University of Southern Queensland

MECHANICAL AND DURABILITY PERFORMANCE OF HYBRID FLAX FIBRES AND GRAPHENE COMPOSITES

A Thesis submitted by

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ABSTRACT

Interest into the research on natural fibre-reinforced polymer (NFRP) composites for different engineering applications has increased significantly because they are environmentally friendly and sustainable renewable materials. However, these NFRP composites degrade when used as outdoor applications due to several environmental conditioning factors including in-service elevated temperature and high moisture. Recently, nanoscale fillers are now being utilised to improve the mechanical and durability performance of these natural composites. Therefore, this study systematically investigated the physical, mechanical and durability properties of hybrid natural fibre composites produced by reinforcing epoxy resin with flax fibres and graphene nanoparticles in elevated temperature, high moisture and hygrothermal environments.

In the first study, hybrid flax composites with graphene at ratios of 0 %, 0.5 %, 1.0 % and 1.5 % by weight of the epoxy resin were prepared and their flexural and inter-laminar shear performance at different temperature conditions, i.e. 20 °C to 100 °C with increments of 20 °C was evaluated. The experimental results showed positive effect of graphene on the flexural and inter-laminar shear (ILSS) properties of hybrid flax composites with the maximum improvements were observed for 0.5 % graphene at room temperature by up to 62 % and 149 %, respectively. These improvements decreased with increasing graphene weight ratio due to filler agglomeration as observed in the scanning electron microscope (SEM). The mechanical properties of hybrid composites started to decrease with increasing temperature but are still significantly higher than those without graphene.

The second study investigated the degradation behaviour of hybrid composites in high moisture environment. Hybrid composites were immersed in water at room temperature for 1000, 2000, and 3000 hours and tested mechanically under flexural and ILSS loading. The moisture absorption and moisture diffusion of flax fibre-epoxy composites was found to be significantly reduce due to the graphene particles providing effective protection layers. While the mechanical properties were found to be affected by high moisture and exposure duration, the maximum retention of the flexural strength by 97 %, 92 % and 86 % and ILSS by 89 %, 84 % and 82 % was achieved in the hybrid composites with 0.5 % graphene for 1000, 2000 and 3000 hours, respectively. The failure mechanisms are also affected by the exposure to high moisture environment.

The combined effect of moisture and in-service elevated temperature on the long-term durability of hybrid composites was investigated as the last study. Hybrid composites were conditioned at a relative humidity of 98 % and a temperature of up to 60 °C for exposure durations up to 3000 hours. The results showed that the addition of graphene can minimise the adverse effects of hygrothermal environments on the flexural modulus, strength and ILSS of hybrid composites. However, the sensitivity of the flexural and ILSS properties of hybrid composites against in-service elevated temperature was much higher than the exposure duration. Arrhenius model predicted that 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.

The results of this study provided a better understanding on the effect of graphene on the mechanical and durability properties of flax fibre-epoxy composites. The optimum ratio among the three tested ones is 0.5 % graphene by weight of the epoxy resin for maximum flexural and ILSS properties. These results also provided a useful guide for the natural fibre composite manufacturer on using additive manufacturing enhancing the long-term behaviour of such materials and be suitable for outdoor applications. It is recommended though to investigate other advance manufacturing process, in industrial scale, to scale up the outcome of this field of study.

CERTIFICATION OF THESIS

I Amer Oun declare that the Thesis entitled *Mechanical and durability performance of hybrid flax fibres and graphene composites* is not more than 100,000 words in length including quotes and exclusive of tables, figures, appendices, bibliography, references, and footnotes. The thesis contains no material that has been submitted previously, in whole or in part, for the award of any other academic degree or diploma. Except where otherwise indicated, this thesis is my own work.

Date: 31 March 2023

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STATEMENT OF CONTRIBUTIONS

The articles produced from this study were a joint contribution of the authors. The details of the scientific contribution of each author are provided below:

Paper 1:

Amer Oun, Allan Manalo, Omar Alajarmeh, Rajab Abousnina, and Andreas Gerdes, (2022) "Influence of elevated temperature on the mechanical properties of hybrid flax-fibre-epoxy composites incorporating graphene". Polymers Journal, vol. 14, no. 9, p.1841.

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The overall contribution of Amer Oun was 60 % related to the data collection, critical review of related literature, analysis, and interpretation of data, drafting and revising the final submission. Allan Manalo, Omar Alajarmeh, Rajab Abousnina, and Andreas Gerdes contributed to the structuring the manuscript, analysis, and interpretation of data, editing, and providing important technical inputs.

Paper 2:

Amer Oun, Allan Manalo, Omar Alajarmeh, Rajab Abousnina, and Andreas Gerdes, (2022) "Long-term water absorption of hybrid flax fibre-reinforced epoxy composites with graphene and its influence on mechanical properties". Polymers Journal, vol. 14, no. 17, p.3679.

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The overall contribution of Amer Oun was 65 % to the concept development, design of experiments, experimental works, analysis, and interpretation of data, drafting and revising the final submission. Allan Manalo, Omar Alajarmeh, Rajab Abousnina, and Andreas Gerdes contributed to the concept development, design of experiments, analysis, and interpretation of data, editing and providing important technical inputs.

Paper 3:

Amer Oun, Allan Manalo, Omar Alajarmeh, Rajab Abousnina, and Andreas Gerdes, (2022) "Durability of hybrid flax fibre-reinforced epoxy composites with graphene in hygrothermal environment". Polymer Degradation and Stability Journal (under review). (Assigned number: PDST-D-23-00017).

The overall contribution of Amer Oun was 70 % to the model development, design of experiments, experimental works, analytical investigations, analysis, and interpretation of data, drafting and revising the final submission. Allan Manalo, Omar Alajarmeh, Rajab Abousnina, and Andreas Gerdes contributed to the concept development, design of experiments, analysis, and interpretation of data, editing and providing important technical inputs.

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CHAPTER 1: INTRODUCTION

1.1 Background and motivation

Synthetic fibre-reinforced polymer composites have been widely used in various engineering applications due to their excellent advantages. However, these fibres have caused environment related issues, as they are non-biodegradable and not environmentally friendly, which means that these fibres will remain on the surface of the Earth for millions of years, unlike many plant fibres. Evidence of this remains in landfills for Municipal Solid Waste (MSW), which are one of the prevailing waste disposal policies in many countries of the world (Cano et al. 2022). In Australia, the direct disposal of MSW in 2002 without pre-treatment of chemicals with high resistance to degradation was 70 % by means of landfills (Laner et al. 2012; Gallen et al. 2016). They also reported that the ratio of MSW landfilled in Finland, the United Kingdom and Greece in 2008 was 77 %, 55 % and 51%, respectively. The Australian Department of Sustainability, Environment, Water, Population and Communities (Randell et al. 2014) reported that the total waste generation in 2010-2011 was approximately 48 million tonnes, and only 19.5 million tonnes of total waste was disposed of annually. Moreover, they reported that the fraction of waste generated by the construction and demolition industries was about 18 million tonnes annually. Recently, there is growing awareness concerning the impact of polymeric materials on the environment and increasing depletion rate of natural resources like minerals and petroleum oil owning to apply new environmental legislations. In developed countries like Australia, these force global material developers and scholars to create new materials as replacement for artificial ones that must be fully compatible with the nature. Producing a new class of environmentally friendly materials with high properties is a major challenge for engineers.

Natural fibre-reinforced polymer hybrid composites have been found to be one of the attractive substitutes for academic researchers and industrial needs. The use of such composites is expected to expand in the coming years, due to their advantages of renewable resources, inexpensive, recyclable, biodegradable, low density, good mechanical characteristics, abundant availability, and light weight nature, which make them more attractive as sustainable renewable materials for the reinforcement of polymer composites for advanced applications. Due to these advantages and the current environmental problems, natural fibres have a proven ability to replace synthetic fibres in polymer composites such as flax fibres for use as sustainable reinforcements, as they are directly applicable to the fibre composite market based on the increasing mechanical and industrial applications. Moreover, natural fibre composites have gained prominence in various engineering applications due to their inherent flexibility in design and relatively low cost. 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. Natural fibres are readily available in many countries of the world, especially in China, Tanzania, Brazil, and India, with many major plant types, namely kenaf, ramie, jute, sisal, flax, and so on (Rogovina et al. 2019). Driven by economical and environmental interests, applications based on plant fibres-reinforced polymer composites can be found in automotive parts, sports, and construction industries in recent years. The potential applications of natural fibre composites are also found in wind turbine blades made of flax fibre-reinforced polyester composites, which would be an alternative option to those produced from glass fibre composites (Shah et al. 2013, Balla et al. 2019). Moreover, natural fibre applications are used in roofing sheets instead of glass and asbestos which is attributed to its advantages like high modulus and strength as has reported by Sahu and Gupta (2017). Furthermore, natural fibre composites have been approved for use in the manufacture of interior panels for the aircraft industry (Ho et al. 2012). In North American automotive industries alone, it was found that by replacing 50 % of artificial fibres with plant-based natural fibres in polymer composites, 1.19 million cubic meters of crude oil use and 3.07 million tonnes of carbon dioxide emissions were avoided (Pervaiz & Sain 2003). They also reported that when substituting 30 % of synthetic fibre in polymer composites with 65 % of natural fibres, it can save 50 000 mega joules (MJ) of net non-renewable energy consumption, which is equivalent to about three tonnes of carbon dioxide emissions per ton of thermoplastic. The feature of using natural fibres to replace synthetic fibre in polymeric matrices not only reduces carbon dioxide emissions but can also make non-renewable resource savings possible.

Flax is a type of bast fibres that is characterized with higher properties than other natural fibres (Haag et al. 2017). These properties of high strength, stiffness, and low density make flax fibre of great interest to scientists and engineers in promoting the sustainability of various engineering industries as well as making it the most widely used fibre in the manufacture of natural fibre composites. In contrast, natural fibres have some drawbacks of low durability, limited processing temperature, water absorption, and compatibility with the matrix resin due to the poor interfacial adhesion property of hydrophilic fibre with hydrophobic matrix (Liu et al. 2019). These issues are the main challenges associated with expanding the engineering application of these sustainable materials. It is therefore critical to focus on these issues that may enhance the outdoor performance of natural fibre composites. Acceptable mechanical and durability properties of natural fibre composites can generally be achieved through preparation procedures, additives and treatment techniques that retain their original properties while enhancing other desirable features such as heat resistance and barrier properties when exposed to thermal, moisture and hygrothermal environments. Improvements in the compatibility and adhesion of the fibre/matrix interface in natural fibre composites have been reported in several research studies after modifying their fibre surface with various chemical and physical treatments (Retegi et al. 2006; Azwa & Yousif 2019). However, the thermal resistance and moisture absorption of plant fibre-based polymer composites remains as one of the major challenges associated with the limitations of their use in outdoor environments. For example, natural fibre composites is reported not suitable for use in high temperature gaskets due to its low heat resistance, and its sensitivity to high moisture absorption (Ouarhim et al. 2019). As a result, natural fibre composites are limited to indoor use such as furniture, packaging industries and housing materials (Potluri & Krishna 2020). It is therefore critical to understand these limitations associated with the application of such composites in outdoor environments and to find possible solutions to those issues.

Several studies suggested the addition of nanomaterials such as graphene nanoparticles to natural fibre composites to improve their outdoor performance (Chaharmahali et al. 2014b; Ashok & Kalaichelvan 2020). Graphene nanoparticles are drawing a great attention for researchers and scholars in different engineering applications due to their excellent properties when incorporated in polymer composites, i.e., improvement in physical, mechanical, and thermal characteristics (Fatima et al. 2021). For example, Mostovoy et al. (2022) investigated the hybrid effect of graphene oxide on the physical, mechanical, and thermal properties of basalt fibre composites. The authors found that the inclusion of 0.05%, 0.075%, 0.1 %, and 0.5 % by weight of graphene oxide to the basalt fibre-reinforced epoxy composites improved their physical, mechanical, and thermal properties. Ferreira et al. (2018) also observed that the addition of graphene into the epoxy matrix improved the hardness property of the developed nanocomposites. Based on the results of these studies, the researchers concluded that there is a key role for graphene in improving the properties of these composites.

The current thesis investigates the long-term durability behaviour of hybrid flax fibre-reinforced epoxy composites with various graphene weights. This thesis focused on studying the reinforcing effects of graphene addition on the mechanical, physical, and microstructure properties of flax fibre composites experimentally and analytically under flexural strength (FS) and interlaminar shear strength (ILSS) tests. Moreover, it identifies the various changes that hybrid composites with graphene undergo when exposed to heat, humidity, and hygrothermal effects to provide a detail understanding of their performance when used in outdoor environments. The experimental data generated from the studies were then used to develop a prediction model describing the degradation mechanism of these hybrid flax composites with graphene under the effect of in-service elevated temperature and high moisture.

1.2 Research Significance

The significance of the results obtained from the current research will have positive effects in economical, industrial, and environmental aspects. This research will also provide useful data contributing new knowledge to design engineers and researchers to use as a guide in the field of composite materials testing. Some of these key significant points, which motivate this research, are highlighted as follows:

1. Dealing with the current gap in knowledge identified by reviewing the literature regarding the influence of various environmental factors on the outdoor performance of natural fibre composites and presenting the benefits of reinforcing natural fibre composites with graphene nanoparticles.

2. Developing an analytical model to accurately predict the long-term service life of hybrid flax composites with graphene in the Australian environment supports the further development of natural fibre composites as well as improving their reliability.

3. Understanding the outdoor durability performance of hybrid flax fibre-reinforced epoxy composites under moisture, thermal, and hygrothermal environments. This will help address the limitations of their use in outdoor environments and make their applications more competitive with traditional synthetic fibre composites.

