Construction and Building Materials 420 (2024) 135584

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Durability of hybrid flax fibre-reinforced epoxy composites with graphene in hygrothermal environment

Amer Oun [a], Omar Alajarmeh [a,*], Allan Manalo [a], Rajab Abousnina [a], Andreas Gerdes [b]

[a] Centre for Future Materials, University of Southern Queensland, Toowoomba 4350, Australia
[b] KIT Innovation Hub, Department of Civil Engineering, Geo and Environmental Sciences, Karlsruhe Institute of Technology, Germany

ARTICLE INFO

Keywords:
Durability
Natural fibre composites
Flax fibre
Graphene nanoparticles
Mechanical strength
SEM

ABSTRACT

Natural fibre composites are highly sensitive to the hygrothermal environment (humidity and elevated in-service temperature). Enhancing the long-term behaviour of such composites can be achieved through additive manufacturing using nanomaterials as a constituent. Thus, this study investigated the mechanical properties of hybrid flax fibre-reinforced epoxy composites with 0%, 0.5%, 1% and 1.5% of graphene nanoparticles after exposure to a relative humidity of 98% for 1000, 2000, and 3000 hours and at temperature of 20°C, 40°C, and 60°C. The degradation behaviour of hybrid natural fibre composites was then evaluated by flexural and interlaminar shear tests. Hygrothermal conditioning simulation of these hybrid composites was then performed using Arrhenius model based on accelerated aging data. The results of this study showed that graphene nanoparticles played a significant role in the reduction of moisture absorption and in the improvement of mechanical properties after hygrothermal conditioning. Compared to the specimens without graphene nanoparticles, the flexural and interlaminar shear strength in hybrid composites with 0.5%, 1.0%, and 1.5% graphene increased by 77.7%, 72.0%, and 77.1%, respectively, and up to 75.5%, 70.6%, and 73.5%, respectively after exposure for 3000 hours at 40°C. However, the degradation of the hybrid composites increased with the increase of conditioning temperature and exposure duration due to the moisture diffusion into the flax fibres and resin plasticisation. Nevertheless, the 0.5% graphene nanoparticles were found optimal in retaining the mechanical properties of aged hybrid composites due to their better distribution within the matrix. Accelerated test results showed that the hybrid composites can retain at least 57% and 49% of its flexural and interlaminar shear strength, respectively, after 100 years in service in hygrothermal environment at a temperature of 30°C representing the average annual temperature in Australia.

1. Introduction

In recent years, plant fibres have become effective reinforcements for polymeric composite materials. These natural fibres reinforced polymer (NFRP) composites are increasingly being used in many mechanical and structural engineering applications due to their economic and environmental benefits. These benefits include low density, good mechanical properties, recyclability, lightweight and relatively low cost, and most importantly being coming from renewable resources and environmentally friendly [1,2]. Gopinath et al. [3] indicated that by replacing steel with composite materials can save 60–80% of the weight of the component and 20–50% of the weight of aluminium components. Natural fibres are considered environmentally friendly materials compared to synthetic fibres due to their recyclability and biodegradability. This was confirmed by evaluating the sustainability of these natural composites in terms of their environmental impact using life cycle assessment analysis. For example, Broeren et al. [4] showed that the production of sisal fibre has approximately (85–95%) lower energy consumption and (75–95%) lower greenhouse gas emissions than glass fibre production on a kg basis. This is in line with life cycle assessments issued for natural plant fibres. Researchers concluded that life cycle assessments show promising uses for natural fibres as an alternative to synthetic fibres to accept the potential environmental and human health consequences of natural fibre composites throughout their life cycle. Thus, NFRP composites have the advantage of lower harmful environmental impacts compared to synthetic fiber-based polymer composites due to the significant contribution of their individual components to natural degradation [5]. Natural fibres consume less energy compared to

---

* Corresponding author.
E-mail address: omar.alajarmeh@usq.edu.au (O. Alajarmeh).

https://doi.org/10.1016/j.conbuildmat.2024.135584
Received 10 July 2023; Received in revised form 7 February 2024; Accepted 21 February 2024

glass, carbon, and aramid fibres during production as reported by Nasihatgozar et al. [6]. Joshi et al. [5] and Balla et al.[7] also reported that the production process of flax fibre consumes energy of about 9.55 MJ/kg while glass fibre consumes 54.7 MJ/kg. Economically, natural fibre-reinforced polymer composites are considered sustainable materials as these materials often used in natural composites are sourced from natural plants or various types of animal skins [8]. Moreover, synthetic fibres, being more expensive materials, limit their use in various industrial applications, as reported by Guijun Xian [9] while natural fibres are relatively low cost [10]. Replacing synthetic fibres with natural fibres in polymer composites is therefore an important approach to encounter this challenge in terms of providing sustainable development of high-performance composites and being environmentally friendly materials. Thus, applications based on natural composite materials have proven successful in contributing effectively to various industries. Although NFRP composites are increasingly used in various engineering applications, their durability properties need to be demonstrated, which can be improved through physical and chemical treatments or hybridisation technique [11]. It should be highlighted that flax is the mostly used fibre for manufacturing natural fibre composites due to its higher characteristics than other plant fibres attributed to its fibre length and small diameter [12]. Balla et al. [13] also highlighted flax fibres have desirable properties including a high cellulose percentage as well as a low micro fibril angle with the fibre axis. Both fibre parameters contribute to the mechanical properties of the fibres and the performance of the composites [13]. Their desirable properties are close to the glass fibre [14]. Dimo Hristozov et al. [15] found that the long-term durability performance of flax fibre composites natural composites was no worse than that of synthetic fibre composites. Similarly, Shah et al. [16] concluded that flax fibre composites are a suitable structural alternative to E-glass fibre composites in small wind turbine blade applications. Moreover, Khotbehsara et al. [17] stated that composites with higher lignin content showed lesser loss in flexural strength and modulus compared to the other composite samples, which was attributed to their hydrophobic surface. Current applications of natural polymer composites are however mostly limited to indoor applications. This is due to the hydrophilic nature and lower thermal degradation property of NFRP composites. Wang et al. [18] also indicated that the limited information on the long-term properties and durability of natural fibre composites in harsh environments contribute to the low confidence in using them for outdoor applications. A better understanding of the durability properties of NFRP composites in harsh environments is therefore required to extend the usage of these sustainable composites worldwide.

Natural fibre composites in outdoor applications are exposed to environmental factors involving high temperature and humidity. Mamalis et al. [19] and Wang et al. [20] mentioned that hygrothermal aging in NFRP composites causes fibre swelling, deteriorates the fibre/matrix interface and finally decreases significantly the original properties of the composite. According to Alessi et al. [21] and Shaohua et al. [22], subjecting fibre matrix composites to hygrothermal conditioning accelerated moisture absorption and was accompanied by matrix plasticisation and fibre swelling due to this absorption causing micro-cracks in the polymer matrix. Both directly affect most of composite properties [23]. These studies showed that the sensitivity of NFRP composites to hygrothermal conditioning is a major challenge for their long-term usage in various industrial applications. Therefore, the reduction of the long-term performance of NFRP composites in hygrothermal environments should be well understood to prevent any unexpected failures during their service life.

A number of researchers have investigated the sensitivity of natural fibre composites in hygrothermal environments [18,24–32]. These researchers concluded that the effect of hygrothermal ageing in the mechanical properties of NFRP composites depends on the type and temperature of the solution, the glass transition temperature (T_g) of the polymer and the length of exposure time. Wang et al. [18] investigated the mechanical strength of ramie fibre-reinforced phenolic composites after exposure to water at 20 °C and 40 °C for 28 days. They found that increasing water temperature from 20 °C to 40 °C increases water absorption from 8.4% to 10.5% after 1 day of exposure and reduced the flexural strength and modulus, respectively by 24.9% and 45.9% at 20 °C, and 28.4% and 58.3% at 40 °C. These mechanical properties continued to deteriorate until 28 days of exposure time. A study by Jiang et al. [25] examined the tensile properties of poly (lactic acid) PLA composite reinforced with jute fibre immersed in water at 50 °C for 56 days and found 78% and 26% reduction in tensile strength and modulus, respectively. Moreover, Scida et al.[33] studied the tensile properties of flax fibre-based epoxy composites aged at a relative humidity of 90% for 38 days at 20 °C and 40 °C. Research results indicated that the tensile properties were affected by hygrothermal conditioning and showed a decrease in strength and modulus by up to 12% and 55%, respectively. It can be concluded from these studies that NFRP composites show negative response to moisture and temperature, but their effects on the mechanical properties occur at varying degrees.

A number of researchers have used different treatment methods to modify the surface of natural fibres and improve their resistance under hygrothermal environments. These methods include physical and chemical treatments that can contribute to enhancing the compatibility and interfacial bonding of the fibre with the matrix, which in turn promotes the hygrothermal ageing behaviour of natural fibre composites [24,34]. Fibre surface treatment methods may enhance the hygrothermal behaviour of these composites in the initial stages of aging, but there is no clear improvement in their hygrothermal behaviour under long-term aging [35]. The reasons for this phenomenon can be explained by the degradation of both the polymer matrix and the fibre/matrix interface of natural fibre composites, resulting by the effect of hygrothermal aging. When natural fibre composites are subjected to water at elevated temperatures, moisture diffuses into the composite matrix or its interface, which then causes microcracks in the matrix by fibre swelling or deteriorating at the composite interface by plasticising effect. Both matrix and interface bond degradation contribute to reducing the surface modification benefits of natural fibres and thus the improvement of hygrothermal aging behaviour becomes unclear under long-term immersion in any solution at elevated temperatures. This means that the effectiveness of fibre surface modification by physical and chemical treatments on the hygrothermal aging behaviour of natural fibre composites becomes limited. It is therefore important to find other effective ways to enhance the properties of natural fibre composites exposed to hygrothermal conditions.

Recent developments in the use of filler materials such as graphene nanoparticles in producing hybrid flax fibre-epoxy composites showed high-quality moisture barrier properties [36] and beneficial effects in retaining their mechanical properties under in-service elevated temperature [37–39]. It is anticipated therefore that the addition of graphene will have a positive effect on the mechanical strength of flax fibre composites under combined moisture and thermal conditioning, which is the main motivation of this study. This hypothesis is supported by the findings of several researchers who studied the long-term durability of particulate-filled polymer matrix composites under hygrothermal conditions. Khotbehsara et al. [17] revealed that epoxy-based matrix system filled with fire retardant and fly-ash subjected to relative humidity of 98% at elevated temperatures can retain most of their mechanical properties as the fillers reduced the rate of moisture absorption and increased the T_g of the composites. More recently, Manalo et al. [40] demonstrated that the negative impact on the flexural and interlaminar shear strength of glass fibre reinforced polymer (GFRP) composites could be efficiently minimized with the use of a particulate-filled polymer-epoxy coating. It can be noted that the hybrid effect of nanomaterials can significantly improve the bonding strength of fibre/matrix interface, which contributed to the increased long-term durability performance of these hybrid composites in hygrothermal environments. The addition of graphene nanoparticles reduces the water absorption rate within the hybrid composite by reducing the volumes of free voids in its matrix. It can also increase the mechanical interlocking of the fibres with the epoxy matrix via additional sites provided by their effective aspect ratio to enhance the bonding strength of these hybrid composites and improve their properties. These mechanisms showed the main role of graphene nanoparticles in acting as an effective barrier to water molecules being transported within the composite matrix, protecting the fibre from swelling, and obstructing the interface from plasticisation. These effect mechanisms showed the key role of nanomaterials in reducing moisture absorption in the composite matrix. Thus, a positive hybrid effect was observed in the higher mechanical properties of the hybrid composites. Therefore, a comprehensive evaluation of the long-term durability of flax fibre composites by reinforcing the polymer matrix with nanomaterials such as graphene nanoparticles will be beneficial to expand their use in outdoor applications.

Durability studies by natural ageing take a long time to obtain service-life results, and are suitable for composites with short-term use but not for long-term use as reported by Brebu [41]. Firdosh et al. [42] also stated that determining the actual service life of composite structures in aggressive environments is impractical because it can take years of waiting. Furthermore, Alam et al. [43] reported that it is difficult to research the damage caused by natural aging in humid environments because real-time aging takes a long period, up to many years, before insightful changes in the original properties of composite materials are observed. Therefore, Jiang et al.[44] highlighted the usefulness and time-effectiveness of accelerated experimental tests to study the long-term durability of such composite materials. Brebu [41] suggested that the design of artificial aging tests is the best technique to accelerate the ageing processes by means of simulating natural weathering in laboratory environments. Moreover, Uthaman et al. [45] mentioned that durability performance can be determined by using different analysis methods based on the exposure of these composite materials to the type of harsh environmental factors such as hygrothermal conditioning, where the parameters of temperature, duration of exposure and water ingress or any other solutions are used to determine the degree of aging. According to Alessi et al. [21], a common method used to accelerate the water absorption process and degradation mechanism is by hygrothermal aging, which involves the absorption of water at elevated temperature. The use of artificial hygrothermal aging to simulate actual in-service exposure in aggressive environments and predict their service lives is an appropriate method as suggested by several researchers including Alam et al. [43] and Manalo et al. [40]. Therefore, ageing tests are used in this study to accelerate the mechanical degradation of flax fibre-reinforced epoxy hybrid composites with different graphene loadings and to help predict their long-term durability based on analytical model.

Natural fibre composites are relatively new to outdoor applications; thus, information of their durability properties is still limited in terms of their expected service life. Lau et al. [46] explained that the reason for this limitation in durability information is related to the difficulty of obtaining accurate input data. Thus, the service life prediction of NFRP composites and their resistance to aggressive environments is a continuing concern as suggested by Bambach [47]. Silva et al. [48] highlighted that most of the studies reported in the literature are about the durability of glass fibre-reinforced polymer composite bars and there is a lack of information data for the long-term predictive behaviour of composite laminates. Moreover, Uthaman et al. [45] suggested that the long-term use of FRP composites in different engineering applications, especially under hygrothermal conditioning, requires further studies, as their use in civil engineering applications is expected to be longer than 50 years. This highlights the increasing importance of using analytical models such as Arrhenius model to predict the long-term durability performance of natural fibre composites.

