initial mass. Prior to immersion in the different water tanks shown in Fig.2a, all samples were oven-dried at 30ºC for 48hrs in order to start at a completely dried state.



(b)

Figure 2. (a) Moisture diffusion principle, (b) samples aged for 112 days vs. as-received sample.

Fig.2b illustrates snapshots of the samples employed to characterize the moisture uptake behaviour. As degradation is manifested, increased temperature levels induce changes in the samples' surface colour indicating potential occurrence of chemical reactions enabled during aging [4].

2.1.2 Mechanical testing

A series of tensile and short beam tests were carried out using a 50kN Instron testing machine. Tensile tests were conducted to assess the tensile strength and stiffness of both reference (un-aged) and aged FRP samples. Short beam tests were conducted to assess the interlaminar shear strength (ILSS) of both reference and aged FRP materials. Batches of 5 (tensile) and 3 (short beam) specimens were tested with a constant displacement rate of 1mm/min.

2.1.3 Computed tomography

The internal structure of the un-aged material was examined via a Nikon XT H 225 CT-scanner, allowing for the identification of any intrinsic hidden imperfections i.e. cracks, voids etc. Samples were interrogated with a view to determining the material's structural architecture.

2.1.4 Scanning electron Microscopy

A JEOL SEM6480LV scanning electron microscope was adopted to scrutinize the aging effects on the micro-structure of the material.

2.1.5 Impedance spectroscopy

The dielectric properties of the material were acquired in order to efficiently monitor the hygrothermal aging process of samples soaked at 60ºC. Scans were conducted with a Numetric PSM3750 impedance

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analyzer. Samples of 6x6x15mm^3 were prepared and appropriate electrical contacts were applied using silver loaded adhesive paste to fix the electrodes on opposing faces in the through-thickness direction.

2.2 Results and discussion

Fig.3 depicts moisture uptake vs. time curves for all interrogated aging temperatures. As is shown, the rate of moisture uptake elevates with the increase in temperature (Fig.3). In addition, increase in aging temperature leads to increase in the maximum absorbed moisture content (*M(%)*). Specimens immersed at 80°C have reached moisture maximum after approximately 30 days whereas the rest of specimens reached a moisture content maximum after approximately 150 days of aging.

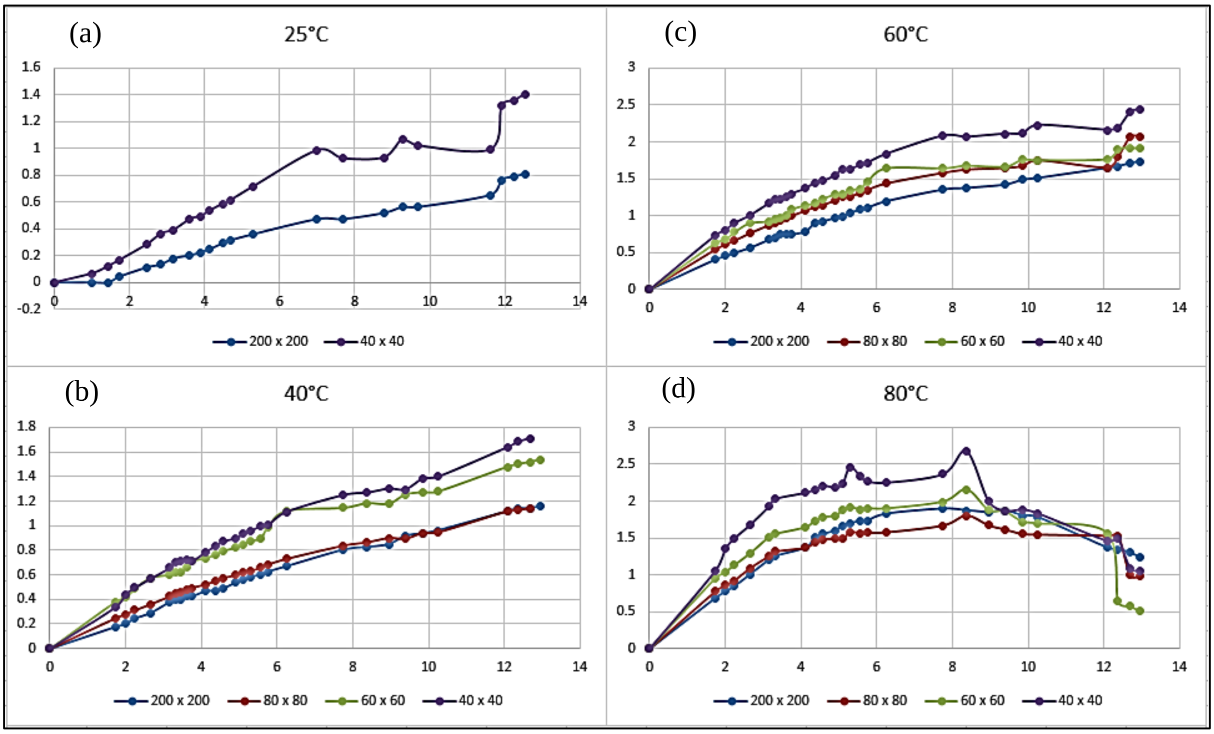

Figure 3. Moisture uptake vs. time curves for all investigated temperatures. (a) 25°C, (b) 40°C, (c) 60°C and (d) 80°C.