1.3 Research Objectives

The main objective of this study is to investigate the durability of flax fibre/ epoxy composites with graphene under thermal, moisture and hygrothermal environments. The specific objectives of this research were as follows:

1. To evaluate the thermal degradation behaviour of flax fibre/epoxy composites with graphene reinforcement subjected to in-service elevated temperature.

2. To examine the effect of graphene nanoparticles on the mechanical and physical properties of flax fibre/epoxy composites in high moisture environment.

3. To study the mechanical performance of flax fibre/epoxy composites filled with graphene exposed to simulated hygrothermal environment.

4. To develop an analytical model to reliably describe the long-term behaviour of flax fibre/epoxy composites with graphene.

1.4 Thesis Layout

This thesis is structured into six major chapters as described in Fig.1. Chapter 1 provides a brief introduction to the motivation and idea of the works carried out in the present thesis in terms of the development of natural fibres composites based on flax fibres and epoxy, and the introduction of graphene to enhance their physical, mechanical and durability properties. The Chapter also explains the specific objectives and significance of the research. In Chapter 2, a comprehensive review of the relevant literature on natural fibre properties and their composites as well as the factors limiting their use in polymer composite applications is presented. Besides, a review of the role of nanoparticles such as graphene in the enhancing the properties of natural fibre composites is conducted. Chapters 3, 4, and 5 cover three experimental studies addressing the research objectives in which experimental tests based on their standard testing methods were prepared and then performed, providing a detailed discussion of the outcomes obtained from these tests. Chapter 5 presents a prediction model system to consider the durability behaviour of the produced composites. Finally, Chapter 6 concludes the main research findings and contributions. This chapter also provides recommendations and new areas for future research work based on the outcomes of this thesis.

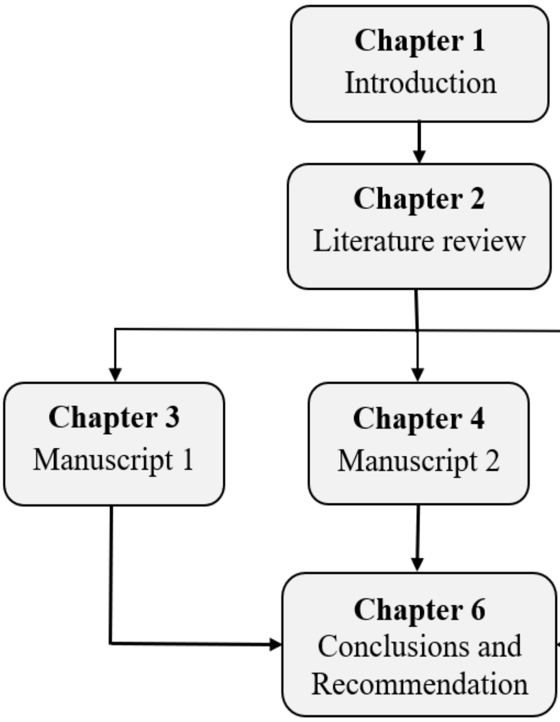


Fig.1.1: Layout of the thesis

From this research work, three international articles were published or are currently under review in high standard journals (Q1) as follows:

Paper 1:

Amer Oun, Allan Manalo, Omar Alajarmeh, Rajab Abousnina, and Andreas Gerdes, (2022) "Influence of elevated temperature on the mechanical properties of hybrid flax-fibre-epoxy composites incorporating graphene". Polymers, vol. 14, no. 9, p.1841.

DOI: https://doi.org/10.3390/polym14091841

The manuscript addresses the first objective of this study where the influence of elevated temperature on the mechanical properties of hybrid flax-fibre-epoxy composites incorporating graphene was evaluated. The thermal degradation study was conducted to determine the reinforcing influence of graphene on the mechanical properties of flax fibre composites after exposure to in-service elevated temperatures. The flexural and interlaminar shear properties of hybrid flax fibre-reinforced epoxy composites with various graphene weights were evaluated experimentally. The results of this study showed an improvement in the mechanical properties of hybrid composites when compared to the flax fibre composites at room temperature but highlighted the challenges associated with in-service elevated temperatures, as the hybrid composites decreased significantly when exposed to a temperature of 40 °C while flax fibre composites decreased gradually up to 60 °C.

Paper 2:

Amer Oun, Allan Manalo, Omar Alajarmeh, Rajab Abousnina, and Andreas Gerdes, (2022) "Long-term water absorption of hybrid flax fibre-reinforced epoxy composites with graphene and its influence on mechanical properties". Polymers, vol. 14, no. 17, p.3679.

DOI: https://doi.org/10.3390/polym14173679

This study focuses on the effect of graphene reinforcement on the water absorption behaviour of flax fibre-reinforced epoxy composites and how this reinforcement is reflected on the mechanical behaviour of these composites. To determine graphene effects on these behaviours, a comparative study was conducted between dry and wet hybrid composites, and the test results were analysed and compared in terms of mechanical strength, failure mode, and modulus of elasticity. From the test results, the inclusion of graphene nanoparticles reduced the moisture absorption and moisture diffusion coefficient of flax fibre composites, but there was a challenge associated with increasing the exposure duration as the absorbed water reduced the mechanical properties of hybrid composites regardless of graphene content. It can be concluded from this study that the addition of graphene nanoparticles has a significant role in improving the resistance of epoxy composites reinforced with flax fibres against the influence of moisture. This will provide the opportunities and possibilities to use this type of natural fibre composite in outdoor applications.

Paper 3:

Amer Oun, Allan Manalo, Omar Alajarmeh, Rajab Abousnina, and Andreas Gerdes, (2022) "Durability of hybrid flax fibre-reinforced epoxy composites with graphene subjected to hygrothermal conditioning”. Polymer Degradation and Stability Journal (under review). (Assigned number: PDST-D-23-00017).

This paper presents a hygrothermal degradation study on hybrid flax fibre-reinforced epoxy composites with graphene to assess the outdoor durability performance. To achieve this, the produced composites were subjected to the combined effect of moisture and temperature. Their degradation behaviours due to hygrothermal conditioning were assessed by flexural and inter-laminar shear tests. Through the experimental results of this study, the addition of graphene nanoparticles demonstrated significant effects and played an important role in reducing moisture absorption and improving mechanical properties after exposure to hygrothermal conditioning.

Based on the accelerated aging data, a new prediction model reflecting Arrhenius concept was developed to reliably predict the durability performance of hybrid flax fibre-reinforced epoxy composites with graphene.

1.5 Summary

Natural fibres have excellent characteristics in terms of low density, recyclability, abundance, low weight, and cost, which are their attractive aspects, and these characteristics provide the opportunity and possibility of using their composite products in different engineering applications such as automotive, construction materials, and aerospace. However, natural fibre composites suffer from durability degradation when exposed to various environmental conditions such as thermal, humid, and hygrothermal environments; understanding the durability behaviour of natural fibre composites is a major issue for their use in outdoor applications. This is the main motivation and justification for the current research. To this end, hybrid flax fibre-reinforced polymer composites with graphene were developed by a vacuum bagging method and intensively investigated wherein the results and significant findings are presented in Chapters 3 to 5.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

A comprehensive review of the relevant literature on mechanical, thermal, and physical properties of plant fibres and nanofillers as well as plant fibre chemical composition and its effects on degradation is introduced. It also includes the mechanical properties and long-term durability of natural fibre composites and nanoparticles/plant fibre-based hybrid polymer composites. A brief introduction to categories, advantages, and disadvantages of polymers, and the effects of natural fibres as reinforcement and nanoparticles as filler on polymeric composite properties are provided. Moreover, a brief overview about the model used to predict the equivalent service life of newly produced hybrid composites is presented.

2.2 Epoxy resin as recent attracted polymer

Among these thermosetting polymers, epoxy resin is used as a matrix in the current study as it has desirable properties in low shrinkage, relatively good mechanical strength, moisture resistance, heat resistance, and high modulus, making it one of the best matrixes for use in fibre polymer composites (Alamri 2012; Manthey 2013). In addition, epoxy resins have advantages over the other polymer matrixes such as polyester resins, vinyl ester resins, and phenolic resins (Gupta & Srivastava 2015). These advantages include high tensile strength and modulus, excellent flexural properties, and high application temperature. They also provide excellent interfacial bonding properties to the fibre required for stiffness and structural behaviour, as shown in Table 1, as well as resistance to chemicals and environmental degradation. Due to these advantages, its applications are widely spread across industries in aerospace structures, adhesives, and electronics. However, epoxy resins have a higher cost than other polymer resins as well as their undesirable brittle behaviour. Therefore, epoxy matrices are usually reinforced with a variety of natural or synthetic fibres for improving their properties.

Table.1: Properties of epoxy resin compared to other thermosets (Gupta & Srivastava 2016b).

Thermosets	TS (MPa)	TM (GPa)	FS (MPa)	FM (GPa)	Glass transition temperature (°C)	Specific gravity
Epoxies	55-130	2.7-4.1	110-150	3-4	170-300	1.2-1.3
Phenolics	50-60	4-7	80-135	2-4	175	1.2-1.3
Polyesters	34-105	2.1-3.5	70-110	2-4	130-160	1.1-1.4
Vinyl esters	73-81	3-3.5	130-140	3	----------	1.1-1.3

Where TS and TM are tensile strength and modulus, and FS and FM are flexural strength and modulus

Replacing traditional materials with biodegradable ones is an important goal that has been articulated in sustainability charters globally. The accumulation of synthetic fibres in the environment or landfill sites and their high cost due to production from non-renewable resources are the main reasons for their limited use (Mochane et al. 2019).

2.3 Natural plant fibres and classification of their composites

2.3.1 Natural plant fibres

The usage of natural fibres like, cotton, kenaf, flax, sisal, coir, bamboo, jute, etc in polymer composites as reinforcement instead of traditional fibres, like glass, Kevlar, and carbon fibres has recently become attractive attention to researchers, experts, and engineers in various industrial applications. This is attributed to the advantageous properties of natural fibres such as renewable resources, availability, no harm to health, low cost compared to synthetic counterparts, good mechanical properties, environmentally friendly, and low weight which is a very important factor for structural applications (Adesina et al. 2019; Lotfi et al. 2019). Natural fibres are sustainable renewable materials and their availability in many countries of the world makes them of great importance for use in future composite products for various engineering and industrial applications. Moreover, the energy consumption for their production is very low compared to the energy needed in the manufacture of synthetic fibres, and these natural fibres are recyclable and biodegradable (Adole et al. 2019; Lotfi et al. 2019). This low energy consumption for making natural fibres is advantageous in terms of their production cost, which contributes to increasing their applications in many industries. Other advantages of these natural fibres are their lower densities than synthetic fibres, and their relatively low cost. These fibres with densities ranging from 1.25 to 1.5 g/cm^3 are lower than for carbon fibre and E-glass fibre, with 1.8–2.1 g/cm^3 and 2.54 g/cm^3, respectively. This means that a natural fibre composite product has a lighter weight than a composite reinforced with synthetic fibres. These are the main reasons why natural fibres are more attractive for use in the automotive and other industries. Natural fibre applications were first used in carpets, ropes, and interior items for the home, and their applications have advanced further to furniture, packing, sporting goods, and inner door panels (Sanjay et al. 2016).

Nevertheless, these natural fibres suffer from some disadvantages when used as reinforcements in polymer composites for advanced applications, namely the limited application temperature, moisture absorption, lower durability, and the incompatibility of the fibres with the matrix resin. This is due to their hydrophilic nature, which is a main concern for their use. Their hydrophilic nature is the main issue associated with the incompatibility of these natural fibres with polymer matrices, resulting in poor adhesive quality at the fibre/matrix interface and high moisture absorption. This affects the final properties of the composite because the interfacial adhesion property plays an important role in improving the mechanical performance and quality of the polymer composite, allowing the matrix resin to transfer uniform stress to the fibres, which act as carriers for the applied load. In addition, these fibres with a low decomposition temperature (~200 °C) are not suitable for use in thermoplastic polymers with application temperatures in excess of 200 °C. This limits their success in the reinforcement of polymer matrices for advanced applications. Although it is emphasised that the price of natural fibres is cheaper compared to their synthetic fibres, these problems associated with natural fibres can be improved by means of chemical and physical treatments that improve their surface (Shuhimi et al. 2017), while incurring additional costs. Surface modification of natural fibres by these processing methods increases the roughness through removing impurities from their surface, and thus enhances the fibre/matrix interface adhesion (Shuhimi et al. 2017). The advantage of surface treatment makes natural fibre composites more competitive with synthetic fibre composites.

Natural fibres are obtained from the main three sources (George et al. 2016; Lotfi et al. 2019), namely plants, animals, and minerals as shown in Fig.2. The source of flax fibre extracted from plants is increased in Western Europe, Eastern Europe, China, and Egypt but Western Europe is the main production area, particularly in France. Flax fibre production in Australia started in1941 where the Flax Production Commission established six flax processing mills in Tasmania, six in Victoria and one mill in Western Australia. Thus, natural flax fibre was grown in Tasmania, South Australia, and Western Australia but Victoria in 1944-45 was the leader with 38,000 acres of a total Commonwealth production of about 61,000 acres. Consequently, Colan Australia Composite Reinforcement has been manufacturing Composite Reinforcement fabrics in Australia for over 50 years and has expanded its manufacturing facilities to be available in a range of weights and fabric constructions such as Weaves: Plain Weave, Twill Weave, and Unidirectional. All of these ranges can be produced from lighter flax fibre with equivalent performance and cost. However, these fibres have various properties because their compositions are very different due to climate and terrain (Asim et al. 2020). Even in the same type of fibre classification there is a slight difference in their properties. For example, protein and cellulose contents are major components of animal and plant fibres, respectively (Chakkour et al. 2022). Plant fibres have proven their potential to be used as the most suitable natural fibres in polymer reinforcement (Parbin et al. 2019). Based on their extraction from plant parts, natural fibres can be categorized into bast, leaf, seed, fruit, stalk, wood, and grass fibres (Lotfi et al. 2019). These natural fibres can be separated from other parts of the plant by several methods such as scrapping, pulping, and retting.