This study is the first to discover the degradation mechanisms of the hybrid natural fibre composites under hygrothermal conditions and establish the 100 years performance prediction considering the effect of graphene nanoparticles. This is achieve by investigating the effects of graphene addition on the long-term and durability performance of flax fibre composites under aggressive environments and predicting their service life using Arrhenius model. The research focused on evaluating the flexural and inter-laminar shear behaviour of hybrid flax fibre composites with 0%, 0.5%, 1%, and 1.5% of graphene by weight of the matrix. These hybrid composites were hygrothermal conditioned at different levels of exposure temperature (20 °C, 40 °C, and 60 °C) and exposure duration (1000, 2000, and 3000 hours). The results obtained from this research will provide a better understanding about the long-term performance of flax fibre composites filled with graphene nanoparticles under hygrothermal conditions. This also will provide comprehensive information useful to expand the applicability of hybrid flax epoxy composites for sustainable applications. Furthermore, this study will provide guidance to engineers and designers on the long-term service life prediction of natural fibre composites in harsh environments based on filler hybrid effect for their safe design and use in outdoor applications.

2. Experimental procedure

2.1. Materials

Kinetix RX240 epoxy resin with H160 medium hardener was used as a matrix in a mixing ratio of 1:4 by weight for the manufacture of test samples. Both epoxy and hardener were obtained from ATL Composites based on Molendinar, Queensland, Australia. Flax fibres, used as reinforcement in the form of a unidirectional fabric with areal density of 200 g/m^2 and a thickness of 0.36 mm, were obtained from Colan Composite Reinforcement, Huntingwood, New South Wales, Australia. Graphene nanoparticles, with an average area of 300 m^2/g used as additives, were purchased from Sigma-Aldrich, Bayswater, Australia. According to the manufacturer's recommendations and from available literature, the properties of these materials are presented in Table 1. Graphene nanoparticles was selected for flax fibre composites to ensure that a positive hybrid effect could be achieved based on their excellent mechanical properties shown in Table 1. The excellent properties of graphene including high surface area, hydrophilic nature, and high tensile strength measured at 130 GPa, which is about 5–200 times greater than of steel, and Young's modulus of 1 tera pascal (TPa) makes it more suitable nanomaterial as polymer reinforcement than other nanoscale fillers [49]. It is worth highlighting that the surface area of graphene is twice the one of carbon nanotubes, i.e., 2630 m^2/g and 1315 m^2/g, respectively, as reported by the extensive review work done by Tareen et al. [49].

2.2. Composite fabrication

Flax fibre composites, with a thickness of 4 mm, were made from six layers of unidirectional flax fibres wet with epoxy resin using a hand lay-up approach. The composite manufacturing process was started by cutting the flax fibres to dimensions of 600 mm in length and 400 mm in width before being placed them in an oven at 40°C for 30 minutes, to remove the moisture content of the fibre as recommended by the fibre

Table 1
Properties of flax fibres, graphene, and epoxy resin used in this study.

Materials	Properties			Reference
	Tensile strength (MPa)	Elastic modulus (GPa)	Density (g/cm^3)	
Epoxy resin	130	3.4	1.12–1.17	Technical Data Sheet [50]
Flax fibre	1400	70.0	1.40	[51]
Graphene	130×10^3	1000	0.03	[52]

manufacturer. An epoxy mixture was then poured over the first layer of fibres and distributed uniformly throughout the layer using a metal roller to ensure proper wettability of the fibres and to eliminate air bubbles from the composite plates or any developed gases before applying the next fibre layer. Wetting the fibres with the epoxy mixture continued until the composite was built with a fibre volume ratio (V_f) of 25%, which was calculated by the weight method. As for the hybrid composite samples, graphene nanoparticles were mixed with epoxy resin at varying weight percentages of 0.5%, 1.0% and 1.5% before a hardener was added [37]. The weighed graphene nanoparticles were mixed in the epoxy matrix using a mechanical stirrer for 5 minutes, to ensure a homogeneous mixture without aggregation of the graphene particles based on the manufacturer's recommendations. The high-speed rotating motion of the mixer creates a shear force that overcomes the filler-filler interaction caused by van der Waals attraction and thus facilitates better dispersion of graphene nanoparticles in the epoxy matrix. After the flax fabric layers were completely infused with epoxy resin, the vacuum bag was sealed around the edges with yellow sealant tape and a constant pressure of 92 kPa applied by the vacuum pump on the composite plates. The curing process involved two steps: the first at room temperature for 24 hours and the second in an oven at 120 °C for 3 hours based on the recommendations of the matrix manufacturer. The standard sizes of mechanical test samples were cut from the treated composites plates using a water jet. Fig. 1 illustrates the entire manufacturing process, and the details of the material contents used in the prepared composite laminates are presented in Table 2.

2.3. Hygrothermal ageing and absorption testing

Aging was performed under combined humidity and temperature in which samples were conditioned in an environmental chamber (with temperature and humidity accuracy of ±0.2°C and ±0.5%, respectively) (Votsch technikat) (see Fig. 2a) at 98% relative humidity and at test temperatures of 20°C, 40°C and 60°C, to simulate the influence of hygrothermal environment on the mechanical properties of hybrid composites with different weight percentages of graphene. These conditioning temperatures were lower than the measured glass transition temperature of hybrid composites of 78 °C, to avoid the exposure of these composite materials to chemical oxidation, which can contribute to the change in the chemistry of the matrix as was also reported by Shaohua et al. [22]. Aging temperatures lower than the T_g can promote the degradation effect of accelerated aging without altering the degradation mechanism of natural aging as suggested by Manalo et al. [53] and Cadu et al. [54].

Table 2
Details of resin, fibre and graphene contents used in the prepared composite laminates.

Composite materials	Content (%)		
	Graphene (Gr)	Epoxy (E) resin	Flax (F) fibre
F-E composite	0	75.0	25
Gr-F-E composite	0.5	74.5	25
Gr-F-E composite	1.0	74.0	25
Gr-F-E composite	1.5	73.5	25

For absorption testing, all samples were initially weighed in a dry state (w_o), after coating their edges with a thin layer of resin to ensure that moisture enters only through the upper and lower surfaces of the composite materials. The water absorption test was performed based on ASTM D570 [55], for all samples under constant humidity conditioning and at three different temperatures. The environmental chamber temperature was monitored by a thermostat installed inside the environmental chamber to accurately determine the target exposure temperature. These samples were taken out of the chamber after 1000, 2000, and 3000 hrs to measure the experimental moisture absorption using a digital scale with an accuracy of 0.001 mg. This time range was selected based on a previous study that showed 3000hrs is sufficient to achieve saturation by the conditioned specimens. Once dried with tissue paper, they were immediately weighed. The average of five measurements was taken as the sample weight. The moisture absorption ratio (M_t %) is then calculated as the difference between the weight of the wet (w_t) and dry (w_o) samples using Eq. (1).

$$M_t\ (\%) = 100 \text{ x } (w_t - w_o) / (w_o) \tag{1}$$

.

2.4. Flexural and interlaminar tests

The long-term and durability performance of the hybrid composites in hygrothermal conditioning were evaluated by testing their flexural and inter-laminar properties. After conditioning the samples in the environmental chamber, the flexural and interlaminar shear tests were

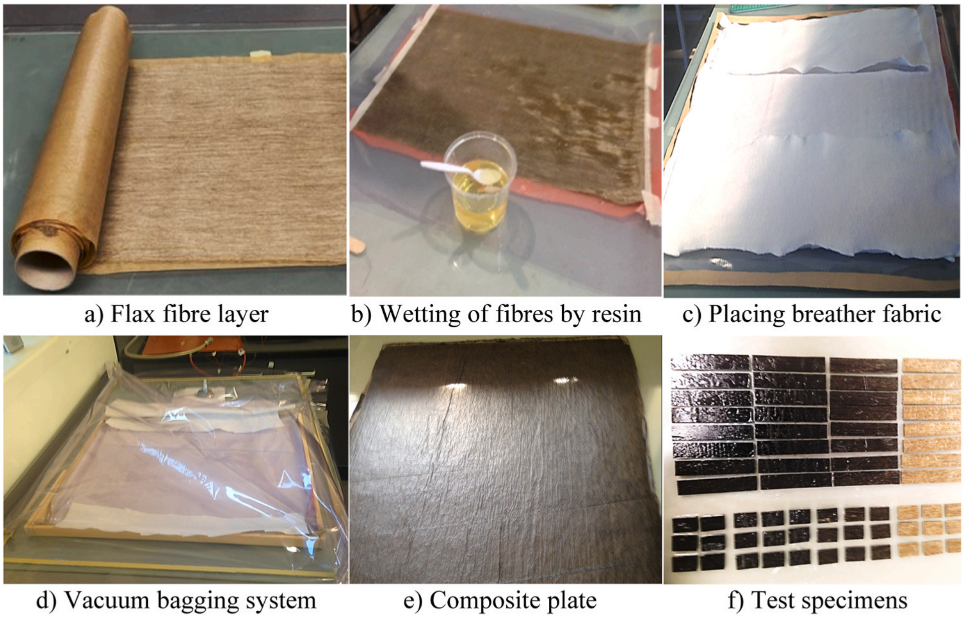

a) Flax fibre layer
b) Wetting of fibres by resin
c) Placing breather fabric
d) Vacuum bagging system
e) Composite plate
f) Test specimens

Fig. 1. Manufacturing process for hybrid composite laminates.

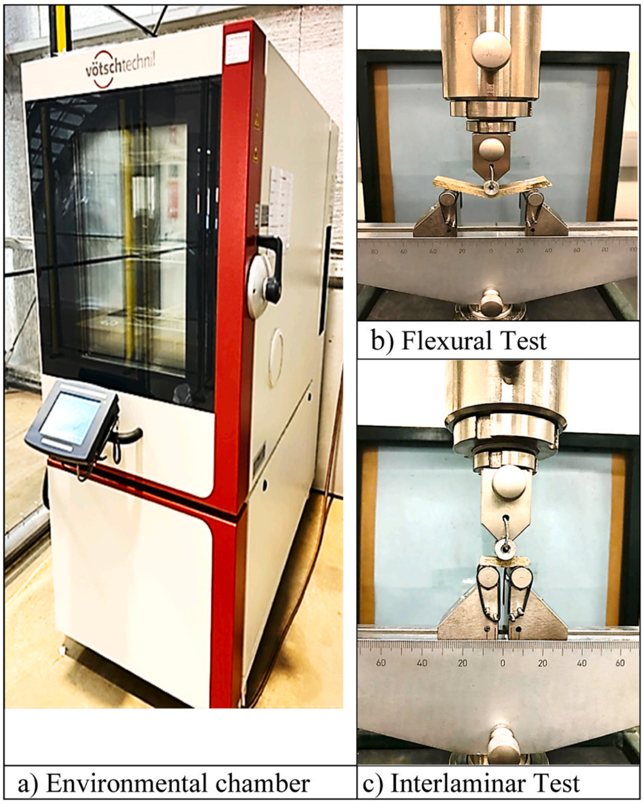


Fig. 2. **:** Aging and mechanical tests for hybrid composites.

performed in a 3-point bending test using a universal testing machine (MTS E43.104) with a mechanical test speed of 1.3 mm/min and a capacity of 10 kN with 1 N accuracy, as shown in Fig. 2(b and c). The flexural and interlaminar properties of the hybrid composites were evaluated following the ASTM D790 [56] and ASTM D2344 [57], respectively. For each mechanical test, five samples were tested, and the average strength value was considered. The flexural test specimens, with dimensions of 80 mm in length, 16 mm in width and 4 mm in depth, are tested over a support span of 64 mm to achieve a span-to-depth ratio of 16:1, whereas the inter-laminar shear strength (ILSS) test was conducted on specimens with a clear support span of 16 mm achieving a support span length-to-sample thickness ratio of 4:1. The investigated mechanical properties (flexural and ILSS) were selected as these properties are the most influential properties to demonstrate the effectiveness of the graphene nanoparticles in the stiffness and strength properties of fibre reinforced composites. Same techniques were adopted in previous studies reported in [53,58].

2.5. *SEM and FTIR analysis*

The fracture surface of the hybrid composites with different graphene weights was analysed using scanning electron microscopy (SEM) JEOL JXA 840 A (Jeol, Tokyo, Japan) and assessed the distribution of graphene nanoparticles in the epoxy matrix composites. The samples were prepared by cutting a section of 10 mm by 10 mm from the fractured specimens from the flexural strength and interlaminar shear strength tests. FTIR spectra is a suitable technique used to confirm the identity of the characteristic functional groups present in the sample structure which in turn allows us to know if there is any significant change in the chemical properties of the sample. This technique was used to collect high spectral resolution data, using a Nicolet 6700 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the range, typically 4500–400 cm^{-1}. The main purpose of the FTIR analysis is to understand if there is any chemical change happened within the composites and to support the measured changes in the mechanical properties of hybrid composites after conditioning.

3. Results and discussion

3.1. *Moisture absorption behaviour*

Fig. 3 shows the moisture absorption behavior of hybrid flax fibre-reinforced epoxy composites with graphene at different temperature and up to a maximum exposure of 3000 hours. The maximum exposure time was taken, in this case, to obtain quantitative information on the mechanical performance of these hybrid composites after hygrothermal conditioning. As can be seen from Fig. 3, the moisture absorption rate is lower for all the hybrid composites with regards to the control samples (without graphene addition). The higher moisture content observed in natural fibre composites is justified, as flax fibres have a higher cellulose content [13,59] consisting of hydroxyl groups that form hydrogen bonds with water molecules. However, the large standard deviation of the results in Fig. 1 can be explained by the formation of micro-cracks in the composite matrix caused by the swelling of natural fibres. Cutting the samples using the water jet method causes the ends of the fibres to be directly exposed to water at the cutting edges, although these edges have been coated with a thin layer of epoxy resin to ensure water absorption from both the upper and lower surface only. The large standard deviation due to the formation of micro-cracks in the composite was also observed by Kamau-Devers, Kortum [60] in their study of wood flour reinforced poly (lactic acid) composites in a hydrothermal environment. After 3000 hours of conditioning in hygrothermal environment, the lowest moisture absorption values of 38.9%, 21.5%, and 55.3% were recorded at room temperature (20 °C) for the hybrid composites with 0.5%, 1.0%, and 1.5% graphene, respectively, when compared to the specimens without graphene. This percentage increased with the increase in the conditioning temperature. When the conditioning temperature was increased to 60 °C, the moisture content of the hybrid composites with 0.5%, 1%, and 1.5% graphene is 18%, 28%, and 11% higher than those measured from composites at room temperature, respectively, but remained lower than the other composites without graphene at the same conditioning temperature. This difference between the absorbed moisture content at 60 °C and 20 °C is an indication of the degradation in the composite materials which have affected their mechanical properties. The higher temperature during the conditioning of the specimens accelerates the degradation rate of the composite materials immersed in water. A similar observation was found by Fergani, Di Benedetti [61] wherein they investigated the long-term durability properties of glass fibre-reinforced polymer (GFRP) bars exposed to severe environments. This behavior means that the flow behaviour of water molecules within the composite matrix is accelerated by the higher conditioning temperature due to water molecules act as a plasticer that increases the ductility of the matrix which contributes to the weakening of the fibre /matrix adhesion. This results in increasing the moisture absorption and the degradation of reinforcing fibres because of the hydrolysis mechanism. When the moisture is absorbed by the polymer matrix, it causes the natural fibres to swell and micro-cracks develop in the composite matrix. These microcracks provide entry passage for the moisture increasing further the mositure absorption and the degradation of the matrix as also observed in SEM images shown in Fig. 10 (2 a, 2 b and 2 d). Moreover, the lower moisture absorption of samples with graphene indicate a beneficial effect of graphene nanoparticles in reducing the amount of moisture. This mechanism can be explained by the higher aspect ratio of the graphene nanoparticles which created a longer and more tortuous diffusion path in the epoxy matrix so that the water molecules have to pass around the platelet layers following this path as was also explained by Damari et al.[62]. Graphene nanoparticles play an important role in improving the bonding performance through additional sites provided by their aspect ratio for mechanical interlocking of the fibres with the resin [36]. Moreover, graphene nanoparticles reduce