Fig.4 illustrates the mechanical performance of FRP samples during and after hot/wet aging. Fig.4a depicts the tensile strength and Fig.4b the tensile modulus (modulus of elasticity) of FRPs aged for 112 days. Samples were tested in the transverse direction (transversely to the UD reinforcement). Fig.4c presents the interlaminar shear strength values during and after aging of FRP samples in hot/wet environment for 112 days. Samples were tested both in the transverse (T, transversely to the UD reinforcement) and longitudinal (L, parallel to the UD reinforcement) directions. The samples were fully immersed in hot/wet water at four different temperatures. As can be seen from Figs. 4a and 4b, tensile values exhibit a general non-linear behaviour during aging. In specific, tensile strength was found to increase with hot/wet aging at 40°C after 28 and 56 days, respectively. This incremental behaviour changed with aging time. FRP samples aged at 40°C, exhibited a 10% drop in tensile strength after 112 days of aging, compared to the un-aged material. This was attributed to the additional cross-linking which occurs due to aging. The additional cross-linking is cancelled and overshadowed by significant plasticization which causes reductions in both strength and stiffness [5].

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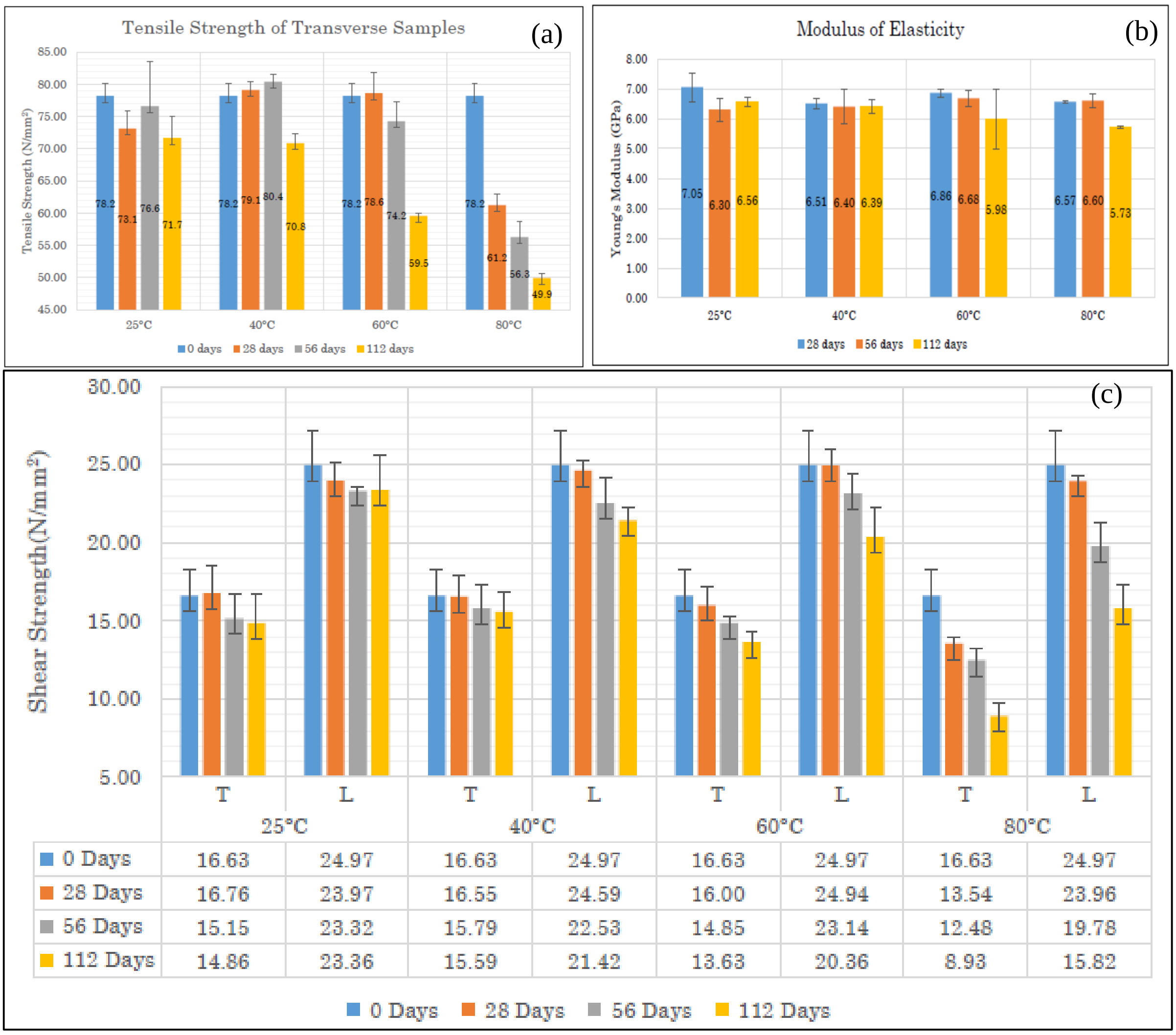