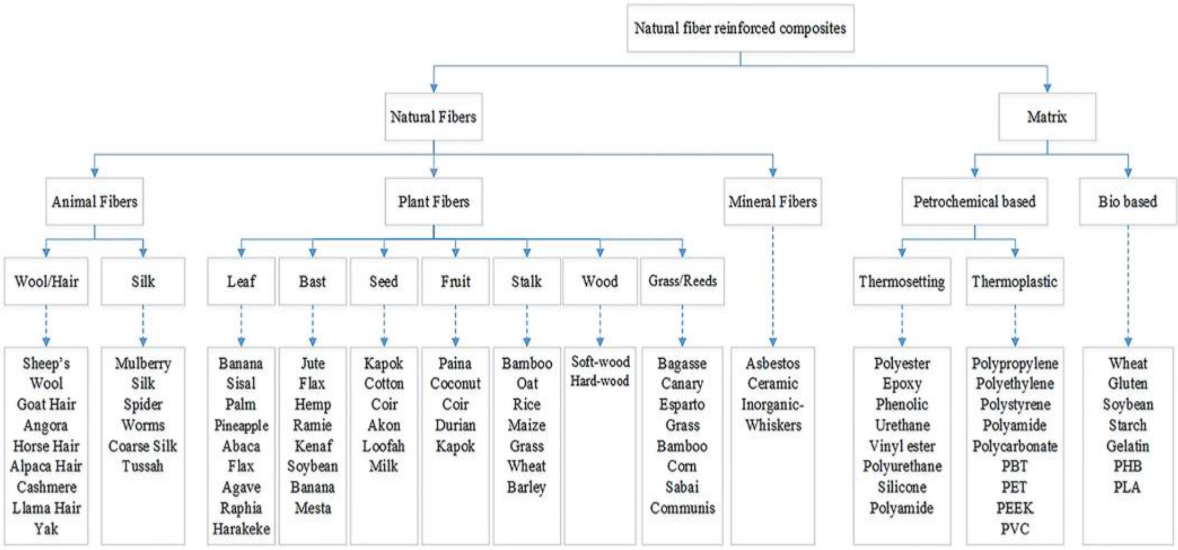


Fig. 2.1: Classification of natural plant fibres , source: (Lotfi et al. 2019)

2.3.1.1 Importance for natural plant fibres

In terms of environmental concerns, natural fibres are environmentally friendly due to their biodegradability, renewable resources, and recyclability and have recently gained much attention from engineers, experts, and researchers alike as a hot topic. This is not only due to these fibres being completely harmless to the nature, but also have the potential to replace inorganic fibres in reinforcing polymer composites such as carbon, glass, and Kevlar fibres (Mishra et al. 2022). The increasing demands for using environmentally friendly materials in various productions such as automotive, packaging, and construction industries have made polymer composites reinforced with natural fibres more importance for research. In addition to this, new legislations have been made by some counties to use recyclable materials in the manufacture of cars for example Japan and Germany. In 2006, the European Union issued new legislations to use 80 % of car components from recyclable materials as a first step to protect the environment and by 2015 recyclable materials would reach 85 % (Alamri 2012; Nirmal et al. 2015; Adesina et al. 2019). The manufacturers for European cars have begun the use of new reinforcing materials produced from natural fibres as reinforcement for thermoplastic and thermoset composites in numerous automobile parts like seat backs, dashboards, panels of the doors, and other internal parts (Lotfi et al. 2019). The same case is reflected in the automotive industry in Japan in 2005 where demand utilisation reached 88 % of vehicle parts from materials that can be recycled and by 2015 it was expected to reach 95 % (Mohd Nurazzi et al. 2017). Their good mechanical properties lead to a significant enhancement in the mechanical properties of polymer composites, and as a results, these fibres are used in many other industries for indoor applications as in furniture and panels, and for outdoor applications such as decking and railings (Alamri 2012). In other words, their relatively high mechanical properties have made these fibres superior alternative reinforcements in polymeric composites in terms of environmental protection from the influences of many engineering applications based on synthetic fibre composites, where the demand for applications made of natural reinforcements with polymer matrixes has increased in recent years. This was confirmed by evaluating the sustainability of these natural composites in terms of their environmental impact such as recyclability, renewability and biodegradability using life cycle assessment analysis. A number of researchers have examined the sustainability of natural fibre composites using life cycle assessment technique. This technique is used to assess the potential environmental impact of natural fibre composites on the earth. Broeren et al. (2017) evaluated the environmental impact of sisal fibre production by measuring the energy consumption and greenhouse gas emissions of sisal fibre manufacturing using life cycle assessment and comparing it to the effect of glass fibre. The results 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. The life cycle assessment analysis conducted by Vidal et al. (2009) on the environmental impact of produced composite materials made from a blend of recycled thermoplastics (polypropylene and high-density polyethylene) with rice husks and recycled cotton, and compared to the impact of conventional virgin polypropylene and high-density polyethylene. The results exhibited that subjecting these composite materials to a life cycle assessment analysis showed a significant reduction in environmental impact compared to that of conventional virgin thermoplastics using 1 kg of material as a functional unit. The 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.

2.3.1.2 Mechanical properties for natural plant fibres

A better understanding of the properties of plant fibres is a very important factor for selecting them as natural reinforcements in polymeric composites to improve their performance. These properties can determine their uses in various engineering applications. The properties of natural plant fibres are mainly dependent on their composition, microfibril angle, and crystallinity as well as their internal structure (Ahmad et al. 2015). Ramu et al. (2019) suggested that their expanded use in polymer reinforcement for advanced applications requires knowledge of the properties of these fibres. Table 2 lists the mechanical properties of natural plant fibres and shows that flax fibre has higher mechanical properties compared to all other plant fibres. This motivates the current research work to use this fibre in epoxy matrix reinforcement. Table 2 shows the tendency of plant fibres with different levels of density ranging from 1.33 to 1.48 g/ cm^3 for a lightweight, and flax fibres have a higher tensile strength and modulus as well as lowering moisture absorption than other natural fibres. This makes them more attractive materials as reinforcement for mechanical and structural applications.

Table 2: Mechanical properties of natural plant fibres (Mallick 2007; Ramu et al. 2019)

Properties	**Fibre**			
	Hemp	**Jute**	**Sisal**	**Flax**
Density (g/cm^3)	1.48	1.46	1.33	1.4
Tensile strength (MPa)	550-900	400-800	600-700	800-1500
Tensile modulus (MPa)	70	10-30	38	60-80
Elongation (%)	1.6	1.8	2-3	1.2-1.6
Moisture (%)	8	12	11	7

Plant fibre has wide range of important characteristics which include length of fibre, cell wall thickness and diameter of fibre. As shown in Table 3 below, the diameters of fibre are available in a range of 5 to 76 microns, the lengths of fibre are ranging from 1.2 to 300 mm, and the widths of fibre bundle are between 10 and 1000 μm as well as a shape of the fibre plays an important role in making the large differences in the properties of the composite materials based on these fibres. Moreover these characteristic differences in natural fibre directly affect in the manufacture process of natural fibre based polymeric composites. Therefore, these characteristics have to take in account during manufacture to achieve and design natural fibre/polymer composites with functional properties (Balla et al. 2019).

Table 3: Important characteristics for plant fibres (Balla et al. 2019).

Fiber	Shape	Dia./ width, μm	Bundle width, μm	Length, mm	Cell width/ dia., μm
Wood	Rectangular to round	5–50	–	1.2–3.6	10–30
Flax	Polygonal	5–76	40–620	4–140	–
Hemp	polygonal or ribbon-shape	5–40	25–500	8–55	4–60
Jute	Rectangular to Polygon	5–30	25–200	1–5	–
Kenaf	Round to polygonal	12–50	30–247	1.5–11	–
Abaca	Polygonal to round	6–46	10–1000	2–12	–
Sisal	Polygonal to round	4–47	9–460	0.5–8	–
Coir	Round to oval	10–30	50–460	150–300	10–30

2.3.1.3 Chemical constituents for natural plant fibres

The major constituent parts of natural plant fibres are cellulose, lignin, and hemicelluloses while the other remaining components include pectin, waxes, and moisture content. These constituents were significantly different according to the source and type of these fibres (Balla et al. 2019). Fibre properties are controlled by these components, which play an important role in improving the properties of natural fibre composites. Natural plant fibres obtained from bast fibres tend to have higher cellulose content (30-76 % by weight) as displayed in Table 3. The cellulose content in natural fibres is one of their main components that gives them strength and stiffness (Sood & Dwivedi 2018). Pappu and Thakur (2017) also indicated that high cellulose content in natural fibre results in increased fibre properties. It was therefore found that the high cellulose content of these fibres have a significant reinforcing effect on their composite properties (Balla et al. 2019). However, cellulose contains hydroxyl groups (OH) that provide potential hydrogen bond sites, making it responsible for moisture absorption (Sweygers et al. 2022). Therefore, the high cellulose content in natural fibres results in a high moisture absorption rate (Huner 2015). Thus, it is necessary to consider the improvement in their moisture resistance before using them in mechanical and structural applications. This can be achieved by modifying their surface with chemical and physical treatments or by means of additives (Asim et al. 2020). The chemical composition of natural plant fibres is shown in Table 4. Low content of lignin in natural fibres provides a higher degradation temperature for polymer composites (Manfredi et al. 2006). Among these natural fibres, flax fibre has low lignin element and thus, tends to have high thermal stability (Manfredi et al. 2006). Ahmad et al. (2015) studied the effect of lignin content on the thermal stability behaviour of jute fibres, sisal fibres, and flax fibres. The results showed that the thermal stability behaviour was similar for both, sisal, and jute fibres due to the same lignin content while flax fibres showed the best thermal stability and decomposed at a high level of temperature because of the low content of lignin in flax. Flax fibre with low lignin content is better for thermal resistance than other natural plant fibres which is the motivation for the current study to use it.

Table 4: Chemical composition of some natural plant fibres (Yan et al. 2016; Ramesh et al. 2017; Balla et al. 2019)

Fibre	Cellulose (wt.%)	Hemi-cellulose (wt.%)	lignin (wt.%)
Hemp	70-74	20.0	4-10
Flax	64-71	14.5	2.2-2.5
Jute	61-72	16.0	12-13
Kenaf	31-39	21.0	9-17
Ramie	68-76	14.0	0.6-0.8

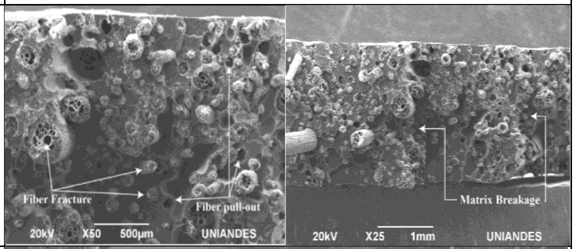
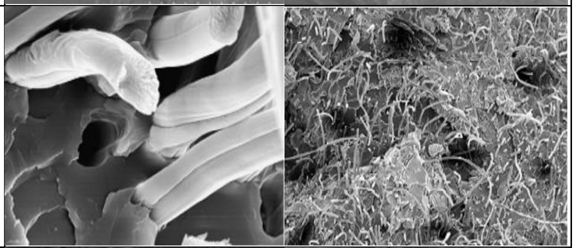
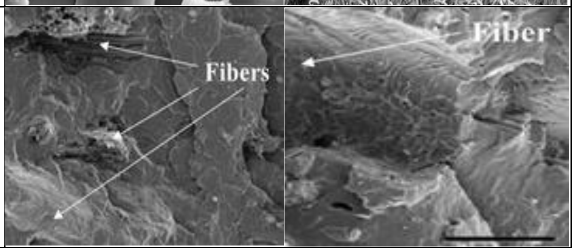
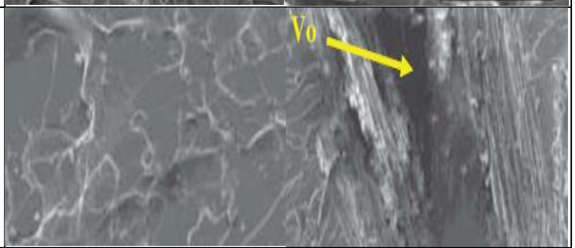
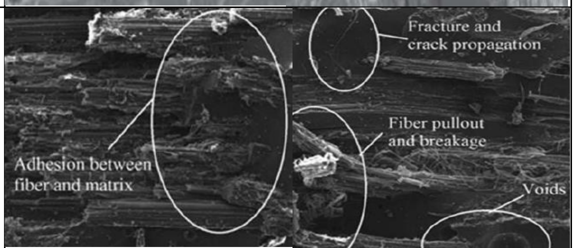
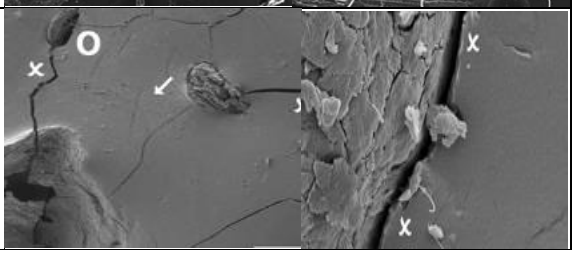
2.3.2 Natural fibre composites