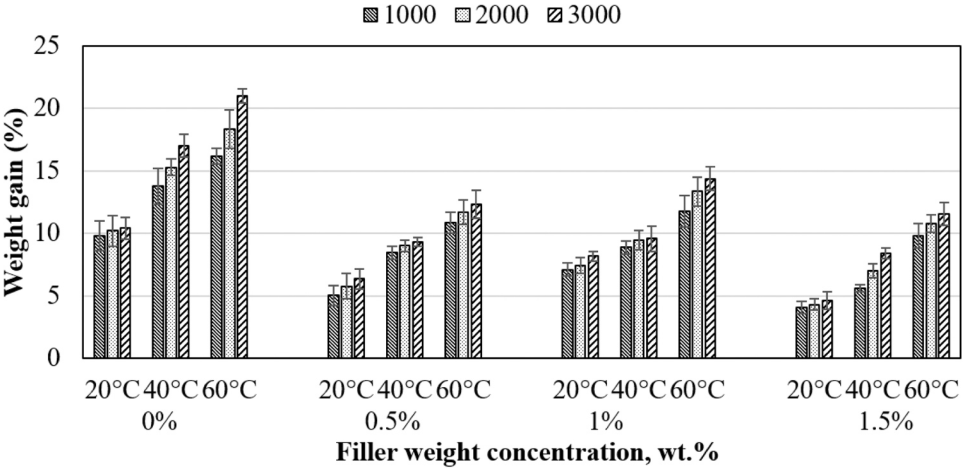


Fig. 3. : Moisture absorption of hybrid composites at different temperatures.

the sizes of free voids within the epoxy matrix as reported in other studies [63,64]. As a result of the reduction of free voids, the volumetric presence of moisture within the composite matrix is naturally reduced and consequently a successive decrease in its diffusion. The aforementioned mechanisms demonstrated the ability of graphene nanoparticles to reduce the rate of moisture absorption even at elevated temperatures by acting as a barrier to prevent penetration of water molecules into the matrix, protect the fibres from swelling, and obstruct the interface from plasticisation.

The moisture absorption behaviour also proves that the increase in conditioning temperature of the environment accelerates moisture penetration within the composite interface for the same exposure duration. This result showed that the conditioning temperature affects the activity of the water molecules responsible for the diffusion of moisture within composites as also suggested by other studies [28]. These sorption results justify the lower strength values recorded for hybrid composites conditioned in humidity at elevated temperatures as described in the next sections for the flexural and inter-laminar properties. It is interesting to note from Fig. 3 that the moisture content in hybrid composites decreases with increasing percentage addition of graphene. Graphene nanoparticles serve as an excellent barrier to the diffusion of water molecules in hybrid composites by creating a long tortuous path that delays this diffusion. Moreover, the reinforcement of the epoxy matrix with higher graphene content makes the matrix more rigid due to its hard particles, which hinders the propagation of cracks in the composite matrix by limiting the expansion of the fibers as supported by previous investigations [36,65,66]. However, the higher amount of moisture absorbed in samples with 1% graphene is due to the formation of more voids and micro-cracks at the composite interface [36]. The inevitable formation of voids and microcracks within the produced composites can be explained by the manufacturing and solidification process as reported by Zhang and Mi [14]. The voids created from the manufacturing process can aid in the penetration of water molecules into the composite matrix by diffusion. These micro-cracks can create new voids through plasticisation of the resin matrix after breaking the chemical bonds in resin chains as also observed by [15]. This will contribute to increasing the moisture absorption content in the composite. Prolongo et al.[67] also explained that the increased amount of moisture absorbed in the sample can be attributed to the weakening at the interface between the graphene nanoparticles and the matrix, allowing water molecules to move between them.

3.2. *Flexural behaviour under hygrothermal condition*

3.2.1. *Flexural strength*

Flexural strength (FS) of hybrid composites with graphene at different weight ratios under hygrothermal conditioning is illustrated in Fig. 4. In general, with increasing aging duration, the FS reduces due to the increase of moisture content inside the composite matrix, but it decreases significantly when the conditioning temperature is increased. A clear indication of these results is the detrimental effect of hygrothermal conditioning at elevated temperature on the quality of the composite interface. As shown in Fig. 4, it is observed that under all conditions, hybrid composites with 0.5%, 1%, and 1.5% graphene by weight have higher FS than other conditioned composites without graphene, which suggested the FS of flax fibre composites could be improved by the addition of graphene nanoparticles. The hydrophilic nature of flax fibres is responsible for the weakening of interfacial adhesion with the epoxy matrix which contributes to the reduction of flexural strength. However, hybrid composites exhibited different degrees of strength loss under hygrothermal conditions at different temperatures due to the acceleration of moisture diffusion in the composite matrix caused by increasing temperature. The FS of hybrid composites with 0.5% graphene exposed to 98% humidity for 3000 hours was recorded 115.5 MPa at 20 °C, 103.6 MPa at 40 °C, and 86.8 MPa at 60 °C while other hybrid composites showed 106.1 MPa, 92.6 MPa and 80.5 MPa in FS for 1% of graphene, and 115.1 MPa, 96.3 MPa and 83.5 MPa for 1.5% graphene, respectively, at the same levels of exposure temperatures. However, the FS of these hybrid composites is still higher than the control composites in all conditions. The results indicated that the strength loss of hybrid composites with 0.5% graphene under hygrothermal conditioning was less than those specimens with 1% and 1.5% graphene, which was attributed to stronger interfacial bonding due to good dispersion of graphene particles, which plays a main role in improving the mechanical properties of these hybrid composites, as reported by Prasad, Joseph [68] for flax fibre reinforced epoxy composite with nano TiO2 addition and Ashok, Kalaichelvan [69] for luffa fibre-reinforced epoxy composites with graphene. In their studies, they found that better dispersion of nanoparticles with their higher aspect ratio in the epoxy matrix improved the interfacial bond strength of hybrid composites by creating a good mechanical interlocking of the epoxy matrix with the fibre. This helps stress transmission from the matrix to the fibre and thereby increasing the mechanical properties of hybrid composites. Filler agglomeration is responsible for more strength loss in the hybrid composites with 1% and 1.5% graphene as evidenced by the SEM image in Fig. 10 (2 c and 2 d right in the bottom images). Moreover, the amount of moisture absorbed in the samples with 1.5% graphene was the lowest (see Fig. 3), confirming that the lower FS compared to hybrid composites with lower amount of graphene is due to agglomeration of the fillers. The reduction of FS by filler agglomeration has been confirmed by other studies [70,71].

The FS retention of conditioned hybrid composites with and without

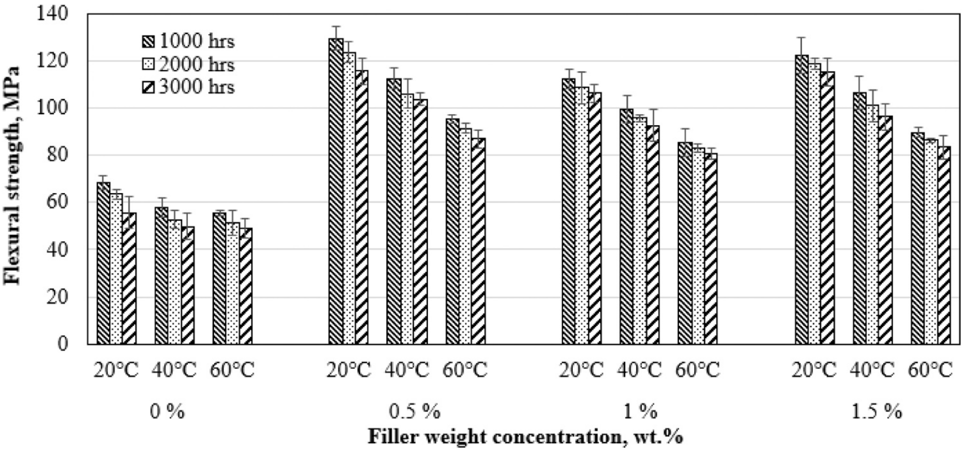


Fig. 4. : Flexural strength of hybrid composites under hygrothermal conditioning.

graphene are presented in Fig. 5. Composites without graphene exhibited FS retention of 83%,77%, and 67% after 1000, 2000, and 3000 hours, respectively after conditioning at 20 °C, while the hybrid composites retained at least 97.7%, 94.8% and 92.1% for 0.5% graphene, 87%, 84.3% and 82.5% for 1% graphene, and 97%, 92.6% and 86.6% for 1.5% graphene of their initial FS at the same conditioning temperature and exposure durations, respectively. This confirms that the higher FS retention associated with the addition of graphene is attributed to the improved interfacial bond strength of the fibres with the matrix. Increasing the conditioning temperature to 40 °C affected the FS retention of the hybrid composites, where 85.1%, 80.8% and 77.7% for 0.5% graphene, 77%, 74.4% and 72% for 1% graphene, and 84.8%, 79.5% and 77.1% for 1.5% graphene of their FS were retained after 1000, 2000, and 3000 hours, respectively. The lower strength retention can be attributed to the mismatch of thermal expansion coefficients for flax fibre, epoxy resin, and graphene particles used in the hybrid composites; where the thermal expansion coefficient of graphene and its derivatives typically ranges from 7×10^{-6} K^{-1} to -0.77×10^{-6} K^{-1} [72], and the flax fibre with a negative thermal expansion coefficient is -8×10^{-6}/°C in its longitudinal direction as reported in the literature [73,74], while the thermal expansion coefficient of epoxy matrix is 64–68 $\times 10^{-6}$ K^{-1} [72]. The resulting difference due to this strong mismatch leads to the development of different points of thermal stress concentration at the composite interface, which in turn weakens the interfacial adhesion strength and thus causes a lower FS. With the conditioning temperature increased to 60 °C, the hybrid composites experienced low strength retention for three conditioning durations. Nevertheless, the FS results of the hybrid composites even after a longer exposure to hygrothermal conditioning at elevated temperature, are still much higher than those of flax fibre composites without graphene. The higher strength retention of the hybrid composites than without graphene is attributed to the hydrophobic nature of the graphene nanoparticles which reduced the moisture absorption by increasing the mechanical interlocking between the fibre and matrix. It can be noted that the effect of increasing the conditioning temperature on FS retention was more pronounced than the effect of increasing the exposure duration. This is evidenced by the comparative results between the samples with 1.5% graphene conditioned at 20 °C for 3000 hours and the same samples conditioned at 60°C for 1000 hours, where the previous samples at 20 °C retained most of their initial flexural strength (86.6%) and the latter retained only 71.6% of their strength. This demonstrated that the degradation at the interface, likely related to the moisture content, of hybrid composites increased at elevated temperature. Thus, the interfacial bond strength becomes weak, causing the fibre to separate from the matrix as shown in the SEM image in Fig. 10 (2 d left). It is worth noting that since the hygrothermal conditioning at elevated temperature (60 °C) is close to the T_g of 78 °C for the hybrid composites, the FS, which is a mechanical property is expected to decrease as reported in the literature [17,37].

3.2.2. *Flexural modulus*

Flexural modulus (FM) of hybrid composites with graphene at different weight ratios under hygrothermal conditioning is illustrated in Fig. 6. A lower flexural modulus was observed for all samples conditioned at higher temperatures with longer duration. The higher temperature accelerates the diffusion of moisture inside the composite matrix which in turn increases the absorbed moisture content. Since this property is mainly controlled by the properties of the fibre, the high

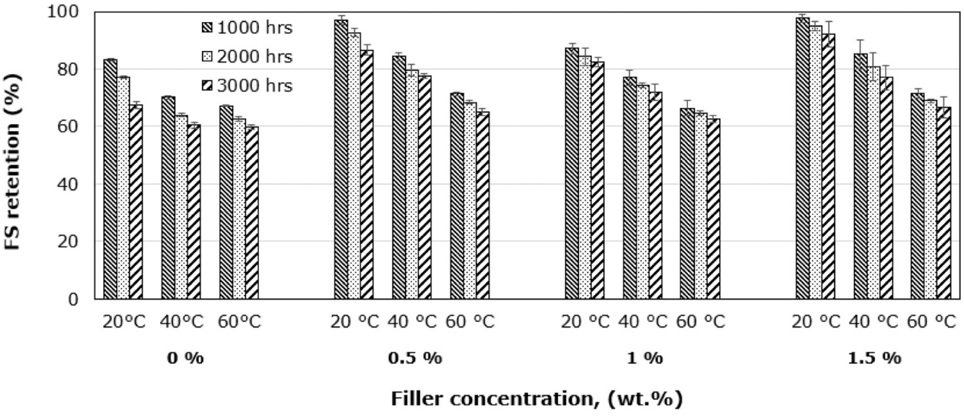


Fig. 5. : Flexural strength retention of hybrid composites under hygrothermal conditioning.