Figure 4. (a) Tensile strength of transverse samples, (b) tensile modulus (modulus of elasticity) of transverse samples and (c) Interlaminar shear strength values (ILSS) of both transverse and longitudinal samples.

As can be seen from Fig.4c, ILSS values exhibit a general reduction with aging. It is also evident that the aging temperature increase results in more severe damage which is reflected by the drop in ILSS. However, ILSS values did not reveal a non-linear behaviour due to aging. The effect of cross-linking and plasticization caused by aging was only distinguished by the matrix-dominated tensile properties of the transversely tested FRP samples.

In Fig. 5 a snapshot of the structural architecture of the examined GFRPs is presented via CT-scanning. A stack of five samples was scanned. Cracks (shown in dark colour) located in between the longitudinal fibre reinforcement (bright colour layers) are clearly visible. The generation of the cracks is mainly attributed to the matrix shrinkage after the curing process, and are responsible for the significant moisture transport in the through-thickness direction. Fig. 6 depicts a SEM snapshot of a sample aged for 56 days at 80°C. SEM photograph justifies that failure in the fibre-matrix interface is inflicted after hygrothermal aging.

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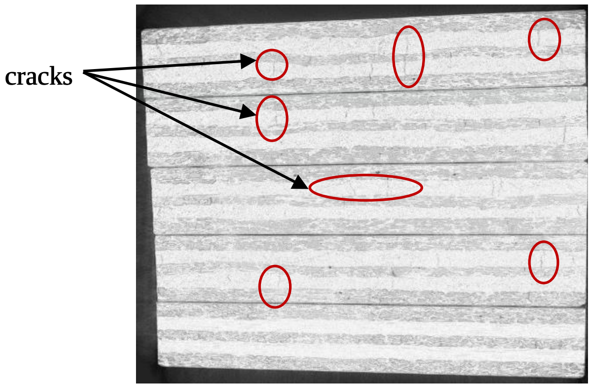

Figure 5. CT-scanning image, showing cracks.

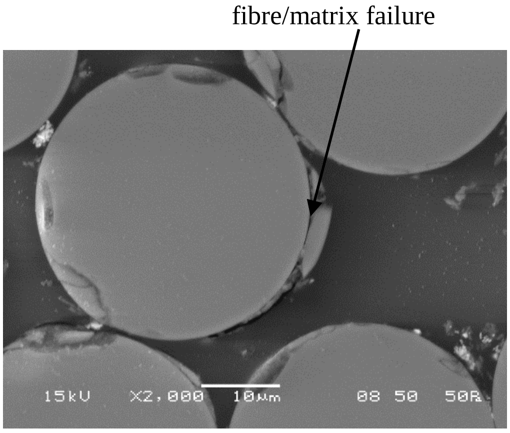

Figure 6. SEM image of fibre/matrix interface failure.

Finally, changes of the material's dielectric properties were captured with a view to monitoring the moisture absorption process. Frequency sweep scans were performed in a range of 1Hz to 10MHz. For this test, the specimens were continuously immersed in water at 60°C. Fig. 7a depicts the changes of tan*δ* values with aging time as a function of frequency. Tan*δ* corresponds to the dielectric dissipation factor [6, 7]. As is shown in Fig. 7a, frequency sweep spectra follow a characteristic trend exhibiting a peak tan*δ* value in the frequency range of 5E-03 Hz to 1E-04 Hz. The max tan*δ* values increase with soaking time. To that end, Fig. 7b plots the tan*δ* peak-values along with aging time juxtaposed with the actual moisture uptake curve obtained through gravimetric measurements. As it is shown in Fig. 7b, the tan*δ* peak-values curve coincides with the moisture uptake curve providing a very promising estimation of moisture absorption behaviour.