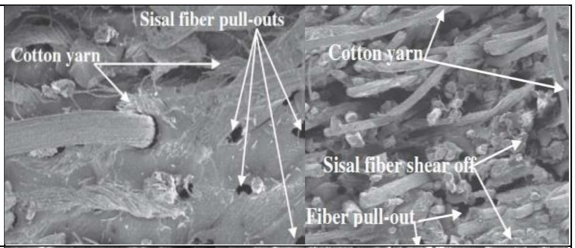
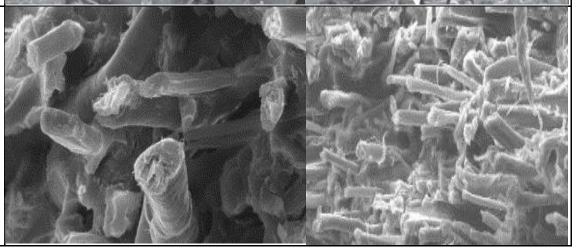
Natural fibre is the first technique for use as a natural reinforcement for polymer matrices to produce engineering materials with lower cost and higher properties (Alamri 2012; Lotfi et al. 2019). In this technique, the principal natural fibres used so far to reinforce polymer composites include sisal, bamboo, jute, ramie, flax, banana, hemp, Kenaf fibre, etc. This is due to their desirable properties which classify them as mechanically strong fibres as mentioned in the previous section. A number of researchers have studied the mechanical, thermal and water absorption properties using natural fibres in polymer reinforcement and found in their studies that improvements in these properties were recorded for sisal fibre/epoxy matrix (Gupta & Srivastava 2016a), woven flex fabric/polyoxymethylene matrix (Xiong et al. 2018), sisal fibre/epoxy composites (Sahu & Srivastava 2019), Kenaf fibre/epoxy composites (Devadas et al. 2018), and jute fibre/epoxy composites (Bisaria et al. 2015). In general, most cases for polymer composites reinforced with natural fibre reinforcements show remarkable properties when compared to the neat matrix. However, these natural composites still suffer from significant limitations such as thermal degradation and moisture resistance that prevent their use in outdoor applications which will be discussed later in this chapter. Interestingly, the field of mechanical characteristics of polymer composites supporting with natural fibres is still a new area and is not well established yet (Saba et al. 2016; Alsubari et al. 2021). Saba et al. (2016) have also stated that the research studies conducted by the researchers and published in literature did not include all types of natural fibres. There are more opportunities for new research in polymer science, especially polymer composites reinforced with natural flax fibres. This may result in new discoveries that contribute toward a great understanding concerning the development of mechanical performance for engineering applications in outdoor environments. In addition, there is a lack of good understanding regarding the effect of fibres extracted from plant resources on the outdoor performance of polymer composites and thereby, more research work needs to be done in this area in order to understand the influence on the durability properties of plant fibre-reinforced polymer composites for use in outdoor applications (Scida et al. 2013; Wang et al. 2014). Therefore, the interest in the present work correlates to the development of new research areas in the long-term durability and mechanical performance of these natural composites with nanoscale fillers. This motivates to be the focus of this study on the potential of the use of unidirectional flax fibres as natural reinforcements for epoxy composite samples with the insertion of graphene nanoparticles.

2.3.2.1 Tensile failure mechanisms in polymer composites reinforced with natural fibre

Natural fibres filled polymer composite have showed a variety of the tensile failure mechanism of type to type as listed in Table 5 below. From those works, it can be explained that failure mechanism is related to the plant fibre in terms of moisture absorption, its orientation within the matrix, impurities on its surface, chemical type used in a treatment process, volume of friction, and its physical properties. These factors result in poor interfacial interaction of the fibre with the polymer matrix, leading to the matrix unable to transfer uniform stresses to the fibre and thereby leading to tensile failure mechanisms such as fibre pull-out and fracture surfaces that can be observed with poly-lactic acid (PLA)/ Manicaria fabric (Porras et al. 2016), moringa oleifera pods/ epoxy (Kumar 2019), PLA/ cordenka composite (Bax & Müssig 2008), and PLA/wood fibre (Huda et al. 2006). Additional void spaces and cracks occurred with Kenaf fibre/epoxy composite (Devadas et al. 2018), unidirectional banana/jute/ epoxy composite (Devireddy & Biswas 2017), and PLA/ sugar beet pulp (LiuLiu et al. 2005). Poor adhesion and fibre broken occurred to cotton/sisal/ polyester (Plackett et al. 2003), and PLA/flax (Oksman et al. 2003).

Table 5: Tensile failure mechanism in natural fibre polymer composites

Reference	Material	Failure mechanism	SEM photographs
Porras, et al. (2016)	PLA/MF composite	Fibre fracture Fibre pull-out Matrix breakage	
Kumar (2019)	Moringa Oleifera Pods/ Epoxy composite	Fibre debonding, fibre breakage and Fracture surfaces	
Bax and Müssig (2008)	PLA/ Cordenka composite	Fibre pull-out Fracture surfaces	
Huda, et al. (2006)	PLA/WF Composite	Fibre pull-outs, and gaps between the fibre and matrix	
Devadas, et al. (2018)	Kenaf fibre/ Epoxy composite	Delamination, voids, debonding and cracks	
Devireddy and Biswas (2017)	Unidirectional Banana/Jute/ Epoxy composite	Fibre pull-out, void, crack propagation, and fibre breakage	
LiuLiu, et al. (2005)	PLA/SBP Composite	Tensile fracture surfaces Gaps and void spaces	

Plackett, et al. (2003)	Cotton/Sisal/ Polyester composite	Fibre shears off, agglomeration, fibre fracture and pull outs	
Oksman, et al. (2003)	Poly lactic acid/ flax composite	Poor adhesion among fibres/ PLA matrix, Fibre pull-outs, and broken	

2.3.3 Natural fibre composites with nanofillers (Hybrid composites)

A hybrid composite is generally a new class of materials design concept represented in the form of natural fibres with nanomaterials such as graphene in a polymer matrix that allows it to have unique properties, not as in the case of individual reinforcement of these materials. The interest in this new concept comes from the fact that a small amount of nanomaterials adding to a polymer matrix can improve its mechanical, thermal, and physical properties (Hong & Chen 2015). This technique is a new reinforcement phase for natural fibre composites to produce hybrid composites with high properties. In this study, the new hybrid composite takes the advantages of natural flax fibres and graphene nanoparticles. Thus, there is a new opportunity to extend the use of natural fibre composites for advanced applications (Mochane et al. 2019). The source of graphene is extracted from natural graphite using a technique called micromechanical cleavage, as reported by Choi et al. (2010) . This technique allowed for the easy production of high-quality graphene crystals and also led to tremendous experimental activities. The derivatives of graphene include graphene oxide and reduced graphene oxide. Graphene oxide is a monolayer material that is produced by exfoliation of graphite oxide. While the reduced graphene oxide can be produced by removing the oxygen lattice from graphene oxide using reduction reagents. Schniepp et al. (2006) reported that there are several methods such as chemical reduction of graphite oxide that can be used to produce reduced graphene oxide by hydrazine known chemically reduced graphene oxide and through thermal reduction method by annealing in hydrogen/argon environment known as thermally reduced graphene oxide. The best way to understand the structure of graphene is by the International Union of Pure and Applied Chemistry (IUPAC) who approved the term graphene and replaced graphite layers wherein graphite is defined as a three-dimensional structure whereas graphene is a two-dimensional structure even though it is a building unit of graphite (Singh et al. 2011). Hybridising natural fibre with nano-fillers such as graphene nanoparticles into polymer matrix can improve the mechanical, thermal and water absorption behaviours of the produced composites through the improvement of fibre/matrix interfacial adhesion. Hybrid flax composites with graphene nanoparticles have the potential to improve their outdoor performance and can be implemented in many industrial applications from automotive parts to building materials. This is due to the excellent properties of graphene including high surface area, high tensile strength measured at 130 GPa, which is about 5 to 200 times greater than that of steel, and Young's modulus of 1 tera pascal (TPa) makes it a more suitable nanomaterial in polymer reinforcement than other nanoscale fillers (Lee et al. 2008). The properties of graphene are listed in Table 6. Furthermore, graphene nanoparticles can help in the uniform distribution of individual fibres by reducing fibre-fibre interactions and fibre entanglement, and they are easier to fill in more spaces leaving less resin. Ghatrehsamani (2016) highlighted that it is possible to find desirable properties that meet the use requirements of each application when these nanomaterials are added as fillers to natural fibre-reinforced polymers. Moreover, its other properties such as small size, high surface area and low density make graphene an ideal reinforcement in polymer composite materials for advanced composites. In nanomaterials field, graphene has the highest strength and hardness compared to other well-known nanomaterials. Comparing the theoretical surface area of graphene with carbon nanotubes shows that it is two times larger for graphene than for carbon nanotubes, i.e. 2630 m/g and 1315 m/g, respectively, as reported by Mehmood et al. (2020b). As a result, graphene has received a lot of attention due to its exceptional properties in various research fields. Considering the above, the current research work is motivated to use graphene as a filler in polymer composites reinforced with natural fibres.

Table 6: Properties of graphene (Mehmood et al. 2020a)

Properties	Value
Young's modulus	1100 GPa
Fracture strength	125 GPa
Thermal conductivity	5000 W m $^{-1}$ k
Charge carrier's mobility	250,000 cm ^{2} v $^{-2}$
Specific surface area	2630 m g
Phenomena of transport	Excellent
Absorption of visible light up to	2.3 %
Minimum Hall conductivity at zero concentration	4 e /h
Second Order Elastic Stiffness (thickness 0.335 nm)	340 ± 50 N/m
Intrinsic Strength	130 GPa
Thickness of monolayer graphene	0.345 nm
Poisson's ratio	0.16
Bandgap	Zero (eV)

2.3.3.1 Characterization of Hybrid composites

Many researchers have studied the mechanical, thermal, and physical properties of hybrid natural fibre-reinforced polymer composites with nanoscale fillers (Borba et al. 2014; Hosseini et al. 2014; Tshai et al. 2016). For example, Chaharmahali et al. (2014a) studied the mechanical and physical properties of hybrid bagasse fibre-reinforced polypropylene composites with graphene. The investigation was conducted to study the reinforcing influence of adding graphene nanoparticles on the tensile, impact, flexural, and moisture absorption properties of hybrid bagasse composites with 0.1 %, 0.5 %, and 1 % of graphene by weight of the matrix. The researchers found in their investigation that by adding 0.1 % of graphene improved the flexural, tensile, and water absorption properties but slightly declined the impact property. Increasing the amount of graphene more than this percentage did not show any improvement in the mechanical properties due to filler agglomeration. A study by Kamaraj et al. (2020) investigated the role of graphic reinforcements on the mechanical, flammability, and water absorption properties of hybrid epoxy composites reinforced with flax fabric. They concluded that graphene nanoparticles have a positive effect on improving the mechanical and physical properties of the hybrid composites. These improvements, due to the high surface area of nanoscale graphene, include tensile strength, flexural strength, and moisture absorption behaviour as well as flammability property due to graphene acting as a flame retardant. Ganapathy et al. (2019) investigated the influence of graphene addition on the mechanical and physical properties of banyan fibre/epoxy composites. Hybrid composites with graphene ranges (2 %, 4 %, 6 %, 8 %, and 10 %) and fibre reinforcements of 40 %, and 60 % by weight of the matrix were prepared. The authors concluded that hybrid composites reinforced with 40 % of banyan fibre content and filled with 4 % of graphene showed the optimum concentrations for developing productive composites with high tensile and flexural strengths, while the highest value for shore D hardness was observed with 6 % of graphene. The water absorption decreased in all the hybrid composites due to the contribution of nanoscale graphene. These studies showed the key role of graphene addition in improving the mechanical properties of natural fibre composites. However, the long-term performance of these natural composites with graphene is still unknown. Therefore, this study will investigate this performance during their service life.

2.4 Durability under harsh environmental factors

The durability of natural fibre-based polymer composites in moisture, heat, and hygrothermal environments is the major challenge for their applications as these conditioning environments directly affect the properties of these composites. Natural fibre durability is associated with the fibre resistance to external conditions that result in decrease in natural fibre strength and therefore decreases its composite performance (Ahmad et al. 2015). The major factors affecting the change of plant fibre properties are in-service elevated temperatures, moisture absorption, and exposure time. Jiang et al. (2019) and Akil et al. (2014) also reported that natural fibre composite durability is mainly affected by some parameters such as temperature and moisture and the combined effect of moisture and temperature (hygrothermal effect). When the composite is subjected to these factors, its fibre-matrix interface deteriorates, which in turn results in a loss of the composite properties. Therefore, an important consideration in using natural fibre composites is the risk of exposure to high temperature, moisture absorption, and the combined effect of moisture and temperature because they are important durability properties. To better understand the effects of these environmental factors on material properties, the following sections will discuss all of these factors in detail as individual cases.