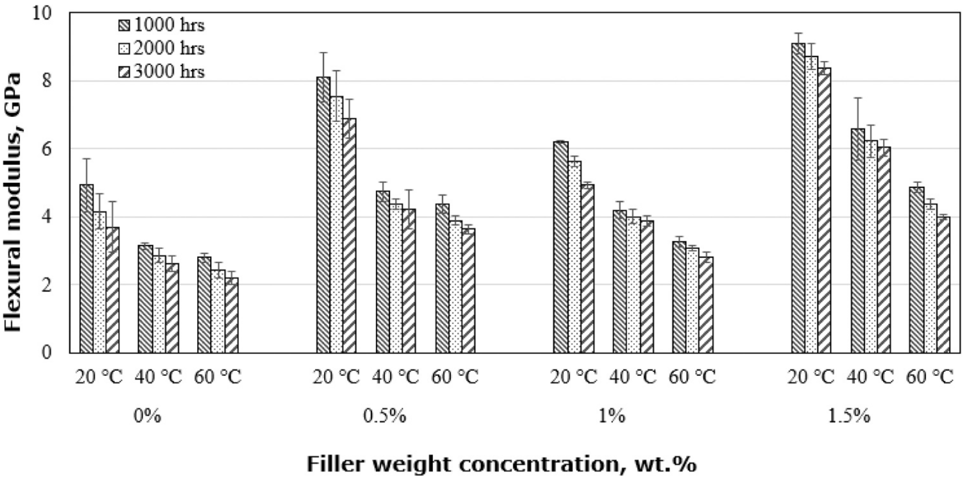


Fig. 6. **:** Flexural modulus of hybrid composites under hygrothermal conditioning.

amount of moisture absorbed by the fibre dramatically reduces the FM values. This is because the higher moisture content facilitates the swelling of the reinforced fibre and plasticises the fibre/matrix interface. Fibre swelling was observed as micro-cracks at the matrix as shown in the SEM image in Fig. 10 (2 c), while the plasticising phenomenon was observed in the form of a decrease in the T_g. According to previous work by Oun et al.[36], graphene reduces the long-term water absorption of hybrid flax fibre-reinforced epoxy composites and helps to retain most of its mechanical properties. The hybrid composites experienced higher FM values relative to the control samples (without graphene addition). This increase in FM values is due to the fact that graphene nanoparticles have higher stiffness than the matrix [75,76], and the protective role of graphene layers contributed to the reduction of the moisture absorption content. The hybrid composites with 1.5% graphene showed lower moisture content with higher FM values than those of samples with 0.5% and 1%. This attributes to the fact that the high amount of graphene made the matrix more rigid which in turn prevented the flax fibre from swelling to a large extent and thus limiting the occurrence of micro-cracks in the composite structure. The SEM image in Fig. 10 (2 d) supports this result, with no cracks visible in the matrix. Therefore, the limited fibre swelling has a positive effect on the FM of the hybrid composites with 1.5% graphene, as this effect confirms the mechanical interlocking of the fibre with the matrix. However, the flexural modulus of hybrid composites with 1% graphene is affected by the higher rate of moisture absorption within their structure. This increase in moisture content appears to be due to the relative increase in voids caused by the increased complexity of the epoxy resin flow path during the composite manufacturing process [77]. Reddy et al. [78] also explained that moisture absorption increases in the samples that have defects during the manufacturing process. Thus, these samples experienced a significant decrease in FM values due to the higher moisture absorption content, which caused swelling and softening of the flax fibre and the matrix, respectively. It is worth mentioning that during the manufacturing of the plate with 1.0% of graphene, a slight air leakage was noted in the vacuum bag during the curing. This may be responsible for the air entertained in the manufactured plate resulting a lower quality composite and with high void content.

Fig. 7 shows the FM retention of conditioned hybrid composites with different graphene weights. Regardless of conditioning temperature and duration, hybrid composites with 0.5%, and 1.5% graphene exhibited higher FM retention relative to the control samples (without graphene addition), due to less moisture absorption, as described in the above paragraph while the conditioned samples with 1% of graphene retained lower values of their initial FM compared to the control samples due to the higher absorbed moisture content. This phenomenon can be explained by the fact that swelling of the reinforced fibres causes stress concentration in the interfacial region of the specimen, which leads to a small cracking mechanism within the epoxy matrix near these swollen fibres. These micro-cracks provide a pathway for the transfer of water molecules by capillaries through the interface as shown in the SEM image of Fig. 10 (2 c). Thus, it caused more interface deterioration and decreased modulus retention. As shown in Fig. 7, the higher modulus

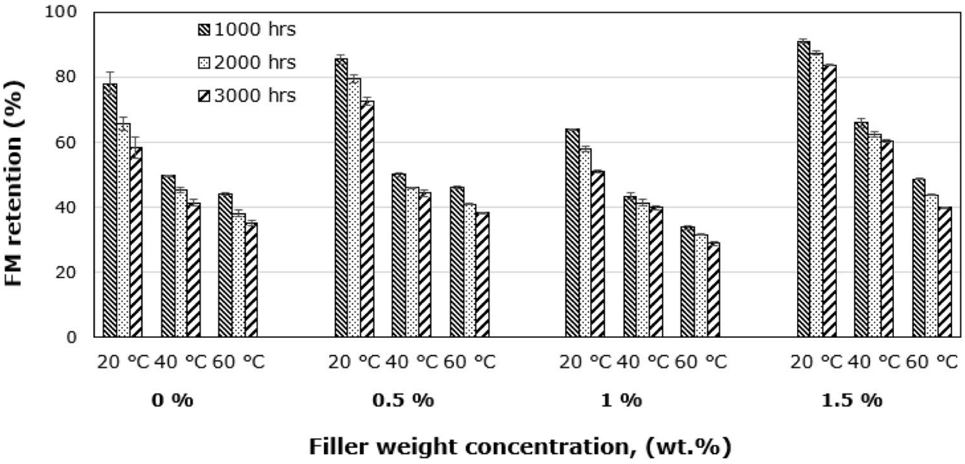


Fig. 7. **:** Flexural modulus retention of hybrid composites under hygrothermal conditioning.

retention was observed at lower temperature and exposure duration. For example, the control samples were able to retain 78%, 66%, and 59% of the initial FM after 1000, 2000, and 3000 hours of conditioning at 20 °C, while hybrid composites retained at least 85.5%, 79.5% and 72.6% for 0.5% graphene, and 91%, 87% and 83.4 for 1.5% graphene, respectively, after 1000, 2000, and 3000 hours of conditioning at the same temperature. However, the further reduction in FM observed in the hybrid composites with 0.5% and 1.5% graphene conditioned at 40 °C is attributed to the extensive differences between the thermal expansion coefficients of the types of materials used in the hybrid composites, where 50%, 46% and 44.4% for 0.5% graphene, and 66%, 62.3% and 60.4% for 1.5% of their initial FM were retained. Further increment of exposure temperature to 60 °C caused a higher decrease in FM of the hybrid composites by 46%, 41.1%, and 38.3% of their FM with 0.5% graphene and 48.7%, 43.8%, 40% with 1.5% graphene at 1000, 2000, and 3000 hours, respectively. This reduction is due to the conditioning temperature which causes the matrix to soften during the aging and to absorb more moisture. From these results, the lower modulus retention of these hybrid composites conditioned at 60 °C compared to room temperature (20 °C) confirms the effect of increasing temperature on accelerating moisture diffusion, regardless of conditioning duration.

3.3. Interlaminar shear strength (ILSS) under hygrothermal condition

The results of interlaminar shear strength (ILSS) tests on hybrid flax fibre-reinforced epoxy composites with different graphene percentages under hygrothermal conditions are shown in Fig. 8. Similar to FS, it can be seen that the addition of graphene enhanced the ILSS because of the decrease in the absorbed moisture. The decrease in moisture content appears to be attributed to the relative improvement in the interfacial adhesion. For all types of hybrid composites, their ILSS are higher compared to the control samples (without graphene addition) in all exposure conditions. The high ILSS strength of the hybrid composites results from the mechanical interlocking of the fibres with the matrix by the active surface area of the graphene nanoparticles as also indicated by Pathak et al. [71]. This result is supported by the FTIR data shown in Fig. 11, where shifting of the peaks to lower wavenumber position in hybrid epoxy composites confirms the hydrogen (H) bonding of graphene with the epoxy matrix. Improving the fibre/matrix interface by the addition of graphene effectively improves the load transfer from the matrix to the fibres, as graphene nanoparticles bridge the matrix and fibre [79]. However, the ILSS results for hybrid composites with higher graphene content were affected by the bonding strength at fibre-matrix interface and the wettability of the epoxy matrix as the viscosity of epoxy resin was increased. This result agrees with the findings obtained by Cheon and Kim [80] for carbon fibre-reinforced thermoplastic composites with multi-walled carbon nanotubes. Moreover, increasing the amount of graphene contributes to increasing the van der Waals' force among graphene particles which affects the dispersion of graphene in the matrix leading to filler aggregation as confirmed by the SEM in Fig. 10 (2 c and 2 d). This aggregation reduces active surface area of graphene particles to interact with the epoxy matrix and thereby decreasing the ILSS strength. Because graphene nanoparticles with higher surface area provide higher load-transfer efficiency when their degree of dispersion is appropriate [67]. Although there was a reduction in the ILSS caused by filler agglomeration, increasing the conditioning temperature had also a significant effect. Fig. 9 illustrates the ILSS retention as a function of the hygrothermal conditioning at elevated temperatures. In all conditions, the ILSS retention of the hybrid composites is higher than that of flax fibre composites, which confirms the beneficial effect of adding graphene nanoparticles to the epoxy matrix. However, the increase of temperature lowered the durability behaviour and ILSS retention of all types of hybrid composites under all conditions. Increasing the conditioning temperature from 20 °C to 40 °C showed a further decrease in the ILSS strength values due to a significant mismatch in the coefficients of thermal expansion between graphene, fibre, and epoxy matrix. The most obvious effect of temperature increase on ILSS retention was when these hybrid composites were conditioned for a longer duration. After 3000 hours of exposure duration, the ILSS strength of conditioned hybrid samples filled with 0.5%, 1%, and 1.5% graphene decreased to 74%, 70%, and 72%, respectively, when the conditioning temperature was increased up to 60 °C. Nevertheless, the hybrid composites benefited greatly from the addition of moisture-resistant graphene nanoparticles, as they were able to retain a higher percentage of their strength than the control samples.

3.4. SEM and FTIR analysis on fracture surface

3.4.1. SEM analysis

Fig. 10 shows the SEM results of hybrid composites with various graphene weights under mechanical tests before and after hygrothermal conditioning in terms of fractured surfaces at the tensile zone of the specimens tested under bending and filler distribution in the hosting matrix. Compared to the samples without hygrothermal conditioning (group1), the SEM images in Fig. 10 (group 2) indicate the strong influence of interfacial adhesion of the composite materials on their strength after hygrothermal exposure. As shown in Fig. 10 (2 a), flax fibre composites had a weak interfacial bond, as evidenced by the clear gaps between the flax fibre and the matrix, with severe fibre pull out present, while flax fibre composites without conditioning showed less fibre pull out and little gabs between the flax fibre and the matrix (see Fig. 10 (1 a). This demonstrates how moisture absorption affects

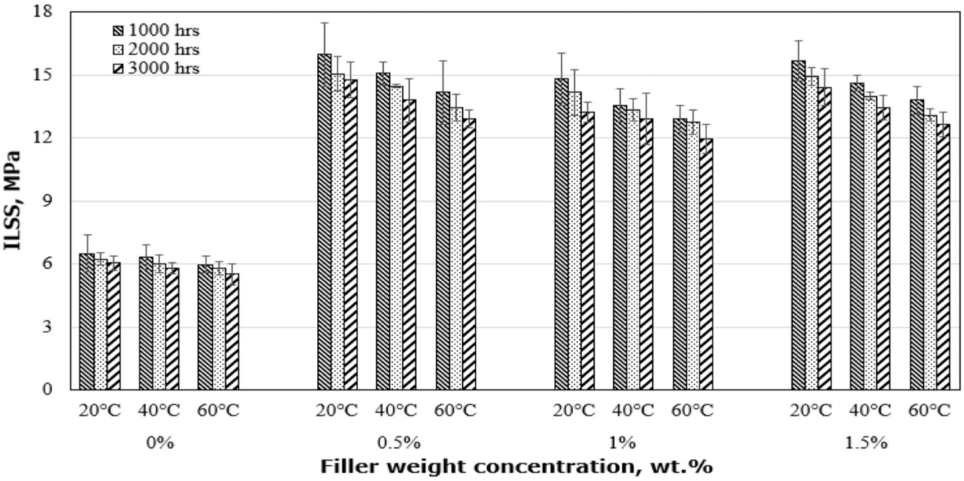


Fig. 8. **:** Interlaminar shear strength of hybrid composites under hygrothermal conditioning.

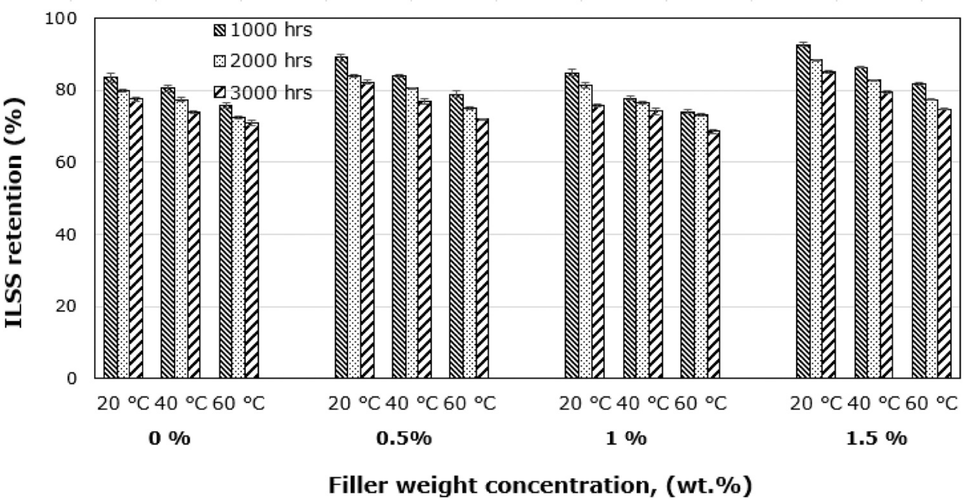
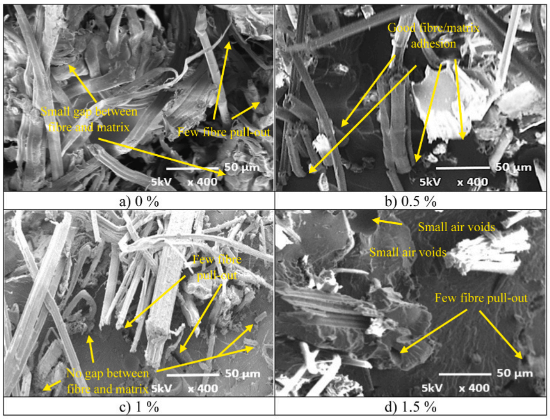


Fig. 9. : ILSS retention of hybrid composites under hygrothermal conditioning.