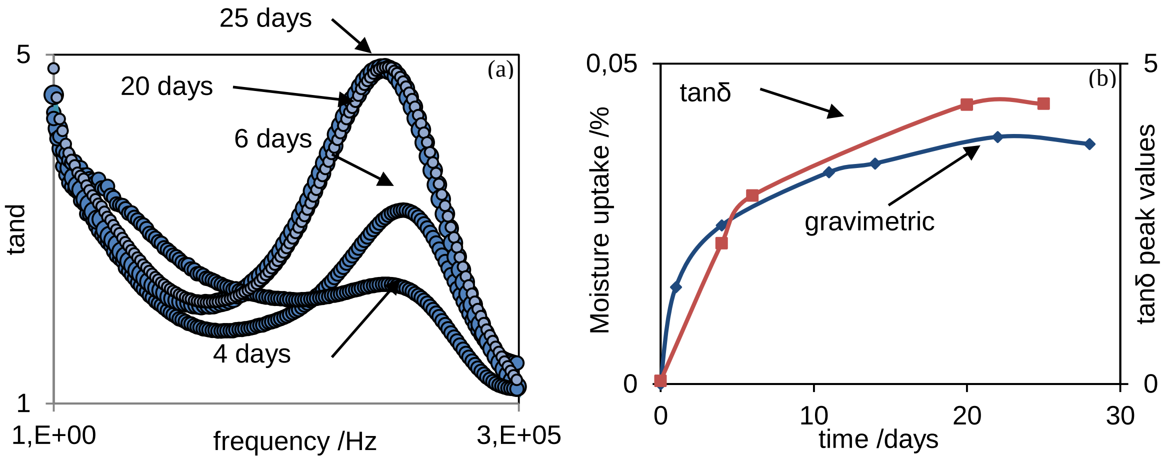

Figure 7. (a) log (tanδ) vs. log (frequency), (b) moisture uptake content (%) and tanδ peak values vs. time.

Conclusions

The hygrothermal degradation of a pultruded glass fibre reinforced composite was investigated by means of moisture absorption, mechanical degradation, micro-structural assessment and non-destructive evaluation. Samples were aged at elevated temperatures and the coupled effects of moisture and temperature were assessed by a variety of methodologies. It was observed that hot/wet

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aging accelerates the moisture uptake rate, maximum moisture content and time to saturation. Tensile mechanical properties exhibited a complex response to aging initiated by an increasing tendency for 56 soaking days and a depression at the end of the aging regime (112 days). However, this was not the case for the ILSS values which revealed a monotonic depression throughout hygrothermal aging. CT-scanning revealed the presence of micro-cracks in the composite structure which is likely to promote the moisture distribution inside the structure. SEM was capable of identifying the presence of fibre/matrix interface failure at aged samples. Lastly, impedance spectroscopy was effectively used to follow the aging effects with soaking time providing an innovative way to monitor the moisture absorption behaviour.

References

[1] Pochiraju KV, Tandon GP, Schoeppner GA. *Long-Term Durability of Polymeric Matrix Composites: Springer*; 2011.
[2] Karbhari V, Chin J, Hunston D, Benmokrane B, Juska T, Morgan R, et al. *Durability Gap Analysis for Fiber-Reinforced Polymer Composites in Civil Infrastructure*. Journal of Composites for Construction. 2003;7:238-47.
[3] Surathi P, Karbhari VM, Project SSR, University of California SDDoSE, Services CDoTDoE. *Hygrothermal Effects on Durability and Moisture Kinetics of Fiber-reinforced Polymer Composites*: Department of Structural Engineering, University of California, San Diego; 2006.
[4] Apicella A, Migliaresi C, Nicolais L, Iaccarino L, Roccotelli S. *The water ageing of unsaturated polyester-based composites: influence of resin chemical structure*. Composites. 1983;14:387-92.
[5] Grammatikos SA, Evernden M, Mitchels J, Zafari B, Mottram JT, Papanicolaou GC. *On the response to hygrothermal aging of pultruded FRPs used in the civil engineering sector*. Materials & Design. 2016;96:283-95.
[6] Patra A, Bisoyi DK. D*ielectric and impedance spectroscopy studies on sisal fibre-reinforced polyester composite*. Journal of Materials Science. 2010;45:5742-8.
[7] Ajaj EAA, S.I.Husaen, H.I.Jafar. *Effect of Water Absorption on Some Electrical and Dielectrical Properties of Epoxy Resin Reinforced with Chopped Carbon Fibers*. Journal of Al-Nahrain University - Science مجلة كلية العلوم - جامعة النهرين. 2011;14:87-94.

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