2.4.1 Moisture durability

Natural fibres have the ability to absorb a high amount of moisture due to their hydrophilic nature when immersed in water or subjected to high wet environments. This results in a loss of their properties and swelling of these fibres causes weak fibre/matrix adhesion at the interface of their composites and therefore affects the performance of these natural composites (Balla et al. 2019; Bachchan et al. 2021; Vinod et al. 2021). This swelling also causes micro-cracks in the composite matrix, directly affecting most of the composite properties (Bachchan et al. 2021; Vinod et al. 2021). Moreover, the porosity and internal structure of natural plant fibres are major challenges associated with moisture absorption that limit their use in outdoor applications. When these natural composites are subjected to humid environmental conditions, moisture penetrates into their matrix through diffusion, transport, and capillary of water molecules (Alomayri et al. 2014; Abd Halip et al. 2019; Zhao et al. 2022). Therefore, prolonged exposure to moisture causes natural fibres to lose their functionality as effective reinforcements in polymer composites. Although physical and chemical treatment methods are used to modify the surface of these natural fibres to improve their resistance in moist environments, their composites still suffer from moisture-related issues. Recently, the use of nanomaterials as secondary reinforcements in neat resin and polymer composites can improve their physical, mechanical, and thermal properties since these nanomaterials have excellent properties such as high surface area and hydrophobic nature. These contribute to achieving the higher bonding strength at the interface. This strategy will contribute to reducing the moisture absorption rate and increasing the durability performance of natural fibre composites.

2.4.1.1 Moisture effects on hybrid composite properties

The effects of moisture on the long-term durability performance of natural fibre composites with nanoscale fillers have been mainly studied through the extensive use of water immersion test in the literature. This is because it is considered to be the most aggressive method of moisture absorption in polymer composites reinforced with natural fibres (Saidane et al. 2016; Chegdani et al. 2021). For example, Prasad et al. (2021) investigated the mechanical and physical properties of hybrid flax fibre-reinforced epoxy composites with nano Titanium dioxide (nano TiO_2) ranging from 0.2 to 0.8 % by weight of the matrix. They found that the highest hybrid effect was present in improving the tensile, flexural, moisture diffusion coefficient, and interlaminar shear strength of hybrid composites with 0.6 % nano TiO_2 by 22 %, 24 %, 42 % and 16 %, respectively, while reducing the moisture absorption rate. Begum et al. (2020) and Ashok et al. (2022) highlighted that hybridisation of natural fibre composites with fillers enhanced their moisture resistance and thus may lead to their potential use in outdoor applications. Vinay et al. (2022) also reported that continuous improvements in their properties make natural fibre composites with the inclusion of a small amount of nanoscale fillers more reliable for use in structural applications. Based on these published studies, it can be concluded that a hybrid solution of natural fibre composites with nanoscale filles is a suitable option for enhancing their mechanical and moisture resistance properties.

2.4.2 Thermal stability

The thermal stability of polymer-based composite materials is generally influenced by some major factors including thermal degradation of the polymer resin and fibre components. Polymer composites supported with natural plant fibres have a higher degradation level than that of synthetic fibre-based polymer composites when exposed to thermal conditions (Balla et al. 2019). This is mainly due to the biodegradation properties of these fibres at lower temperatures, as their thermal decomposition temperature is less than 200 °C. It is expected therefore that this will affect the mechanical and durability properties of natural fibre composites and limit their use in outdoor engineering applications. When these composites undergo a high conditioning temperature, this conditioning temperature leads to some physical and mechanical changes, namely dehydration, hydrolysis, oxidation, and discoloration as reported by Balla et al. (2019). These changes have negative effects on the thermal stability of these natural composites and therefore affect their performance. Nanofillers such as graphene with a high aspect ratio have the potential to provide thermal insulation layers that are effective in improving the thermal stability of natural fibre composites.

2.4.2 .1 Thermal degradation effects on hybrid composite properties

A number of researchers have studied the properties of hybrid natural fibre composites with nanoscale fillers under in-service elevated temperatures. Prasob and Sasikumar (2019) investigated the influence of elevated temperature on the viscoelastic and mechanical properties of hybrid jute fibre-reinforced epoxy composites with reduced graphene oxide (rGO) and Zirconium dioxide (ZrO2). They found that all hybrid composites showed a decrease in their tensile strength, compressive strength, and flexural strength with increasing conditioning temperature because the increase in temperature led to the development of different thermal expansion coefficients in the hybrid composites based on the reinforcing materials. This contributed to the increase in thermal stresses and their effect on the interface of these hybrid composites. However, the mechanical properties of hybrid jute fibre-epoxy composites incorporating ZrO2 were found to be higher for all temperature conditions than those of the samples with rGO due to better fibre-matrix adhesion caused by its good dispersion in the matrix. The highest glass transition temperature value was also recorded for hybrid jute composites with ZrO2. The authors concluded that temperature causes the thermal stresses from direct thermal expansion of reinforcing materials in natural fibre composites due to differences in their thermal coefficients, which in turn affects their thermal stability. A study by Sajna et al. (2017) investigated the thermal stability and fire retardancy of poly (lactic acid)

(PLA) matrix and banana /PLA composites and compared them with hybrid banana fibre-reinforced PLA composites incorporating nano clay. Thermogravimetric analysis of pure PLA, banana/PLA composites and hybrid banana fibre-reinforced PLA composites with nano clay showed that the amount of nano clay addition improved the thermal stability of hybrid composites compared to banana fibre composites and neat PLA. It was also found that hybrid composites revealed an improvement in their flame-retardant behaviour. Based on the results of these studies, it can be concluded that the addition of nanomaterials to natural fibre composites is introduced to ensure better thermal resistance. Therefore, the optimum amount of nanoscale fillers should be added to achieve a good balance between the mechanical strength and the thermal resistance of natural fibre composites.

2.4.3 Hygrothermal environment

A hygrothermal condition is known as an environment associated with moisture and in-service elevated temperatures in which fibre reinforced polymer composites are subjected to the most challenging environmental conditions at the same time. This will damage the fibres, matrix and interface of these composites causing them to lose their overall performance (Yang et al. 2019; Xu et al. 2020). The high temperature in a hygrothermal environment played an important role in accelerating the moisture absorption rate of natural fibre composites, which contributed to the swelling of the fibres and plasticization of the matrix. This led to the deterioration of the composites' properties. The durability of natural fibre composites may limit their use in outdoor environments (Christian 2020). This is due to their hydrophilic behaviour which results in poor moisture resistance and low durability performance, therefore additional protection for these natural fibre composites is vital as it is well known that moisture damage is accelerated when the temperature rises. For outdoor applications, these natural composites are expected to be subjected to hygrothermal conditions and improving their hygrothermal durability using nanomaterials is an effective option to obtain hybrid composites with higher properties than those using natural fibres alone as reinforcement for polymer matrices. This behaviour will be discussed further in the next section.

2.4.3.1 Hygrothermal degradation effects on hybrid composite properties

To understand whether there are any effects of these harsh environmental conditions on changes in the properties of natural fibre-reinforced polymer (NFRP) hybrid composites with nanoscale fillers, a number of researchers have investigated the mechanical and long-term properties of these NFRP hybrid composites. Wang et al. (2019) investigated the tensile and moisture absorption properties of hybrid flax fibre-reinforced epoxy composites with nano-clay exposed to a relative humidity of 80 % for 12 weeks at 20 °C, 40 °C and 70 °C. The authors found a decrease in the moisture absorption rate and diffusion coefficient of the hybrid composites compared to the control ones. They also found that hybrid composites exhibited higher tensile modulus retention as well as better dimensional stability than flax fibre composites after six weeks of exposure. However, there was a slight decrease in their tensile strength retention. A study on the hygrothermal ageing behaviour of hybrid flax fibre-epoxy composites with different weights of carbon nanofibres (CNFs) was undertaken by Wang et al. (2021). The study conducted to investigate the hybrid effect of CNFs on the tensile and water absorption properties of flax fibre composites immersed in water for 180 days at 23 °C, 40 °C, and 60 °C. The authors found in their study that the best hybrid effect was in the moisture absorption and tensile properties of hybrid composites with 1.0 % CNFs among other samples with 0.25, 0.5, and 2 % CNFs after hygrothermal exposure. Although these durability studies showed that adding nano-fillers to natural composites improved their short-term strength, the reinforcing effect of these nano-fillers on long-term strength is not well established yet and requires further investigation. The next section will focus on this area.

2.5 Long-term prediction

The denominated theory of Arrhenius is one of the most successful accelerated aging methods that can be used to determine the long-term prediction of composite materials subjected to accelerated aging conditions as reported by many researchers such as (Aiello et al. 2006; Wang et al. 2016; Ali et al. 2018; Manalo et al. 2020). According to Naya et al. (2013), Arrhenius rate model is considered to be the accurate method used for estimating the long-term and durability properties of polymer composite materials subjected to temperatures lower than their glass transition temperatures. Silva et al. (2014) also considered this model to be a new technique of technology often used to associate accelerated performance with actual behaviour by estimating the effects on the properties of polymer composites after long-term exposures using the experimental results of short-term exposure tests at in-service elevated temperatures. Regarding to this technique, Artificial Neural Network (ANN), Virtual Element Method (VEM), Two-way Analysis of Variance (ANOVA) and Finite Element Method (FEM) are different prediction methods that are used to estimate the durability performance of these materials using the accelerated test results after hygrothermal exposure as have been reported by many scholars such as (Adeyi et al. 2018; Yin & Zhang 2019; Khotbehsara et al. 2020; Velasco-Parra et al. 2022). The fundamental assumption of using Arrhenius rate model to predict long-term behaviour is mainly based on the fact that temperature is the dominant factor in accelerating the aging process without affecting the mechanism of material strength degradation, but the degradation rate will accelerate with increasing temperature (Hota et al. 2020). Based on the theory of this model, at least three temperature levels and three exposure durations are required to achieve reliable predictability (Robert & Benmokrane 2013), and the relationship of this model is written as shown in Equation 1.

$$k = A\,exp\left(\frac{-E_a}{RT}\right) Or\; ln\,k = ln\,A + \frac{-E_a}{RT} \text{ ………………….. Eq.1}$$

Where: k is degradation rate (1/time); A is constant of the material and degradation process; Ea is activation energy (energy required to accelerate degradation); R is universal gas constant; and T is temperature in Kelvin. The logarithm of 1/k is the time for a material property to achieve to a given value is a linear function of 1/T and with the slope Ea/R.

The purpose of using Arrhenius model is to investigate the flexural and inter-laminar shear properties of hybrid flax fibre-reinforced epoxy composites with graphene after the influence of hygrothermal aging conditions. Considering that graphene nanoparticles have excellent properties, namely high tensile strength, Young's modulus, small size, and high surface area, they should have some effects on the interfacial bonding strength and matrix plasticisation.

In recent years, many scholars have been used an Arrhenius rate model to predict the durability and mechanical characteristics of polymer composites. For example, Manalo et al. (2020) studied the long-term interlaminar shear strength (ILSS) retention of glass fibre-reinforced polymer (GFRP) bars immersed in a conditioning solution of alkaline, saline, and tap water at 23 °C, 60 °C and 80 °C for 28, 56, 112 days. The authors used the concept of master curves along with the time shift factor (TSF) in predicting service life, demonstrating that the ILSS retention of GFRP bars was more affected by alkaline solution than tap water or saline solution. The GFRP bars at a reference temperature of 30 °C will retain at least 54 %, 68 %, and 68 % of the original ILSS after 100 years of hygrothermal exposure. A study by Uthaman et al. (2020) investigated the service life prediction of neat epoxy and carbon fibre-reinforced polymer (CFRP) composites exposed for periods of 20, 40 and 80 days at 20 °C, 40 °C and 60 °C. The prediction results based on Arrhenius analysis showed that CFRP composites in alkaline solution exhibited better durability than in acidic environment but lower than that in tap water. These results also showed that the tensile strength retention of CFRP composites at five annual service temperatures obtained after 20 years, was 63.6 – 48 %, 49.8 – 32.7 %, and 44.9 – 29.1 % in tap water, alkaline, and acidic solutions, respectively.

2.6 Research gaps

Based on the previous studies reviewed in this Chapter, natural fibre composites have some drawbacks of thermal stability and moisture absorption that limit their use in outdoor applications. Although several researchers have used physical and chemical treatment methods of fibre surface modifications to improve the mechanical performance of their composites under different environmental conditions, these treatment methods could improve this performance in short-term exposure. However, there are no clear benefits of fibre surface modification in improving the long-term behaviour of their composites. Therefore, the hybridisation approach is a good option for producing hybrid composites with high properties. Nanomaterials such as graphene nanoparticles can be adopted to improve the durability of natural composites against the environmental degradation. In the literature, most of durability studies have dealt with the effect of these environmental factors on the properties of natural fibre composites in the case of individual weathering. There is therefore a need for a comprehensive assessment of the long-term durability of flax fibre composites by reinforcing the epoxy matrix with graphene under different weathering conditions. Through a detailed literature review of existing studies, major research gaps have been identified as follows:

- There is a lack of good scientific understanding regarding the effect of elevated temperature on the mechanical properties of hybrid flax fibre-reinforced epoxy composites incorporating graphene. Since the use of their applications in outdoor environments is expected to undergo thermal exposure, it is important to further understand the thermal durability of newly produced hybrid composites.
- The effect of long-term properties of hybrid flax fibre-reinforced epoxy composites in humid environments is not well known. It is important to have a basic understanding of the moisture absorption behaviour and how the nano-fillers considered for natural fibre composites affect their moisture absorption and durability.
- There is less understanding about the long-term durability of hybrid flax fibre-reinforced epoxy composites with graphene after hygrothermal condition. These hybrid composites in outdoor applications are often subjected to the combined effect of humidity and in-service elevated temperature, it is therefore necessary to increase the knowledge of their effects at the same time using Arrhenius rate models based on accelerated test results for long-term use predictions.

These research gaps are the main motivation and justification behind this research. The effects of these environmental conditions on the physical, mechanical and durability properties of hybrid flax fibre composites are investigated, wherein the results and significant findings are presented in Chapters 3 to 6.