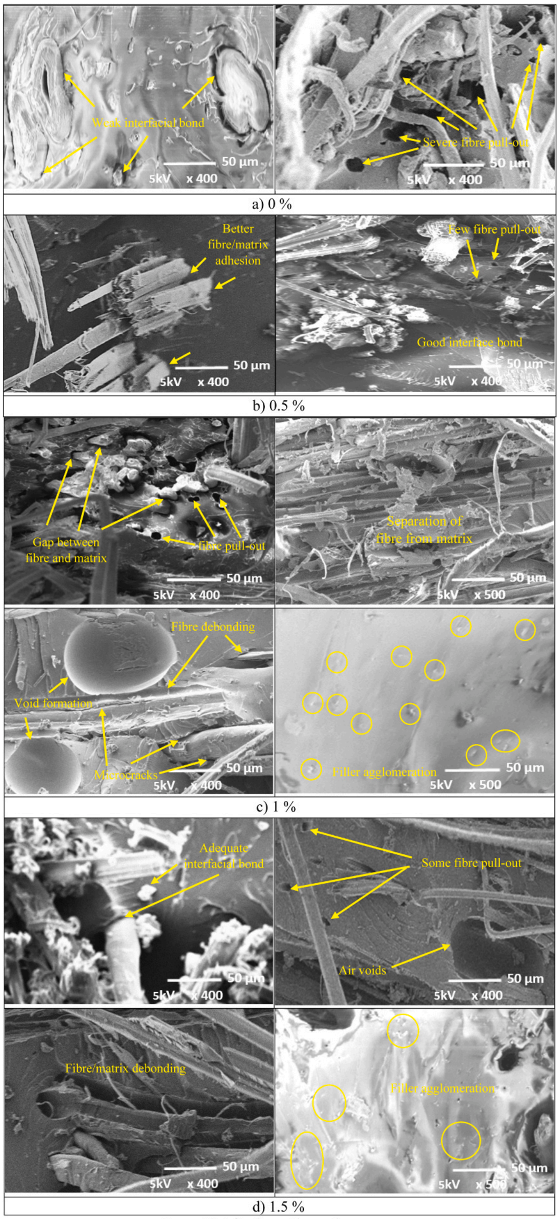
interfacial bond strength after immersion in water which is characterised by the appearance of a gap between the epoxy matrix and flax fibre, and fibre pull out in the microstructure of flax fibre composites. The explanation of moisture absorption mechanism is that the internal composition of natural plant fibre containing cellulose fibrils is responsible for the strength of the fibre since the cellulose molecules in natural plant fibre are tightly bound to each other by means of close intermolecular bonds in the cellulose network structure of the fibre. When the samples are immersed in water, the water molecules diffuse between fibre and matrix through capillary mechanism. This diffusion forces the cellulose molecules to separate and destroys the structural rigidity of the cellulose molecules by reducing the holding force between them in the cellulose network structure due to the action of the water molecules as a plasticizer, thus the cellulose molecules move freely resulting in the softening of the cellulose mass. This can easily contribute to fibre dimension changes when mechanical loads are applied. This effect of moisture absorption on the interfacial bond strength was reported by Alomayri, Assaedi [81] who investigated the effect of water absorption on mechanical and physical properties of cotton fabric reinforced geopolymer composites. A similar remarkable effect in interfacial adhesion was also reported by Dhakal, Zhang [82] who studied the influence of water absorption on the mechanical properties of unsaturated polyester composites reinforced with hemp fibres. This explains their low mechanical strength after hygrothermal conditioning. However, the incorporation of graphene nanoparticles into the epoxy matrix improved the fibre/matrix interface adhesion, which results in the high mechanical strength retention of hybrid composites even after subjecting to hygrothermal environment. This improvement was observed in the hybrid composites with 0.5% graphene, with few fibre pull out detected (see Fig. 10 in 2 b right). Fig. 10 (2 b left) shows a complete adhesion of the flax fibre to the epoxy matrix as also shown in the samples without conditioning (see Fig. 10 in 1 b), which explains less moisture absorption content. The SEM micrograph in the Fig. 10 (2 b right) did not show filler aggregation or air voids in the interface of the composites with 0.5% graphene, which indicates good interface. Further amount of graphene in flax fibre composites affects the interface negatively, resulting in filler agglomeration, and finally decreasing their strength retention, but still higher than flax fibre composites. Fig. 10 (2 c and 2 d right in the bottom photos) shows that hybrid composites with 1% and 1.5% graphene had filler agglomeration in the matrix, indicating a reduced quality of the interface bond between the fibre, matrix, and filler. Moreover, there were more voids observed by SEM at the interfaces of composites with higher graphene content (see Fig. 10 in 2c left in the bottom photo). A higher number of voids observed in the composites with 1% graphene, could be related to the fabrication process, and these air voids may have contributed to the diffusion of water molecules within the microstructure which in turn explains the higher content of moisture absorption and lower mechanical strength retention of these samples. The SEM micrograph of the specimens with 1% graphene obviously showed a prominent gap between the flax fibre and the epoxy matrix due to higher moisture absorption (see Fig. 10 in 2c left). Thus, the expansion of these micro-gaps at the interface with increasing moisture content caused the fibre to separate from the matrix as shown in Fig. 10 (2c right). Micro-cracks developed in the interface of specimens with 1% graphene caused by swelling of the fibre were shown in Fig. 10 (2c left). Micrographs of the hybrid composites with 1.5% graphene revealed that the tracks of fibre pull-out were lower than in the samples with 1% graphene (see Fig. 10 in 2 d right), with lower fibre/matrix debonding present in Fig. 10 (2 d left in the bottom image), indicating adequate interfacial bond as shown in Fig. 10 (2 d left in the above image). However, hybrid composites with 1% and 1.5% graphene after hygrothermal conditioning (see Fig. 10 in 2c and 2 d left and right) exhibited higher volume of voids and more separation of fibres from the matrix than the same samples with 1% and 1.5% graphene before hygrothermal conditioning as shown in Fig. 10 (1 c and 1 d). The observed damage to the interfacial bond of the fibres with the matrix due to the combined effect of moisture and high temperature resulted in a decrease in the mechanical properties over time. Berges et al.[83] observed that moisture absorption can degrade the adhesion of fibre to matrix at the composite interface, which reduces the effectiveness of stress transfer from the epoxy matrix to the fibres via the interfacial region. Akil et al.[84] also explained that moisture absorption causes the fibre to swell which in turn creates swelling stress points located at the interface region. This results in a weakening of the fibre/matrix interface and thereby in the properties of the composites. Guermazi et al.[85] indicated that the absorbed moisture increases the plasticity of the composite when exposed to high temperature for a longer duration. The phenomena of matrix plasticization and fibre swelling weaken the strength of the fibre/matrix interface, resulting in lower mechanical properties of the composite.

3.4.2. FTIR analysis

Fig. 11 compares typical FTIR spectra analysis of hybrid composites with different graphene loadings before and after conditioning. No changes in functional groups were observed between the conditioned samples and the control sample except for a shift in some bands indicating that there is no chemical change has occurred during the hygrothermal conditioning. Therefore, the infrared spectra were analysed only for the samples without graphene. As shown in Fig. 11, three functional groups present in samples without graphene are considered



Group 1) Before hygrothermal exposure



Group 2) After hygrothermal exposure

Fig. 10. : SEM micrographs of hybrid composite surfaces before and after hygrothermal exposure.

as major spectral regions.

The first group of infrared analysis revealed a broad band in the range of 3600–3200 cm^{-1} caused by the stretching vibration of hydroxyl (OH) groups [86], for all samples, indicating the presence of water in the polymeric matrix. The second group of spectral band appearing at 2930–2890 cm^{-1} is related to the stretching vibration of carbon hydrogen (CH) groups [87,88], and the characteristic absorption band at 2180 cm^{-1} is associated with CO [89]. The third group includes spectral bands in the region below (2000 cm^{-1}). The spectral position of absorption band at around 1730 cm^{-1} is attributed to the C = O stretching vibration in the ester group [90]. The sharp absorption bands at 1615 and 1507 cm^{-1} can be assigned as C═C, which is attributed to the stretching in alkenes and aromatics, respectively [91]. The sharp absorption band found at 1300–1200 cm^{-1} is due to the C-O stretching vibration in the ester group [92]. The apparent bands around the 1237 and 1035 cm^{-1} region are associated with the asymmetric and symmetric stretching vibration of C-O-C [93]. The spectral absorption band located in the region of about 827 cm^{-1} corresponds to the C–H bending in the benzene ring [87]. For comparison purpose, shifting the OH peak to lower wavenumber position is attributed to the increase of intermolecular hydrogen bonding caused by the increased amount of filler in the epoxy matrix [94–96]. For example, the stretching vibration of the OH peak at about 3372 cm^{-1} for the sample without graphene shifted to 3360, 3353, and 3341 cm^{-1} for samples with 0.5, 1%, and 1.5% graphene, respectively, as shown in Fig. 11. This confirms the occurrence of hydrogen bonding in the graphene/epoxy matrix composites as was also observed by Yousefi et al.[97] for the mechanical, electrical and thermal properties of reduced graphene oxide/epoxy composites. From FTIR spectra analysis, there is no signs of chemical degradation in the epoxy matrix during hygrothermal aging. This fact was confirmed by the absence of changes in the infrared spectra of the conditioned samples when compared to the control sample in Fig. 11.

4. Service life prediction of hybrid composites using Arrhenius rate model

The experimental results in this study showed deterioration of the hybrid composites materials under the combined effect of high moisture and in-service elevated temperature. Thus, the accelerated test results of these composites were used with the Arrhenius concept to develop master curves for predicting their service life. The predicted service life of NFRP composites with graphene will assist in the effective design of these materials.

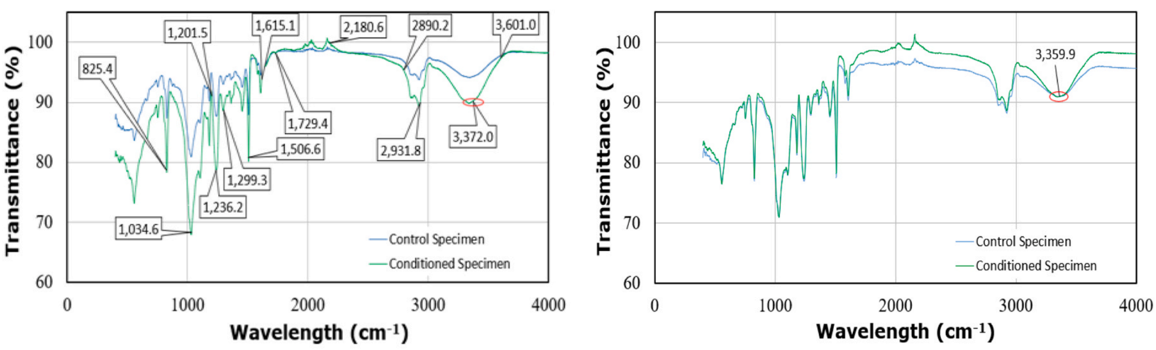
4.1. Arrhenius rate model

Arrhenius rate model is commonly applied in an accelerated life model based on the assumption that there is no change in a single dominant mechanism of deterioration either over time or within the accelerated aging temperature range, but only the deterioration rate accelerates with increasing temperature. The results for the accelerated aging tests of this study validated this assumption. Thus, the Arrhenius relationship can be expressed in terms of the rate of deterioration by Eq.2.

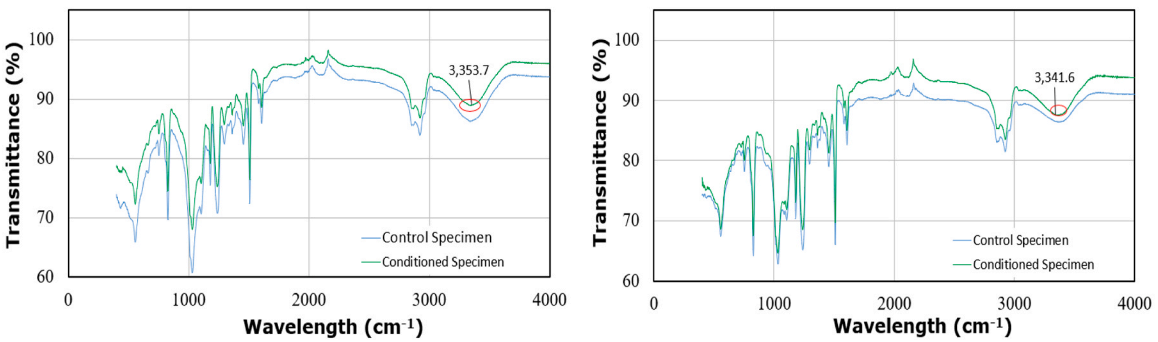
$$K = A \exp [-E_a / RT] \tag{2}$$

The symbols K, E_a, R, T, and A in the Arrhenius equation indicate the deterioration rate, activation energy, universal gas constant, absolute temperature in Kelvin scale, and material constant, respectively. The deterioration rate K shown in Eq. 2 can be transferred to the inverse of time required for the material property to reach a certain value by taking the natural logarithms on both sides of this equation, to give a linear fit of the Arrhenius relation, in the form provided by Eq.3.

$$\ln (1/ k) = E_a / RT(1/T) - \ln (A) \tag{3}$$



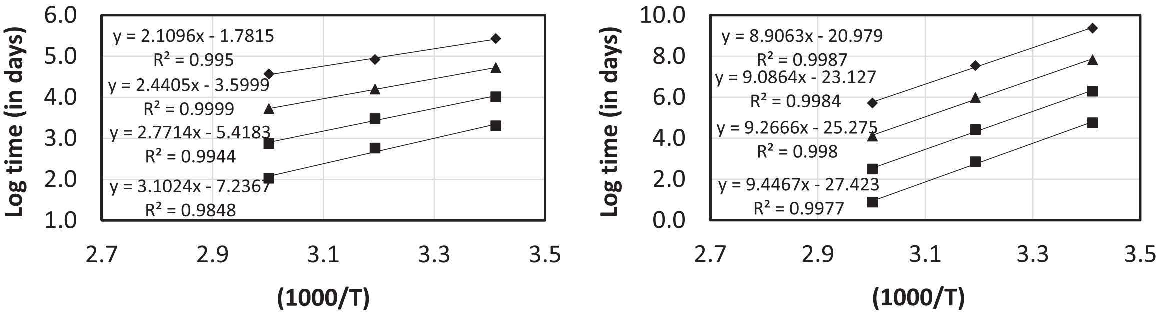
a) Specimen with 0 % b) Specimen with 0.5 %



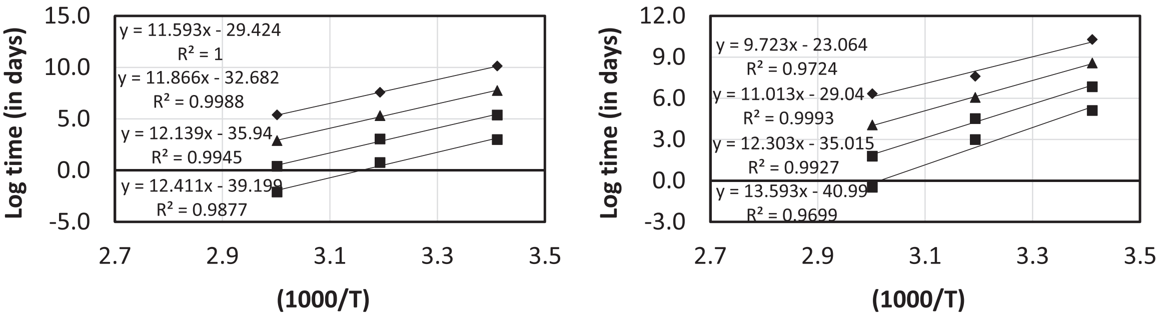
c) Specimen with 1 % d) Specimen with 1.5 %

Fig. 11. : FTIR spectra of hybrid composites.

Based on the average experimental results of this study, the strength retention values of mechanical property at different exposure time are found by dividing the average mechanical strength of the conditioned specimens by the control specimen. The time in days to attain specific mechanical strength retention levels of 90%, 80%, 70% and 60% at conditioning temperature of 20 °C, 40 °C, and 60 °C was then estimated by applying these different mechanical strength retention values to the regression equations. When plotting the logarithm of time required for the FS and ILSS retention levels at different conditioning temperatures (in the y-axis) versus the inverse of absolute temperature (1000/T) (in



a) 0 % b) 0.5 %



c) 1 % d) 1.5 %

Fig. 12. Arrhenius plot for FS retention of hybrid composites with various levels of graphene.

the x-axis), the regression coefficient (Ea/R) can be estimated. The slopes of all temperature regression curves have to be approximately equal, otherwise the deterioration mechanism of these composite materials is temperature dependent. In this study, the relationships between the regression results of Eq. (3) showed parallel straight lines, as shown in Figs. 12 and 13, and validated our data for accelerated aging tests. Arrhenius plot regression analysis was then performed to determine a linear fit for each data set at a given temperature and the average slopes of these straight lines represent the values of E_a/RT. Similar slopes shown in Figs. 12 and 13 for these conditioning temperatures with the regression values R^2 of at least 0.90 as were also observed by Silva et al. [48] and Manalo et al.[53], indicating that this kind of deterioration rate in FS and ILSS for the hybrid composites with graphene can be reliably predicted by the Arrhenius model. However, there are some major limitations in this model as follows: (i) the use of Arrhenius model cannot always describe the effects of temperature on degradation kinetics[98,99]. (ii) there is no hypothesis associated with the dominant degradation mechanism of the materials, and it is just a phenomenological analysis to represent the experimental data [100].

4.2. *Time shift factor (TSF)*

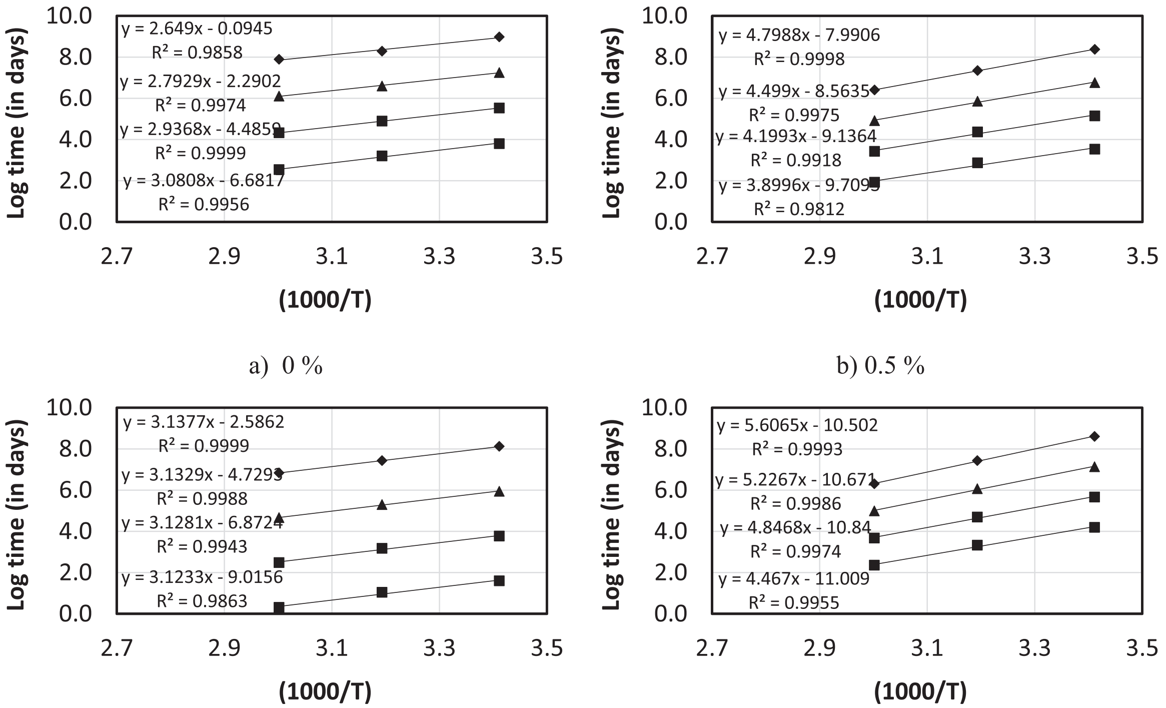
The time shift factor (TSF) is the ratio among the times required for a given reduction in a property retention at two various conditioning temperatures as defined by Dejke [101]. By using the average values of the regression coefficient (E_a/R) obtained from the previous Arrhenius plots, it can determine the time shift factor. The results are summarized in Table 3 obtained from Eq. 4, where t_1 and t_2 are the times in days that were used to predict a certain strength retention at the reference temperature (T_0) and exposure temperature (T_1), and the degradation rates at t_1 and t_2 are k_1 and k_2, respectively.

$$TSF = \frac{t1}{t2} = \frac{k2}{k1} = \frac{A \quad X \quad e^{\left(\frac{-Ea}{RT1}\right)}}{A \quad X \quad e^{\left(\frac{-Ea}{RT0}\right)}} \quad = \quad e^{\left(\frac{-Ea}{R}\right)\left(\frac{1}{T1}-\frac{1}{T0}\right)} \tag{4}$$

Table 3
Time-shift factor and Ea/R values of hybrid composites at different temperatures.

Type of Test	Graphene content (%)	E_a/R	Time Shift Factor (TSF) at temperatures			
			20 °C	30 °C	40 °C	60°C
Flexural	0.0	2.6	1.0	1.3	1.8	2.9
	0.5	9.2	1.0	2.8	7.4	42.9
	1.0	12.0	1.0	3.9	13.7	136.3
	1.5	11.7	1.0	3.7	12.7	118.5
Interlaminar	0.0	2.9	1.0	1.4	1.9	3.2
	0.5	4.3	1.0	1.6	2.6	5.9
	1.0	3.1	1.0	1.4	2.0	3.6
	1.5	5.0	1.0	1.8	3.0	7.9

The TSF can then be used to shift the strength retention plots obtained from accelerated aging tests in laboratory conditions to a longer-term degradation plot. The reference temperature in this study was set at room temperature (20 °C) and the time safety factor was considered to be 1.0 at this temperature since degradation rates are measured very low when such composite materials are exposed to this level of temperature [102]. Therefore, the time safety factor was not measured to account for 20 °C due to its lower degradation rates. The calculation of time shift factors increases with increasing conditioning temperature for faster degradation rates. The level of temperature in all exposure conditions is carefully selected such that it will not have an effect the degradation of the hybrid composites. This approach is widely accepted in this area and adopted by many researchers in investigating the degradation and stability of polymeric composites. The TSF values in our study were calculated for temperatures up to 60 °C which are much lower than the glass transition temperature for the composites. For the purpose of predicting the long-term durability performance based on the Arrhenius equation, experimental short-term data have to be collected with a minimum of three different conditioning durations for three different conditioning temperatures. The selection of these conditioning durations and temperatures must be clearly spaced within a certain range to



a) 0 %

b) 0.5 %

c) 1 %

d) 1.5 %

Fig. 13. Arrhenius plot for ILSS retention of hybrid composites with various levels of graphene.

have a clear degradation mechanism resulting from the accelerated tests.

4.3. Development of master curves

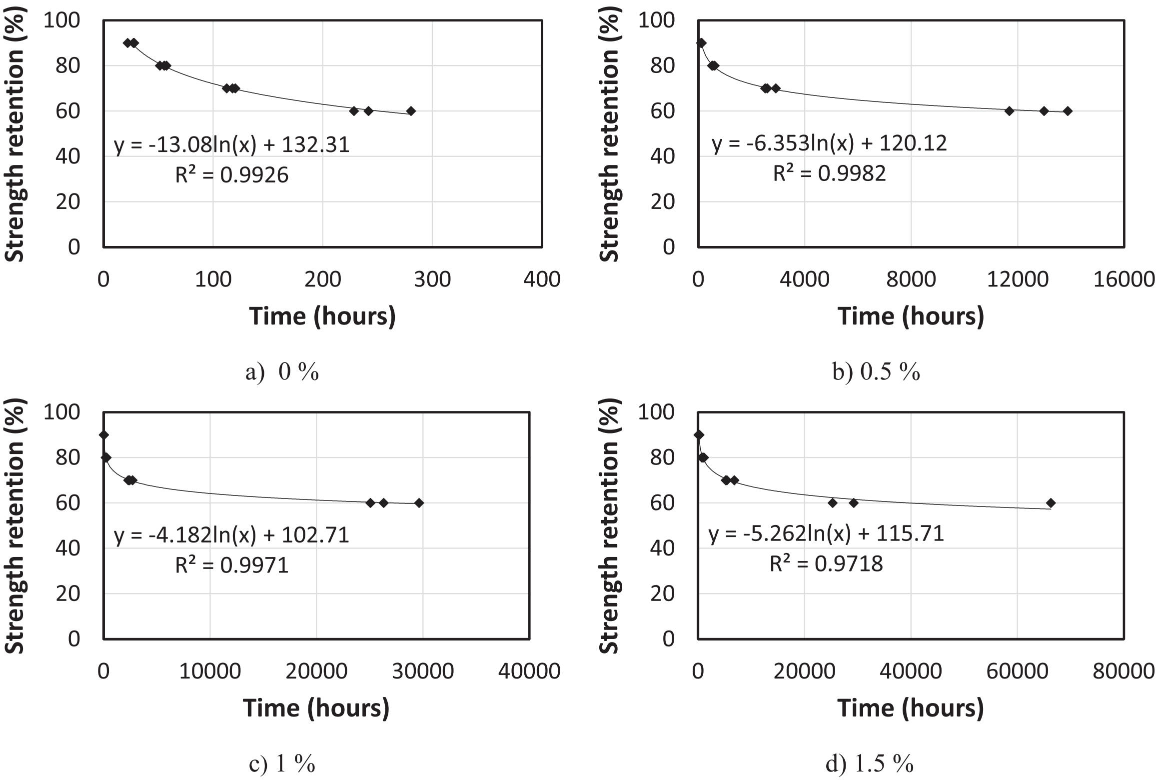
The master curves were developed using accelerated aging tests for this study along with the concept of Arrhenius model. These curves can provide all the data required for every retention level as suggested by Ali et al.[103], corresponding to its TSF obtained from Eq. 4. The master curves at conditioning temperature of 20 °C shown in Figs. 14 and 15 represent the relationship between the strength retention (in y-axis) of hybrid composites and exposure time (in x-axis). The master curves for long-term strength prediction had high correlation coefficient values of at least 0.98 in all cases, indicating a high level of consistency in the analysis of the results.

4.4. Long-term durability prediction using master curves

The best way to predict the long-term durability of hybrid composites is to use the master curves developed in this study based on the accelerated aging data as suggested by Chen et al.[104]. The time in years to attain specific mechanical strength retention levels for hybrid composites with graphene was predicted by multiplying the accelerated aging time with the time shift factor for a given temperature and environment. The aging process varies with the average annual temperature of the site where the strength degradation requires to be known. The predicted strength retention in flexural and ILSS test specimens was made for 100 years of service life since the design of civil engineering structures in Australia should be in service for this period of time [17]. Based on the average annual temperature of Australia (30 °C), the developed master curves shown in Figs. 14 and 15 are transformed into Figs. 16 and 17, which present the equivalent service life of hybrid composites at this annual temperature. These master curves were generated based on the calculated TSF values at the annual temperature of 30 °C (Table 3) for the hybrid composites with and without graphene and using the resulting Arrhenius relationships in the form SR = a ln (t) + b, where SR, t, and (a and b) represent the strength retention, aging time, and regression constants, respectively.

It can be observed from Fig. 16 a-d that the FS retentions of hybrid composites with 0.5%, 1%, and 1.5% graphene would drop to 60% after 4500, 6300, and 11100 hours, respectively, while in the case of flax fibre composites could retain 60% after only 190 hours. This shows the role of the graphene filler blocking the infusion to the fibres assisting in significantly prolong the durability performance of the specimens tested under flexure which is a fibre-based structural property. The corresponding ILSS retention shown in Fig. 17 a-d for samples with 0.5%, 1%, and 1.5% graphene decreased to 60% for up to 2550, 2300, and 3000 hours. Whereas in the flax fibre composites, they were able to retain 60% of their ILSS after 6000 hours. As ILSS is mainly a resin-based structural property, the contribution of the filler to the resin property is insignificant. However, the reduction in the durability performance for the filled specimens is attributed to the time taken to defuse the moisture to the flax fibre evidenced by the less notable reduction compared to the specimens tested under flexure.