CHAPTER 3: PAPER 1- INFLUENCE OF ELEVATED TEMPERATURE ON THE MECHANICAL PROPERTIES OF HYBRID FLAX-FIBRE-EPOXY COMPOSITES INCORPORATING GRAPHENE

3.1. Introduction

From the detailed literature review in Chapter 2, in-service elevated temperature is one of the most aggressive environmental factors affecting the properties of natural fibre/polymer hybrid composites. To address Objective 1, this chapter presented an evaluation of the mechanical properties of hybrid flax fibre-epoxy composites with graphene under the effect of in-service elevated temperatures. Hybrid composites with graphene ranging from 0, 0.5, 1.0 and 1.5 % by weight of the matrix were prepared and tested at a temperature of 20 ℃ to 100 ℃ with increments of 20 °C. Flexural and inter-laminar shear strength (ILSS) properties were investigated, and microstructure analysis and microscopic observations were implemented using a scanning electron microscopy (SEM). The results from this study indicated that the flexural and ILSS properties of flax fibre composites at room temperature increased by up to 62 % and 149 %, respectively, with the addition of graphene but did not improve at in-service elevated temperature. Moreover, the dispersion of graphene nanoparticles has a significant influence and plays an important role in improving these properties. Agglomeration of the filler due to the increased viscosity of the epoxy resin caused by the increased addition of graphene led to void formations in hybrid composites. Hybrid composites under flexure failed by fibre breakage at room temperature and by fibre pull-out at in-service elevated temperature while failure is due to tensile crack at room temperature and fibre pull-out at high temperature under ILSS. Humidity is considered as another environmental factor affecting the outdoor performance of natural fibre composites. Therefore, the reinforcing effect of graphene addition on the mechanical properties of flax fibre composites in a humid environment was studied and the test results will be displayed in the next chapter.

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Influence of Elevated Temperature on the Mechanical Properties of Hybrid Flax-Fiber-Epoxy Composites Incorporating Graphene

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Abstract: Natural fibers are now becoming widely adopted as reinforcements for polymer matrices to produce biodegradable and renewable composites. These natural composites have mechanical properties acceptable for use in many industrial and structural applications under ambient temperatures. However, there is still limited understanding regarding the mechanical performance of natural fiber composites when exposed to in-service elevated temperatures. Moreover, nanoparticle additives are widely utilized in reinforced composites as they can enhance mechanical, thermal, and physical performance. Therefore, this research extensively investigates the interlaminar shear strength (ILSS) and flexural properties of flax fiber composites with graphene at different weight percentages (0%, 0.5%, 1%, and 1.5%) and exposed to in-service elevated temperatures (20, 40, 60, 80, and 100 °C). Mechanical tests were conducted followed by microscopic observations to analyze the interphase between the flax fibers and epoxy resin. The results showed that a significant improvement in flexural strength, modulus, and interlaminar shear strength of the composites was achieved by adding 0.5% of graphene. Increasing the graphene to 1.0% and 1.5% gradually decreased the enhancement in the flexural and ILSS strength. SEM observations showed that voids caused by filler agglomeration were increasingly formed in the natural fiber reinforced composites with the increase in graphene addition.

Keywords: elevated temperature; flax fiber; natural fiber composite; mechanical properties; graphene nanoparticles; SEM

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1. Introduction

Synthetic-fiber-based polymer composites are now being used in a number of industrial applications including civil engineering and construction, packaging, and automotive industries due to their high strength, stiffness, and durability. However, the manufacturing and use of synthetic fiber composites have some detrimental effects on the environment due to their nondegradable nature, reduced recyclability, and toxicity [1]. Moreover, manufacturing of synthetic fibers such as glass, carbon, and aramid consumes more energy compared with that of natural fibers [2]. For example, the energy needed for flax fiber production is 9.55 MJ/kg while for glass fiber it is 54.7 MJ/kg, as reported by Joshi et al. [3] and Balla et al. [4]. The associated problems with the use of artificial fibers in manufacturing polymeric composites have led to an increased interest in plant-based fibers [5,6]. Using natural fibers can also result in high-performance composites [7] and renewable composites [8] at a relatively low cost [4]. Natural-fiber-based composites are now being used for automotive parts, construction elements [9], and wind turbine blades [10]. One major reason behind the increasing attraction of using natural fibers is their renewable nature, which can address the production instability issue of synthetic fibers associated with the shortage of oil resources [11,12]. Moreover, natural fiber composites can result in new materials that will not add to the growth of waste and promote sustainability [13]. Thus, interest has increased in exploring the use of different types of natural fibers as new reinforcements in polymeric composites.

Among many different types of plant fibers, flax is the most commonly used fiber for manufacturing natural fiber composites. Flax fibers are extracted from bast, which has a high cellulose percentage (approximately 30–76% by weight) as well as a low microfibril angle of 2 to 8 degrees. The cellulose percentage is responsible for the strength of the fibers while the microfibril angle controls the stiffness. Both contribute to the mechanical properties of the fibers and the performance of the composites [4]. Xiong et al. [14] stated that the addition of woven flax fibers into polyoxymethylene (POM) matrix improved the properties of flexural strength and tensile strength of POM composites compared with the control specimens. Prasob and Sasikumar [8] also indicated that polymer composites incorporating flax fibers and nanofillers have the same mechanical strength as glass-fiber-based polymer composites. Wang et al. [15] found that flax-based epoxy grafted with nanoparticles can significantly improve the flexural properties of the composites. In another investigation, Foruzanmehr et al. [16] observed that the graft of nanofillers can significantly enhance both the mechanical and physical properties of flax and polylactic acid (PLA) matrix nanocomposites. Nabinejad [17], on the other hand, indicated that the hybridization of natural fiber composites with nanoparticles requires more attention and suggested that further investigation is needed to determine the effects of nanofillers such as graphene nanoparticles on the mechanical properties of hybrid composites.

One limitation of natural fibers as effective internal reinforcements in polymeric composites is their lower thermal degradation property when compared with synthetic fibers [4]. This property of natural fiber composites restricts their widespread use in industrial and engineering applications. Many researchers have highlighted the sensitivity of synthetic-based fiber-reinforced polymer (FRP) composites at in-service elevated temperatures, due to the decomposition processes and glass transition of the polymer matrix material [18]. Although the structural performance of FRP composites at room temperature is considered acceptable, the behavior of composite materials under elevated temperatures is complex—a factor that Manalo et al. [19] highlighted still has limited awareness and requires a more detailed investigation. A better understanding of the behavior of natural fiber composites filled at in-service elevated temperature is therefore crucial for their wide acceptance and use in mechanical and structural engineering applications.

A number of investigations have evaluated the performance of synthetic-based FRP composites with and without nanofillers at in-service elevated temperatures under different loading conditions including tension, compression, interlaminar shear (ILSS), and flexure [8,20–25]. These researchers have concluded that the exposure of FRP composite materials to elevated temperatures resulted in a decrease in the mechanical properties but at different magnitudes depending on the type of resin systems, fiber reinforcements, and nanofillers. Moreover, the degradation of mechanical properties can be related to their glass transition temperature, which mainly depends on the type of resin used. However, the strength retention of polymer against in-service elevated temperature can be improved with the addition of particulate fillers [26,27]. Thus, the effects of nanofillers on the behavior of natural fiber composites under in-service temperatures require a more detailed consideration.

This study investigates for the first time the effectiveness of graphene nanoparticles in improving the performance of flax-fiber-based natural composites at in-service elevated temperatures. The experimental investigation focuses on the flexural and interlaminar shear performance of hybrid flax-reinforced epoxy-based composites with different levels of graphene by weight (0, 0.5, 1.0, and 1.5%) and tested at different levels of elevated temperature (RT, 40, 60, 80, and 100 °C, where RT is the room temperature of 20 °C). The results of this study will provide comprehensive information on the effect of graphene addition on natural fiber composites and their performance at in-service elevated temperatures. Moreover, it will support the development and application of cost-effective and eco-friendly biocomposites for industrial and engineering applications.

2. Experimental Program

2.1. Materials

Epoxy resin (R246TX) mixed with hardener (H160 Kinetix Medium Hardener) supplied by ATL Composites, Molendinar, Australia was used as a matrix in the manufacturing of the composites. The resin to hardener ratio used was 1:4 by weight, as recommended by the supplier. Graphene nanoparticles with average specific area of 300 m^2/g and elastic modulus of 340 GPa were supplied by Sigma-Aldrich, Castle Hill, Australia. The unidirectional flax fibers with density of 200 g/m^2 were supplied by Colan Composite Reinforcement, Huntingwood, NSW, Australia. Table 1 lists the properties of neat epoxy resin, natural fibers, and graphene based on the available literature and as provided by the supplier.

Table 1. Properties of flax fibers and neat epoxy resin.

Material	Density (g/cm^3)	Elastic Modulus (GPa)	Tensile Strength (MPa)	Reference
Flax fibers	1.40	70	1400	[28]
Epoxy resin	1.12–1.17	3.4	130	Technical Data Sheet [29]

2.2. Specimen Preparation

The flax fibers were arranged in a longitudinal direction and prepared as a sheet with dimensions of 600 mm in length and 400 mm in width (see Figure 1a). These sheets were placed in an oven set at a temperature of 40 °C for 30 min to move moisture before fabricating the composites. Hand layup technique was implemented to manufacture 4 mm-thick laminates, which were achieved by using 6 sheets of unidirectional flax fibers. Epoxy resin was mixed and poured onto the fiber sheet until saturated and the sheets were then placed on top of each other to make the composites where the fiber volume ratio (V_f) was maintained at 25%. This is based on a previous study, which showed that the weight proportion of the fiber content is in the range of 23% to 34% influenced by several factors including the resin and fiber type and the manufacturing process (hand layup and vacuum bagging processes) [30]. Our study lies in between. Similar findings have been reported in other works [31,32]. A metal roller was used to distribute the resin evenly over the fibers, ensuring good wettability of the fibers and to free any trapped air, as shown in Figure 1b. For the flax-reinforced composites with nanoparticles, different percentages of graphene—i.e., 0.5%, 1.0%, and 1.5% by weight—were mixed into the epoxy resin before being applied to the fibers. An electric shear mixer was used to ensure a homogeneous mix and to prevent aggregation of the graphene particles, as suggested by the graphene supplier. High-shear mixer facilitates the dispersion of graphene particles within the epoxy matrix by creating the shear force through the high-speed rotary motion of the mixer. This allows less aggregation and good dispersion of these nanoparticles in the epoxy matrix. The flax fibers moistened with resin were placed in the vacuum bag and sealed to start the vacuuming process at a constant pressure of 92 bar (see Figure 1c). This manufacturing technique was also implemented by Muralidhara et al. [33], Geren et al. [34], and Huang et al. [35] to produce high-quality composites. The manufactured sheets were left for 24 h under vacuum to cure initially and then post-cured for 3 h at 120 °C to enhance the heat distortion temperature (HDT) of epoxy (65 °C), as recommended by the manufacturer. The sheets were then cut to the required specimen dimensions for interlaminar shear and flexural tests.

(**a**) (**b**) (**c**)

Figure 1. (**a**) Unidirectional flax fibers. (**b**) Wetting the fibers. (**c**) Vacuum bagging.

2.3. Mechanical Testing

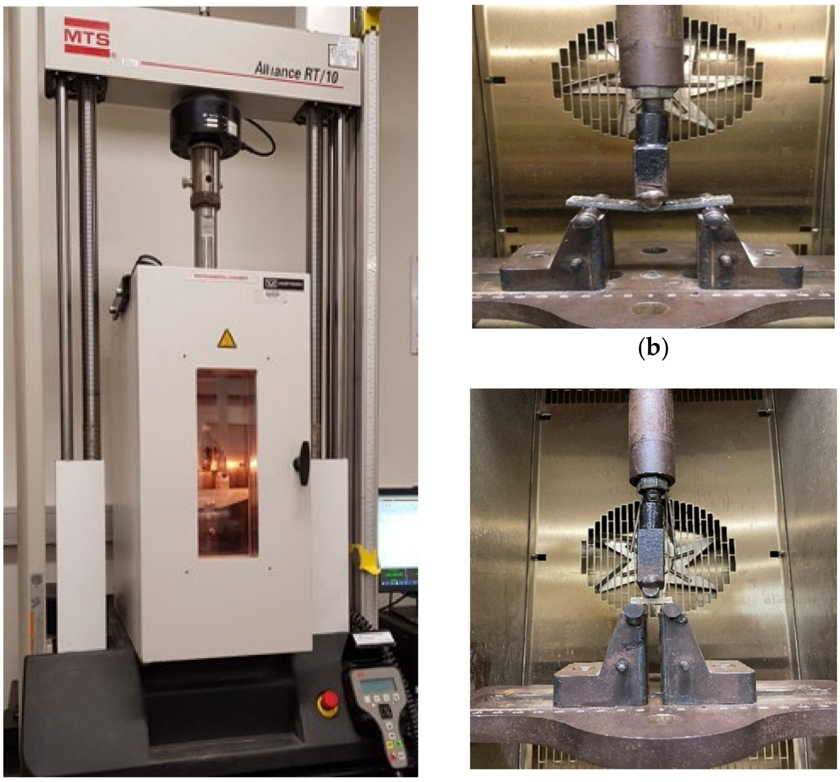
The flexural and interlaminar shear properties of flax-fiber-reinforced epoxy composites with different graphene percentages under in-service elevated temperature were characterized following ASTM D790 [36] and ASTM D2344 [37], respectively. Table 2 shows the standard sample dimensions for different mechanical tests based on the ASTM standards and the required number of samples for each test. At elevated temperature, the specimens were tested using an Instron 3119 (Illinois Tool Works Inc., Norwood, MA, USA) environmental chamber (Figure 2a) at RT, 40, 60, 80, and 100 °C, where RT refers to the reference specimens tested at room temperature (20 °C). The specimens were preheated in the oven at the target exposure temperature for at least 45 min prior conducting the test to ensure consistent temperature throughout the thickness, as recommended by Alajarmeh et al. [38]. The test commenced once the chamber reached the target temperature and was maintained for 5 min. All test samples were performed in a steady state using the 100 kN MTS machine (see Figure 2b,c) at a loading rate of 1.3 mm/min.