Based on these master curves developed with an average annual temperature of 30 °C in Figs. 16 and 17, the predicted FS and ILSS retentions in hybrid composites with different levels of graphene for 100 years of service at 30 °C are shown in Fig. 18. It is worth noting that normal natural fibre composites are not recommended for flexural applications as they can only retain 50% of their strength after 5 years in service. Whereas the hybrid composites showed significantly longer durability with a retention of 45–55% after 100 years (Fig. 18a). It should highlighted that FS is a complex property associated with a combination of compressive and tensile strength, which is directly different with ILSS [105]. The inferior durability behaviour with lower FS retention in flax fibre composites could be attributed to the degradation on the compressive and tensile surfaces (reduction in the effective thickness of the specimen). This finding also agrees with the results of study conducted by Khotbehsara et al. [96] for particulate filled epoxy polymers and they found that flexural samples showed lower strength



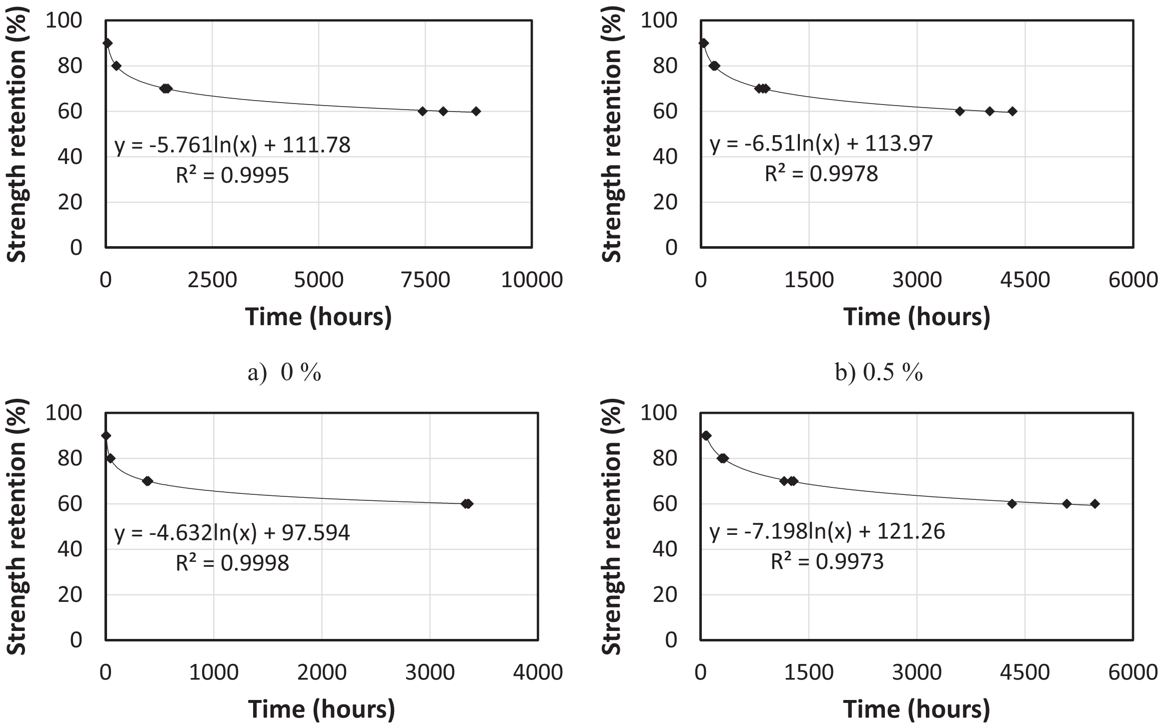
a) 0 %

b) 0.5 %

c) 1 %

d) 1.5 %

Fig. 14. **:** Master cures for FS retention of hybrid composites at 20 °C.



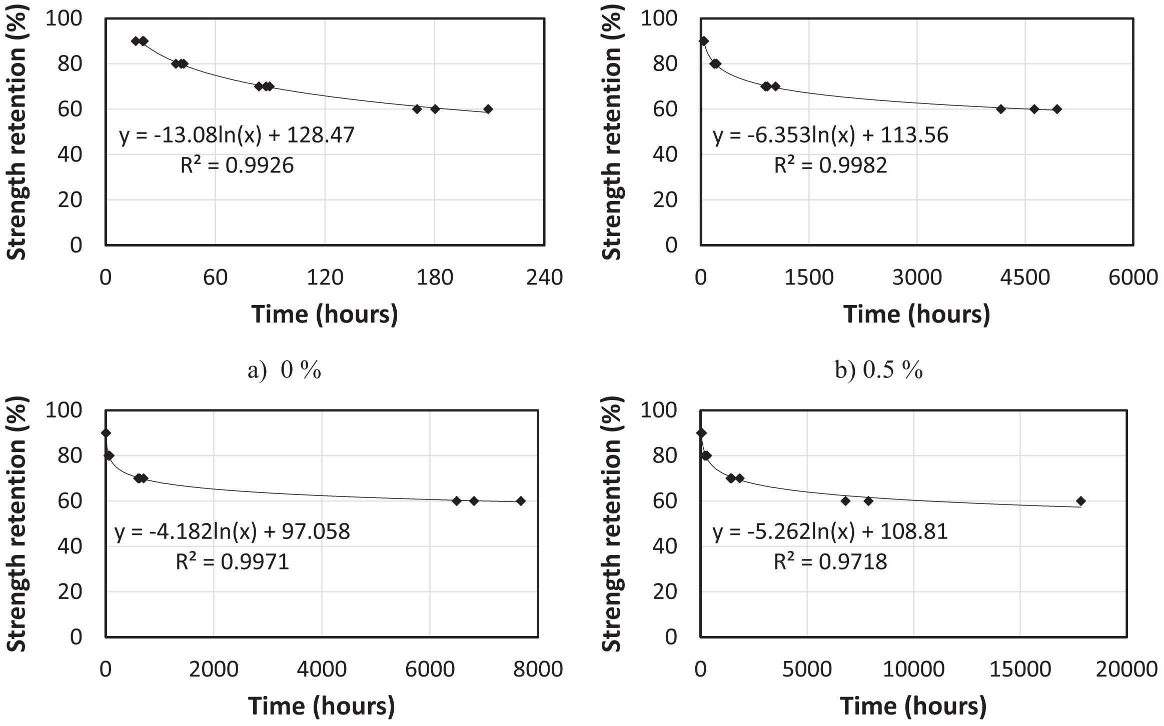
a) 0 %

b) 0.5 %

c) 1 %

d) 1.5 %

Fig. 15. : Master cures for ILSS retention of hybrid composites at 20 °C.



a) 0 %

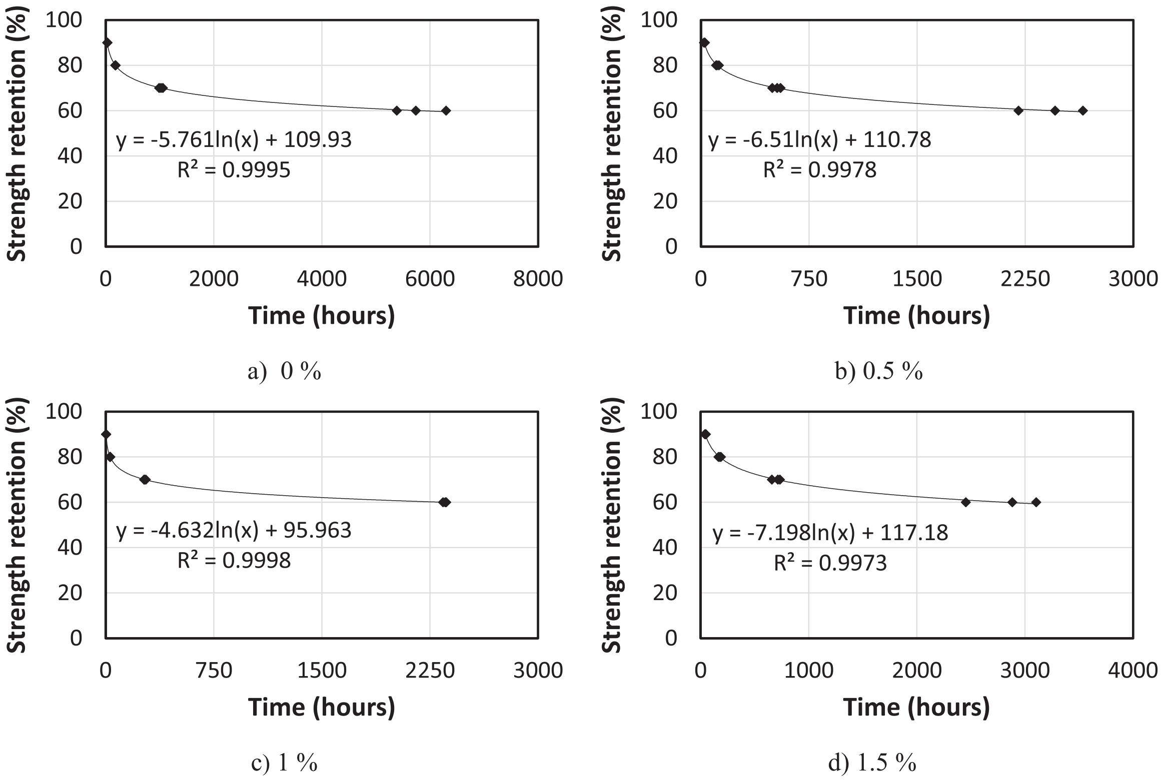
b) 0.5 %

c) 1 %

d) 1.5 %

Fig. 16. : Master cures for FS retention of hybrid composites at 30 °C.

retention than splitting tensile strength and compressive strength. The authors attributed this low flexural strength retention to degradation on the top and bottom surfaces of the sample caused by moisture absorption. Huner [106] investigated the mechanical properties of flax fibre/epoxy composites exposed to moisture environment and concluded that the properties of the specimen near the upper and lower surfaces strongly affect the flexural strength. On the other hand, graphene filler showed insignificant effect on the durability performance of



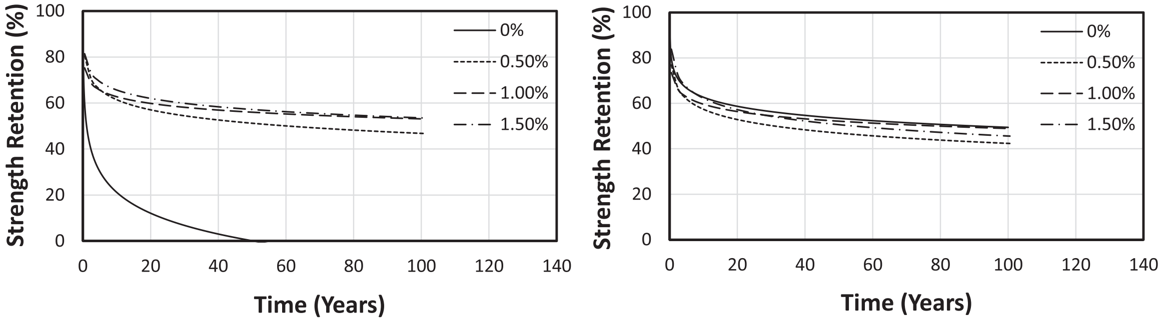
a) 0 %

b) 0.5 %

c) 1 %

d) 1.5 %

Fig. 17. : Master cures for ILSS retention of hybrid composites at 30 °C.



a) Flexural

b) Interlaminar

Fig. 18. : Service life of hybrid composites at 30 °C.

the natural fibre composites after 100 years which shows a strength retention of 40–50% regardless the graphene filler content. However, graphene filler played a major role to increase the ILSS strength of the flax fibre composites (up to 2.5 times, as shown in Fig. 8).

5. Conclusion

This study investigated the influence of hygrothermal conditioning on the flexural and interlaminar shear properties of hybrid flax fibre-reinforced epoxy composites with graphene. Hybrid composites with graphene ranging from 0, 0.5, 1.0, and 1.5% by weight of the hosting matrix were prepared and conditioned at 98% relative humidity for 1000, 2000, and 3000 hours at 20 °C, 40 °C, and 60 °C. Based on the experimental results, the main conclusions of this study can be drawn as follows:

- The moisture absorption of hybrid composites was significatly reduced by adding 0.5% graphene nanoparticles. The rate of moisture absorption decreased with the increase of graphene percentage. However, the moisture absorption rate increased with the increase of exposure duration and conditioning temperature.
- The influence of temperature on flexural and ILSS properties was more pronounced than exposure duration. After 3000 hours of conditioning at 20°C, the hybrid composites retained at least 82% of its flexural strength but only 66% when conditioned at 60 °C for 1000 hours. On the other hand, the ILSS retention of hybrid composites was 82% after conditioning at 20 °C for 3000 hours relative to 78% when conditioned at 60 °C for 1000 hours.
- The flexural modulus was more sensitive to moisture absorption and exposure temperature than the flexural strength because of high diffusion of the flax fibres. Regardless of conditioning temperature and duration, a higher modulus retention was observed in the natural fibre composites with graphene due to their role in blocking the moisture absorption.
- Hybrid composites with graphene can retain at least (45−55) % and (40−50) % of their ILSS and flexural strength, respectively after 100 years of service at an average annual temperature of 30 °C. This demonstrates the positive role played by graphene nanoparticles

enhancing, to a larger extent, the durability of flax fibre composites in outdoor application.

This study shows a guide for the natural fibre composite manufacturer on using additive manufacturing enhancing the long-term behaviour of such materials. It is recommended though to investigate other advanced manufacturing process, in industrial scale, (i.e., hot compress, prepreg or pultrusion processes) to scale up the outcome of this field of study. Similarly, other type of tests including Differential Scanning Calorimetry, TGA, Ellipsometry and among others can be conducted to support the observed degradation mechanisms of hybrid flax fibre-reinforced epoxy composites with graphene in hygrothermal environment.

CRediT authorship contribution statement

Allan Manalo: Writing – review & editing, Supervision, Conceptualization. **Rajab Abousnina:** Writing – review & editing, Supervision, Conceptualization. **Amer Oun:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Omar Saleh AlAjarmeh:** Conceptualization, Methodology, Formal analysis, Writing - review & editing, Supervision. **Andreas Gerdes:** Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors would like to declare and confirm that there is no conflict of interest of this manuscript.

Data availability

Data will be made available on request.