Table 2. Test specimen geometry and a number of coupons based on ASTM standard for evaluating mechanical properties.

Type of Test	Standard	No. of Coupons	Dimensions (mm)		
			Length	Width	Thickness
Flexural test	ASTM D790:2007	5	80	16	4
Interlaminar test	ASTM D2344:2016	5	24	16	4

2.4. Scanning Electron Microscope (SEM) Observation

The scanning electron microscope (SEM) JEOL JXA 840A (Tokyo, Japan) was used to examine the damage features, fracture surface, and fiber–matrix interface of the samples with and without graphene tested under different levels of temperature. SEM observations were also conducted to evaluate the distribution of the graphene nanoparticles within the composite matrix. The samples were carefully prepared by cutting around 10 mm by 10 mm from the tested specimens and then observed under the SEM.



(b)

(a) (c)

Figure 2. Mechanical tests for flax composites with various weights of graphene: (**a**) Instron Environmental Chamber; (**b**) Flexural Test; (**c**) Interlaminar Test.

3. Results and Observations

3.1. Flexural Behavior of Hybrid Flax Fiber-Reinforced Epoxy Composites

3.1.1. Flexural Strength and Modulus under Elevated Temperature

Figure 3 shows the flexural behavior of hybrid flax-fiber-reinforced epoxy composites with different graphene percentages at different levels of in-service elevated temperature. The values of 0%, 0.5%, 1.0%, and 1.5% in Figure 3 represent the amount of graphene nanoparticles by weight of the matrix. From Figure 3, significant improvements of flexural strength (FS) can be observed in composites with the addition of nanoparticles. It is worth mentioning that the highest average FS value at room temperature was obtained from the samples with 0.5% graphene (see Figure 3a). Adding more than 0.5% graphene, however, showed a consistently negative effect on the FS. The increase in temperature resulted in a significant reduction in the FS of the composites (Figure 3a), regardless of having graphene or not. This can be due to matrix softening. It was observed in Figure 3a that the composites without graphene showed a gradual decrease in the FS as the temperature increased to 60 °C. At a temperature above 60 °C, the FS of the composites dropped significantly. Beyond 8 °C, steady state in the FS was observed for all composite samples. This behavior can be explained by softening the matrix at higher temperatures. Since the test temperature is higher than the T_g of the composite, indicating a change in the molecular chain movement of the epoxy matrix, the bonding strength of the fibers with synthetic resin deteriorates at elevated temperature. Thus, this bonding is unable to mediate load transfer from the matrix to the fibers and the role of graphene addition is insignificant, but some of the fibers that remain intact can bear some load at this temperature level. Figure 3b shows the effect of the amount of graphene on the flexural modulus (FM) of flax-fiber-based epoxy composites at elevated temperature. A significant improvement in FM can be observed when adding graphene nanoparticles. At RT, adding 0.5% of graphene increased the FM by 50.8% (see Figure 3b). However, increasing the graphene content by 1.0% and 1.5% briefly increased the FM by 2.1% and 5.3%. At elevated temperature, linear reductions of 11.4%, 7.1%, 10.7%, and 16.6% in the FM values until 60 °C can be observed in the tested samples with graphene contents of 0%, 0.5%, 1.0%, and 1.5%, respectively, compared with the samples tested at room temperature.

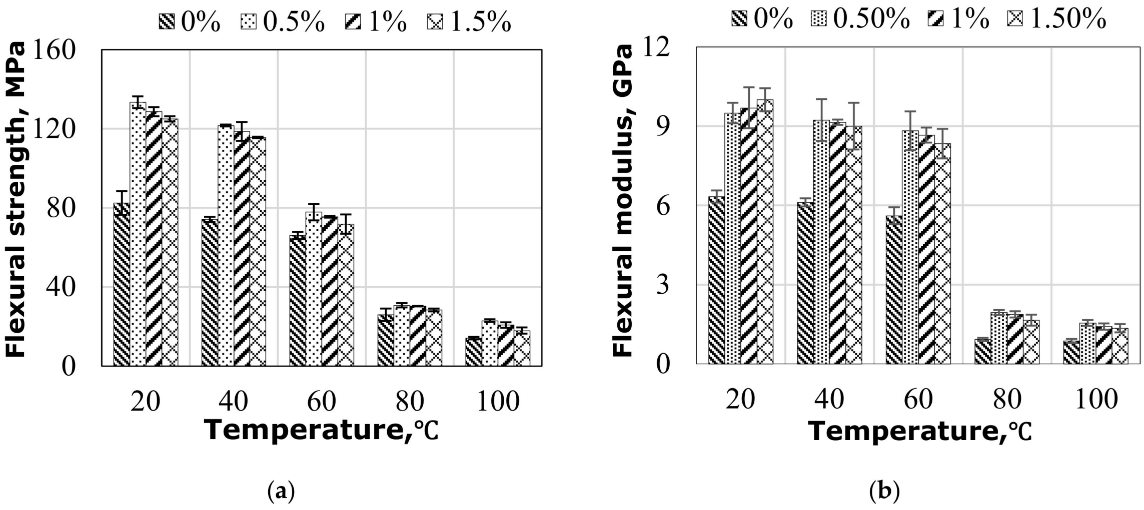


Figure 3. Temperature influence on the flexural properties of hybrid composites: (**a**) Flexural strength; (**b**) flexural modulus.

It is worth highlighting that the increase in graphene addition percentage indicates the high sensitivity of the composite samples with higher graphene content to elevated temperature due to other phenomena arising from the presence of graphene, which contributed to obtaining the trend of mechanical strength values for hybrid composites at elevated temperature. This trend of reduction in mechanical strength can be explained by the thermal effect from the vast differences in the thermal expansion coefficients of flax fiber, epoxy resin, and graphene particles in the hybrid composites. Flax fibers have a negative coefficient of thermal expansion in their longitudinal direction (-8×10^{-6}/°C) [39]. As for graphene and its derivatives, thermal expansion coefficient ranges from -7×10^{-6} K^{-1} to -0.77×10^{-6} K^{-1} as reported by Gangineni et al. [40], while epoxy matrix has a thermal expansion coefficient of 64–68 $\times 10^{-6}$ K^{-1} [40]. This means that there is a difference between the thermal stress values developed at the interface layers reinforced with various materials. As such, the deterioration at the interface increases with increasing temperature at the presence of graphene and thus results in lower mechanical performance. At 80 °C and 100 °C, in contrast, samples with 0%, 0.5%, 1.0%, and 1.5% graphene content show almost a retention of the FM in a range of 14.6% to 16.3%. This is because composite samples with graphene recorded a T_g temperature of 78 °C (for all samples with various graphene percentages), where the influence of the graphene addition becomes insignificant.

3.1.2. Failure Behavior in Flexure under Elevated Temperature

The failure modes in flexure of hybrid flax-fiber-reinforced epoxy composites under elevated temperatures are shown in Figure 4, which can be classified into four modes: (1) Tensile Failure (TF) at lower surface, (2) Fiber Breakage (FB), (3) Fiber Pull-out (FP), and (4) Interlaminar Failure (IF). All these modes of failure were accompanied by cracking in the matrix. The mechanisms of the different failure modes are described below.

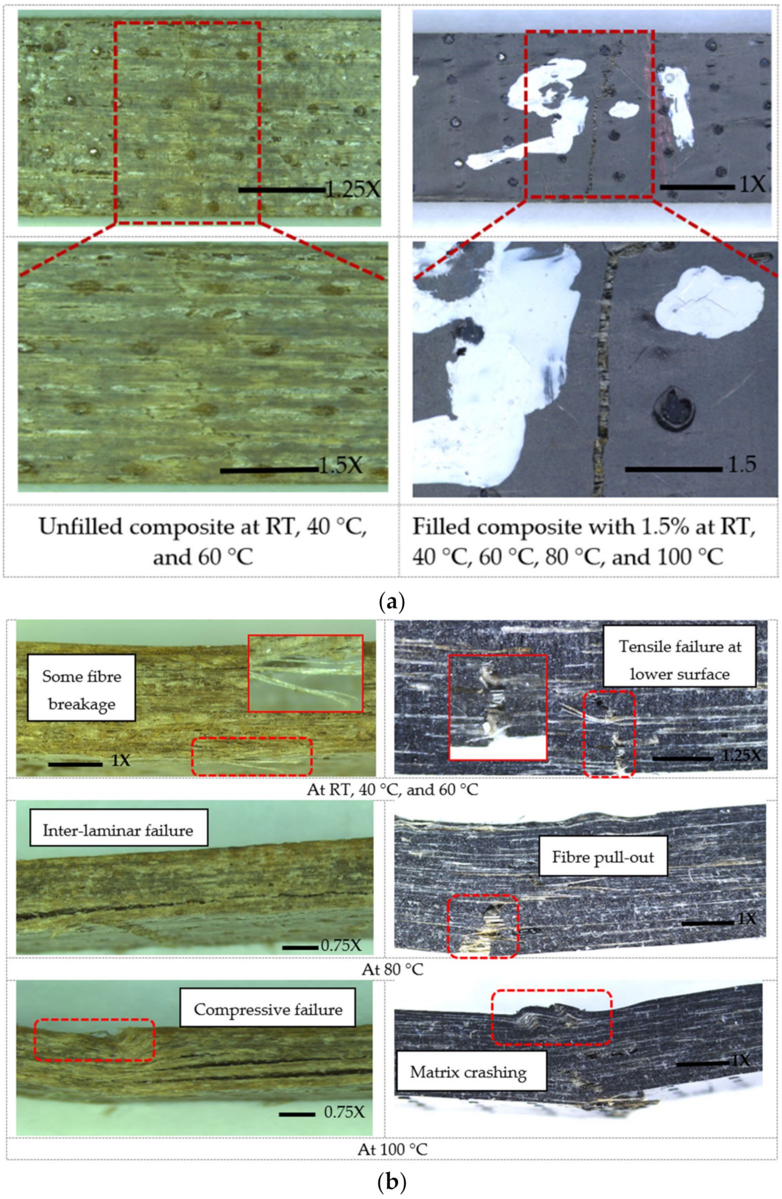


Figure 4. Flexural failure mechanisms for filled and unfilled composites at elevated temperature: (**a**) Tensile failures of hybrid composites with 0% and 1.5% at elevated temperature; (**b**) description of failure from the side view of the sample with 0% and 1.5%.

TF: This failure occurs when the load stress applied on a sample exceeds the material's strength [41]. This load stress causes individual fibers to break in the matrix. With an increase in the applied load, more fiber breakage occurs near the neighboring fractured fibers and then total tensile failure occurs. The tension region (lower surface) is the critical zone for the sample under these stresses. This failure was observed in specimens without graphene and tested at 20 °C, 40 °C, and 60 °C (see Figure 4a). This failure has also been observed for composites with graphene at different weight percentages and tested at levels of in-service elevated temperature. Due to this failure, a flexural crack intruded a few millimeters into the sample thickness (see Figure 4b) from the lower surface up towards the loading point.

FB: This failure occurs when local high stresses associated with the cracks of the cross-matrix and the intersection of the cracks of polymer matrix and ply interfaces occurred, as also observed by Jawaid et al. [42]. This means that when the fiber's tensile strength is exceeded, the FB occurs. This was observed in specimens without graphene and tested at

RT, 40 °C, and 60 °C (see Figure 4b). Hybrid nanocomposites tested at RT, 40 °C, 60 °C, 80 °C, and 100 °C also failed because of fiber breakages.

FP: This failure occurs when the interfacial bonding is weak, causing the fibers to slip out of the matrix. Exposure of the hybrid composites to the in-service elevated temperature caused softening of the epoxy matrix allowing the fibers to slide in the direction of flexural loading. This type of failure was observed in specimens with various graphene weight percentages and tested at 80 and 100 °C (see Figure 4b).

IF: Interlaminar failure is caused by the high interlaminar stresses developed between the layers of the fibers [43,44]. This failure is often described, as the separation of layers within composite laminates caused by matrix failure was observed in all specimens with graphene when tested at 100 °C and for composites without graphene when tested at 80 °C and 100 °C. The difference, however, is that the IF failure occurs parallel to the direction of reinforcement for composites without graphene (see Figure 4b), but this failure was propagated in an inclined plane through the sample thickness for composites with graphene (see Figure 4b).

3.2. Interlaminar Shear Behavior of Hybrid Flax-Fiber-Reinforced Epoxy Composites

3.2.1. Interlaminar Shear Strength under Elevated Temperature

Figure 5 displays the effect of the amount of graphene along with temperature on interlaminar shear strength (ILSS) of flax-fiber-based epoxy composites. The addition of the nanoparticles revealed a significant increase in the ILSS of hybrid composites. The ILSS of the tested composites with 0.5%, 1.0%, and 1.5% graphene at room temperature increased by 148.6%, 138.9%, and 134.7%, respectively, when compared with the specimens without graphene. On the other hand, the composites without graphene showed a progressive and uniform reduction in the ILSS of around 15% for every level of temperature considered in this study. On the contrary, the composites with graphene showed only a 10% reduction in ILSS when the test temperature increased from RT to 40 °C. A 45% reduction in ILSS was then observed once the temperature was increased from 40 °C to 60 °C. A further reduction of 68% in ILSS was noticed when tested at 100 °C.