References

[1] D.S. Bajwa, S.G. Bajwa, G.A. Holt, Polym. Degrad. Stab. 120 (2015) 212–219.
[2] A. Lotfi, H. Li, D.V. Dao, G. Prusty, J. Thermoplast. Compos. Mater. (2019), 0892705719844546.
[3] A. Gopinath, M.S. Kumar, A. Elayaperumal, Procedia Eng. 97 (2014) 2052–2063.
[4] M.L. Broeren, S.N. Dellaert, B. Cok, M.K. Patel, E. Worrell, L. Shen, J. Clean. Prod. 149 (2017) 818–827.
[5] S.V. Joshi, L. Drzal, A. Mohanty, S. Arora, Compos. Part A: Appl. Sci. Manuf. 35 (3) (2004) 371–376.
[6] M. Nasihatgozar, V. Daghigh, T.E. Lacy Jr, H. Daghigh, K. Nikbin, A. Simoneau, Polym. Test. 56 (2016) 321–328.
[7] V.K. Balla, K.H. Kate, J. Satyavolu, P. Singh, J.G.D. Tadimeti, Compos. Part B: Eng. 174 (2019) 106956.
[8] M.Y. Khalid, A. Al Rashid, Z.U. Arif, W. Ahmed, H. Arshad, A.A. Zaidi, Results Eng. 11 (2021) 100263.
[9] G. Xian, R. Guo, C. Li, Compos. Struct. 281 (2022) 115060.
[10] M. Suriani, R. Ilyas, M. Zuhri, A. Khalina, M. Sultan, S. Sapuan, C. Ruzaidi, F. N. Wan, F. Zulkifli, M. Harussani, Polymers 13 (20) (2021) 3514.
[11] R. Latif, S. Wakeel, N. Zaman Khan, A. Noor Siddiquee, S. Lal Verma, Z. Akhtar Khan, J. Reinf. Plast. Compos. 38 (1) (2019) 15–30.
[12] K. Haag, J. Padovani, S. Fita, J.-P. Trouvé, C. Pineau, S. Hawkins, H. De Jong, M. K. Deyholos, B. Chabbert, J. Müssig, Ind. Crops Prod. 98 (2017) 1–9.
[13] V.K. Balla, K.H. Kate, J. Satyavolu, P. Singh, J.G.D. Tadimeti, Compos. Part B: Eng. (2019) 106956.
[14] Y. Wang, W. Zhu, B. Wan, Z. Meng, B. Han, Compos. Part A: Appl. Sci. Manuf. 140 (2021) 106142.
[15] D. Hristozov, L. Wroblewski, P. Sadeghian, Compos. Part B: Eng. 95 (2016) 82–95.
[16] D.U. Shah, P.J. Schubel, M.J. Clifford, Compos. Part B: Eng. 52 (2013) 172–181.
[17] M.M. Khotbehsara, A. Manalo, T. Aravinthan, W. Ferdous, K.T. Nguyen, G. Hota, Constr. Build. Mater. 249 (2020) 118846.
[18] H. Wang, G. Xian, H. Li, L. Sui, Fibers Polym. 15 (5) (2014) 1029–1034.
[19] D. Mamalis, C. Floreani, C.M.Ó. Brádaigh, Compos. Part B: Eng. 225 (2021) 109281.
[20] A. Wang, G. Xian, H. Li, Polymers 11 (8) (2019) 1278.
[21] S. Alessi, G. Pitarresi, G. Spadaro, Compos. Part B: Eng. 67 (2014) 145–153.
[22] M. Shaohua, Y. He, L. Hui, L. Xu, Adv. Compos. Mater. 29 (1) (2020) 55–72.
[23] Bachchan, A.A., P.P. Das, and V. Chaudhary, Materials Today: Proceedings, 2021.
[24] Z. Azwa, B. Yousif, Proc. Inst. Mech. Eng., Part L: J. Mater.: Des. Appl. 233 (6) (2019) 1065–1079.
[25] N. Jiang, T. Yu, Y. Li, T.J. Pirzada, T.J. Marrow, Compos. Sci. Technol. 173 (2019) 15–23.
[26] Z. Yang, G. Xian, H. Li, Polym. Compos. 36 (9) (2015) 1590–1596.
[27] Y. Li, B. Xue, Polym. Degrad. Stab. 126 (2016) 144–158.
[28] I. Widiastuti, Y.R. Pratiwi, D.N. Cahyo, Open Eng. 10 (1) (2020) 814–819.
[29] G. Ma, L. Yan, W. Shen, D. Zhu, L. Huang, B. Kasal, Compos. Part B: Eng. 153 (2018) 398–412.
[30] F.K. Sodoke, L. Toubal, L. Laperrière, Polym. Degrad. Stab. 161 (2019) 121–130.
[31] A. Regazzi, S. Corn, P. Ienny, A. Bergeret, Polym. Degrad. Stab. 130 (2016) 300–306.
[32] W. Wang, M. Sain, P. Cooper, Polym. Degrad. Stab. 90 (3) (2005) 540–545.
[33] D. Scida, M. Assarar, C. Poilâne, R. Ayad, Compos. Part B: Eng. 48 (2013) 51–58.
[34] A. Retegi, A. Arbelaiz, P. Alvarez, R. Llano-Ponte, J. Labidi, I. Mondragon, J. Appl. Polym. Sci. 102 (4) (2006) 3438–3445.
[35] W. Chunhong, L. Shengkai, Y. Zhanglong, J. Reinf. Plast. Compos. 35 (13) (2016) 1062–1074.
[36] A. Oun, A. Manalo, O. Alajarmeh, R. Abousnina, A. Gerdes, Polymers 14 (17) (2022) 3679.
[37] A. Oun, A. Manalo, O. Alajarmeh, R. Abousnina, A. Gerdes, Polymers 14 (2022).
[38] K. Eayal Awwad, B. Yousif, K. Fallahnezhad, K. Saleh, X. Zeng, Friction 9 (2021) 856–875.
[39] K.E. Awwad, B. Yousif, A. Mostafa, O. Alajarmeh, X. Zeng, J. Reinf. Plast. Compos. 42 (17-18) (2023) 939–952.
[40] A. Manalo, O. Alajarmeh, W. Ferdous, B. Benmokrane, C.-D. Sorbello, A. Gerdes, Constr. Build. Mater. 339 (2022) 127687.
[41] M. Brebu, Polymers 12 (1) (2020) 166.
[42] S. Firdosh, H.N. Murthy, R. Pal, G. Angadi, N. Raghavendra, M. Krishna, Compos. Part B: Eng. 69 (2015) 443–451.
[43] P. Alam, C. Robert, C.M.Ó. Brádaigh, Compos. Part B: Eng. 149 (2018) 248–259.
[44] X. Jiang, H. Kolstein, F. Bijlaard, X. Qiang, Compos. Part A: Appl. Sci. Manuf. 57 (2014) 49–58.
[45] A. Uthaman, G. Xian, S. Thomas, Y. Wang, Q. Zheng, X. Liu, Polymers 12 (3) (2020) 614.
[46] K.-t Lau, P.-y Hung, M.-H. Zhu, D. Hui, Compos. Part B: Eng. 136 (2018) 222–233.
[47] M. Bambach, Compos. Part C: Open Access 2 (2020) 100013.
[48] M.A. Silva, B.S. da Fonseca, H. Biscaia, Compos. Struct. 116 (2014) 377–387.
[49] A.K. Tareen, K. Khan, M. Iqbal, Y. Zhang, J. Long, F. Nazeer, A. Mahmood, N. Mahmood, Z. Shi, C. Ma, J. Mater. Chem. C. 10 (32) (2022) 11472–11531.
[50] M.K. Gupta, R. Srivastava, Am. J. Polym. Sci. Eng. 4 (1) (2016) 1–7.
[51] P. Ramu, C.J. Kumar, K. Palanikumar, Mater. Today.: Proc. 16 (2019) 1287–1296.
[52] A. Mehmood, N. Mubarak, M. Khalid, R. Walvekar, E. Abdullah, M. Siddiqui, H. A. Baloch, S. Nizamuddin, S. Mazari, J. Environ. Chem. Eng. 8 (3) (2020) 103743.
[53] A. Manalo, G. Maranan, B. Benmokrane, P. Cousin, O. Alajarmeh, W. Ferdous, R. Liang, G. Hota, Cem. Concr. Compos. 109 (2020) 103564.
[54] T. Cadu, L. Van Schoors, O. Sicot, S. Moscardelli, L. Divet, S. Fontaine, Ind. Crops Prod. 141 (2019) 111730.
[55] ASTM D570, Editorˆ Editors. 2010, ASTM International West Conshohocken.
[56] ASTM D790, 2007.
[57] ASTM D2344, ASTM: West Conshohocken, PA, USA, 2016.
[58] A. Manalo, G. Maranan, S. Sharma, W. Karunasena, Y. Bai, Compos. Struct. 173 (2017) 255–267.
[59] L. Yan, N. Chouw, K. Jayaraman, Compos. Part B: Eng. 56 (2014) 296–317.
[60] K. Kamau-Devers, Z. Kortum, S.A. Miller, Constr. Build. Mater. 214 (2019) 290–302.
[61] H. Fergani, M. Di Benedetti, C.M. Oller, C. Lynsdale, M. Guadagnini, Constr. Build. Mater. 170 (2018) 637–648.
[62] S.P. Damari, L. Cullari, R. Nadiv, Y. Nir, D. Laredo, J. Grunlan, O. Regev, Compos. Part B: Eng. 134 (2018) 218–224.
[63] M. Chaharmahali, Y. Hamzeh, G. Ebrahimi, A. Ashori, I. Ghasemi, Polym. Bull. 71 (2) (2014) 337–349.
[64] S. Sharma, P. Pujari, Prog. Polym. Sci. 75 (2017) 31–47.
[65] M. Kamaraj, E.A. Dodson, S. Datta, Adv. Compos. Mater. (2020) 1–16.
[66] S. Wang, M. Cao, G. Wang, F. Cong, H. Xue, Q. Meng, M. Uddin, J. Ma, Compos. Struct. 281 (2022) 114977.
[67] S.G. Prolongo, A. Jiménez-Suárez, R. Moriche, A. Ureña, Appl. Sci. 8 (9) (2018) 1550.
[68] V. Prasad, M. Joseph, K. Sekar, Compos. Part A: Appl. Sci. Manuf. 115 (2018) 360–370.
[69] K. Ashok, K. Kalaichelvan, A. Damodaran, J. Nat. Fibers 19 (4) (2022) 1472–1489.
[70] M. Kamaraj, E.A. Dodson, S. Datta, Adv. Compos. Mater. 29 (5) (2020) 443–458.
[71] A.K. Pathak, M. Borah, A. Gupta, T. Yokozeki, S.R. Dhakate, Compos. Sci. Technol. 135 (2016) 28–38.
[72] P.K. Gangineni, S. Patnaik, B.G. Gupta K, R.K. Prusty, B.C. Ray, Polym. Compos. 42 (11) (2021) 5893–5903.
[73] J. Thomason, L. Yang, F. Gentles, Fibers 5 (4) (2017) 36.
[74] C. Cerbu, H. Wang, M.F. Botis, Z. Huang, C. Plescan, Mech. Mater. 149 (2020) 103538.
[75] S. Muhammad Firdaus, M. Mariatti, J. Mater. Sci.: Mater. Electron. 23 (7) (2012) 1293–1299.
[76] Ashok, Kalaichelvan, Polym. Compos. 41 (11) (2020) 4716–4726.
[77] K.L. Pickering, M.A. Efendy, T.M. Le, Compos. Part A: Appl. Sci. Manuf. 83 (2016) 98–112.
[78] G. Reddy, V. Krishna, K. Sshanker, Procedia Eng. 173 (2017) 1684–1691.

[79] A. Oun, A. Manalo, O. Alajarmeh, R. Abousnina, A. Gerdes, Polymers 14 (9) (2022) 1841.
[80] J. Cheon, M. Kim, Compos. Part B: Eng. 217 (2021) 108872.
[81] T. Alomayri, H. Assaedi, F. Shaikh, I.M. Low, J. Asian Ceram. Soc. 2 (3) (2014) 223–230.
[82] H.N. Dhakal, Za Zhang, M.O. Richardson, Compos. Sci. Technol. 67 (7-8) (2007) 1674–1683.
[83] M. Berges, R. Léger, V. Placet, V. Person, S. Corn, X. Gabrion, J. Rousseau, E. Ramasso, P. Ienny, S. Fontaine, Compos. Part A: Appl. Sci. Manuf. 88 (2016) 165–177.
[84] H.M. Akil, C. Santulli, F. Sarasini, J. Tirillò, T. Valente, Compos. Sci. Technol. 94 (2014) 62–70.
[85] N. Guermazi, A.B. Tarjem, I. Ksouri, H.F. Ayedi, Compos. Part B: Eng. 85 (2016) 294–304.
[86] M. Al Rifai, H. El-Hassan, T. El-Maaddawy, F. Abed, Constr. Build. Mater. 243 (2020) 118258.
[87] Y. Ngono, Y. Maréchal, N. Mermilliod, J. Phys. Chem. B 103 (24) (1999) 4979–4985.
[88] Z. Wang, X.-L. Zhao, G. Xian, G. Wu, R.S. Raman, S. Al-Saadi, Constr. Build. Mater. 156 (2017) 985–1004.
[89] X. Wang, Y. Hu, L. Song, H. Yang, W. Xing, H. Lu, Prog. Org. Coat. 71 (1) (2011) 72–82.
[90] Wang, B., S. Ci, C. Di, J. Yu, B. Zhu, and K. Qiao, 2022.
[91] Socrates, G. 2004: John Wiley & Sons.
[92] Smith, B. 2018: CRC press.
[93] Y. Yang, G. Xian, H. Li, L. Sui, Polym. Degrad. Stab. 118 (2015) 111–119.
[94] W. Zhang, A.A. Dehghani-Sanij, R.S. Blackburn, Prog. Nat. Sci. 18 (7) (2008) 801–805.
[95] H.C. Kim, P.S. Panicker, D. Kim, S. Adil, J. Kim, Sci. Rep. 11 (1) (2021) 1–12.
[96] M.M. Khotbehsara, A. Manalo, T. Aravinthan, K.R. Reddy, W. Ferdous, H. Wong, A. Nazari, Polym. Degrad. Stab. 170 (2019) 108994.
[97] N. Yousefi, X. Lin, Q. Zheng, X. Shen, J.R. Pothnis, J. Jia, E. Zussman, J.-K. Kim, Carbon 59 (2013) 406–417.
[98] M. Celina, K.T. Gillen, R. Assink, Polym. Degrad. Stab. 90 (3) (2005) 395–404.
[99] Le Saux, V., P.-Y. Le Gac, Y. Marco, and S. Calloch, Polymer Degradation and Stability 99 (2014) 254–261.
[100] J.F. Davalos, Y. Chen, I. Ray, J. Compos. Mater. 46 (16) (2012) 1899–1914.
[101] Dejke, V., 2001.
[102] G. Hota, W. Barker, A. Manalo, Constr. Build. Mater. 256 (2020) 119462.
[103] A.H. Ali, H.M. Mohamed, B. Benmokrane, A. ElSafty, O. Chaallal, Compos. Part B: Eng. 157 (2019) 248–258.
[104] Y. Chen, J.F. Davalos, I. Ray, J. Compos. Constr. 10 (4) (2006) 279–286.
[105] P.K. Kushwaha, C. Pandey, R. Kumar, J. Indian Acad. Wood Sci. 11 (1) (2014) 82–86.
[106] U. Huner, Adv. Sci. Technol. Res. J. 9 (26) (2015) 1–6.