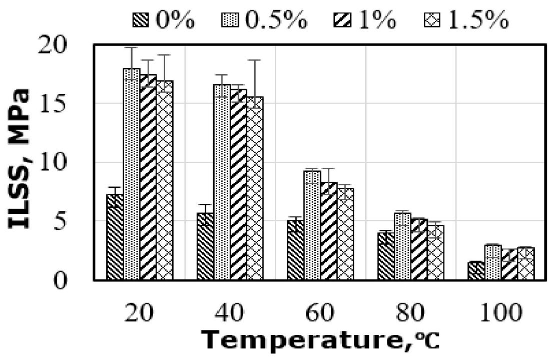


Figure 5. Relationship between temperature and ILSS results.

3.2.2. Failure Modes in ILSS under Elevated Temperature

The failure modes of composites with and without graphene in ILSS under elevated temperature can be categorized as (1) End-ply Delamination (ED), (2) Compressive Failure (CF), (3) Matrix Deformation (MD), and (4) Mid-span Delamination (SD). A description of these failure modes is provided below:

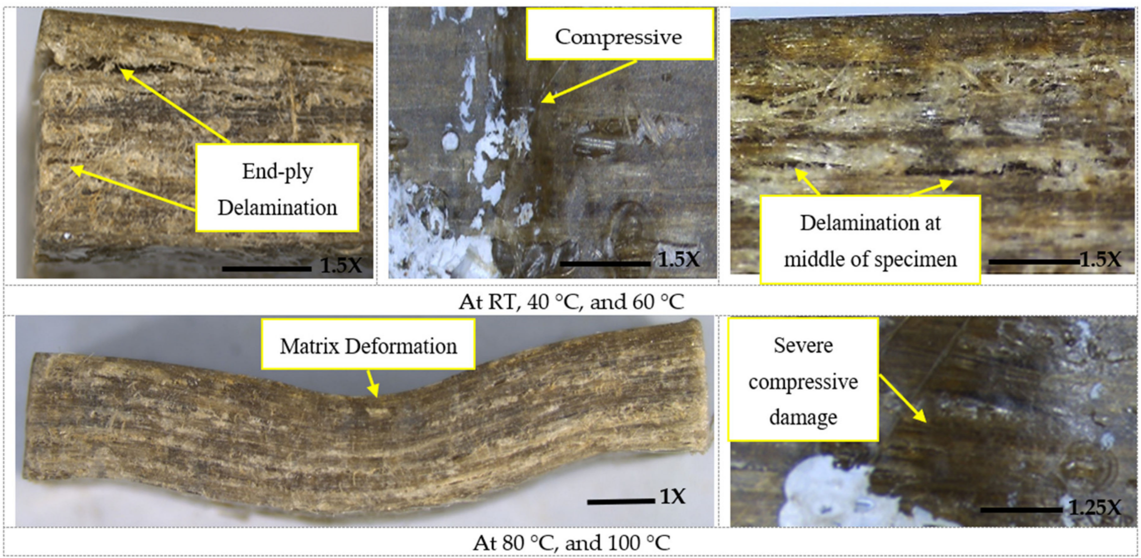
- ED: This failure can be identified as a horizontal interlaminar crack initiated at the end of the specimens and propagated to the mid-span of the sample (Figure 6a). This failure occurs due to the composites exceeding their interlaminar shear strength at the ends due to the applied stress. ED was observed in specimens without graphene at RT, 40 °C, and 60 °C. This failure in samples with graphene changed to tensile failure at lower surface and distributed through the thickness in an inclined plane due to the increase in matrix stiffness caused by graphene addition at RT and 40 °C (see Figure 6b).

- CF: This type of failure occurs by compressive stresses on the upper surface and was observed in specimens without graphene when tested at different levels of temperature, as can be seen in Figure 6a. As for specimens with different levels of graphene by weight, compressive damage was observed in their top surface when tested at 60 °C, 80 °C, and 100 °C (see Figure 6b).
- MD: This mode of failure appeared as permanent deformation in the specimens without graphene nanoparticles and tested at 80 °C and 100 °C (see Figure 6a). This permanent deformation is accompanied with compression at the top surface for all the specimens with graphene and tested at 80 °C and 100 °C, as shown in Figure 6b. The tested composites failed by MD were able to retain a part of their original straightness after the removal of the applied load.
- SD: Increasing the temperature up to 80 °C and 100 °C for composites without graphene and with graphene resulted in failure by severe horizontal interlaminar cracks. SD failure initiated at the mid-span and propagated towards the supports because of the high mid-span deflection under loading, as shown in Figure 6a,b. This failure was also accompanied with matrix deformation under the loading point as it became soft at elevated temperatures.

3.3. SEM Image Analysis

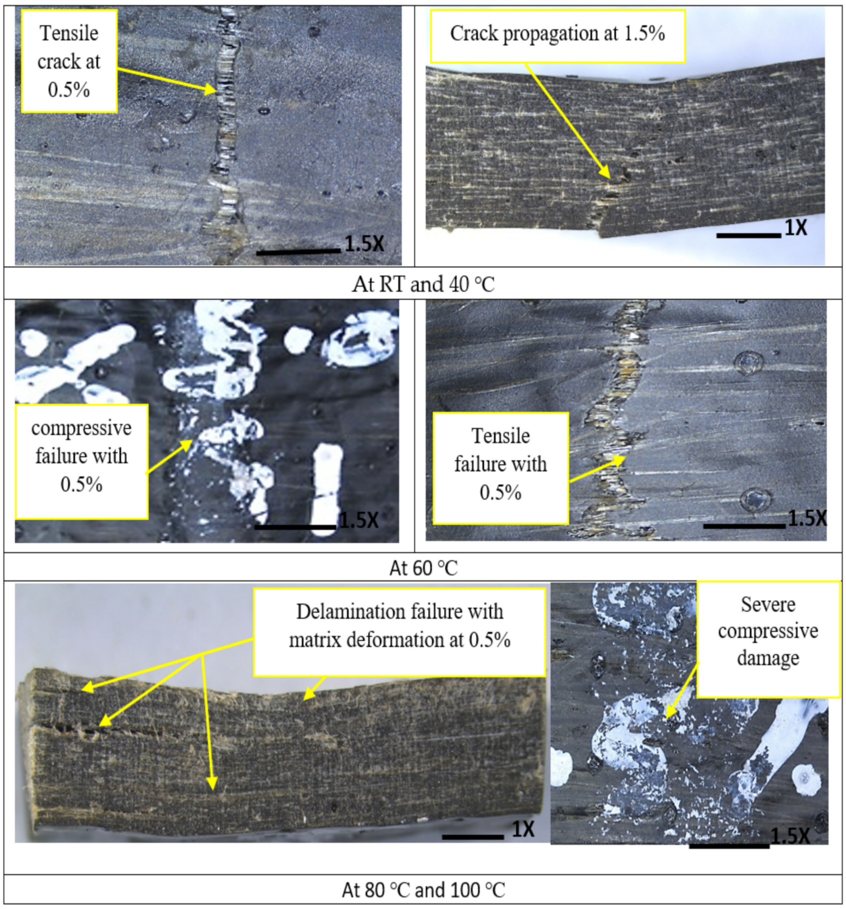
The microstructure of flax fiber composites with various amounts of graphene at room and at elevated temperature was analyzed by Scanning Electron Microscope (SEM), as shown in Figure 7. The SEM image (up to magnification of ×500 times) also provided information of the internal structure showing the distribution of the fibers and the dispersion of the graphene to the epoxy matrix. It is worth mentioning that the analysis was conducted on the fracture surfaces of the tested specimens to evaluate the effect of the graphene and temperature on the observed failure modes.

Figure 7a shows large voids in the resin matrix of the control specimen, with weak fiber–matrix adhesion at room temperature. For specimens with 0.5% graphene, Figure 7b exhibits well-distributed and properly bonded graphene particles to the epoxy resin with a lower content of voids in the matrix where these voids were not around the fibers. Better fiber–matrix adhesion was also clear on these specimens, which was evident from the absence of fiber pull-out.



(**a**)

Figure 6. *Cont.*



(**b**)

Figure 6. Short beam failure features under elevated temperature: (**a**) Failure mode of flax fiber composites; (**b**) failure mode of hybrid nanocomposites with 0.5% and 1.5%.

In contrast, the specimens with higher graphene percentages (1.0% and 1.5%) showed a greater number of void formations caused by filler agglomeration induced by the increase in the viscosity of the epoxy resin (see Figure 7c). These voids are clearly observed around the flax fibers, indicating that the fibers are not bonded properly to the epoxy resin at these locations. This also led to the formation of more weak points where failure can be initiated by fiber breakage. The formation of voids due to filler agglomeration in the filled composites contributes to poor interfacial bonding. This weakness in interfacial bonding can also explain the observed interlaminar failure of all composites. As such, increasing the viscosity by adding nanoparticles has been affirmed in other investigations [45].

At a higher temperature, the SEM images were chosen at 60 °C because this temperature is the HDT of the epoxy at which the resin begins to soften [26]. Further, according to the supplier instructions, the HDT of epoxy is 65 °C after 3 h curing time at 120 °C, as mentioned in the previous specimen preparation section. The T_g for epoxy was also measured by DMA test, which was 64.6 °C. In the case of softening, although reducing the size of voids in all composites, regardless of filled or not, softening of the resin resulted in a continuous decrease in mechanical properties. For the control specimen tested at 60 °C, more pores were observed due to fiber pull-out, as shown in Figure 7d. The specimens with 0.5% graphene had good fiber–matrix interface adhesion, with less fiber pull-out present (see Figure 7e). However, specimens with 1% and 1.5% showed more fiber pull-out, indicating evidence of poor fiber–matrix interface adhesion (see Figure 7f).

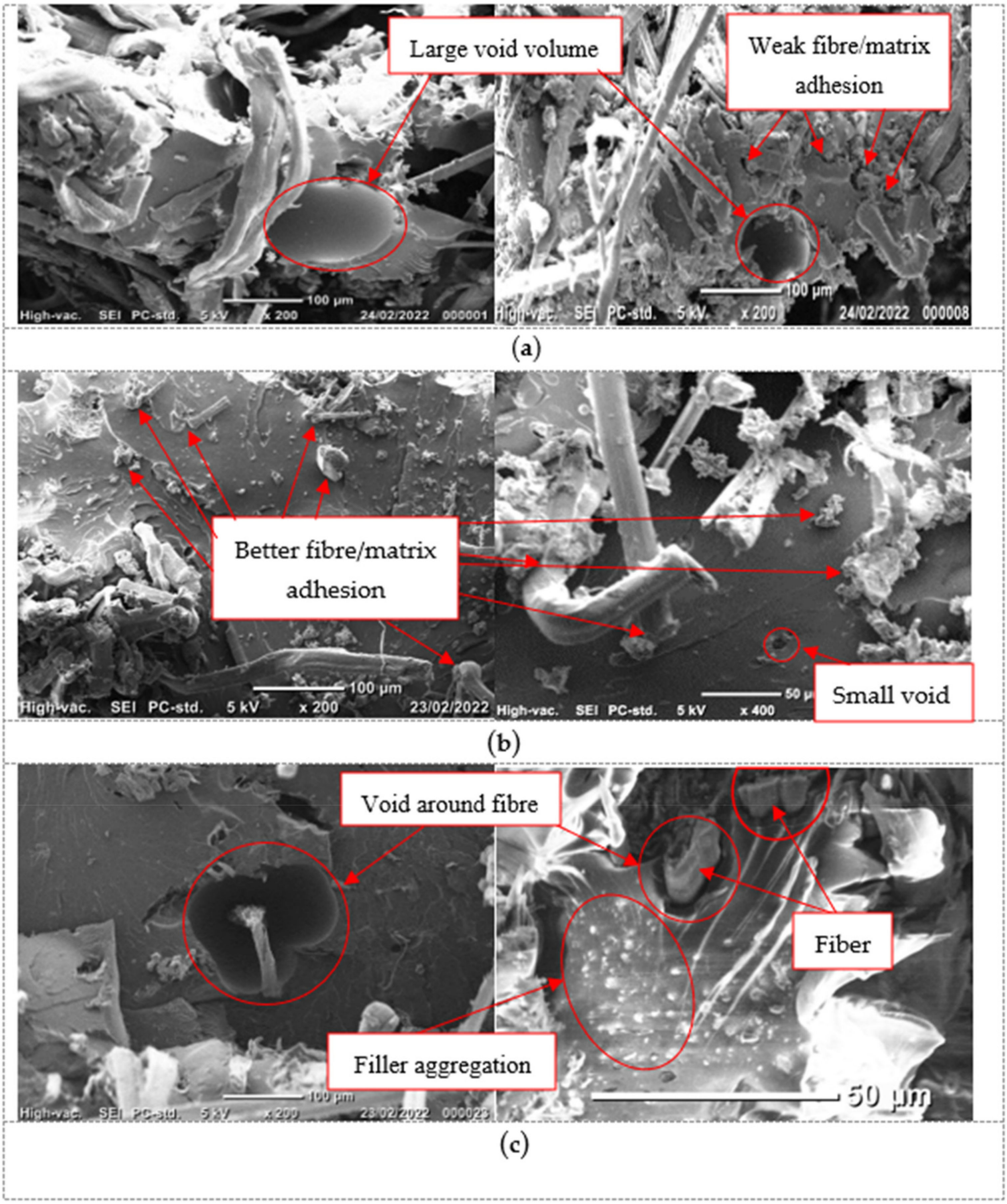
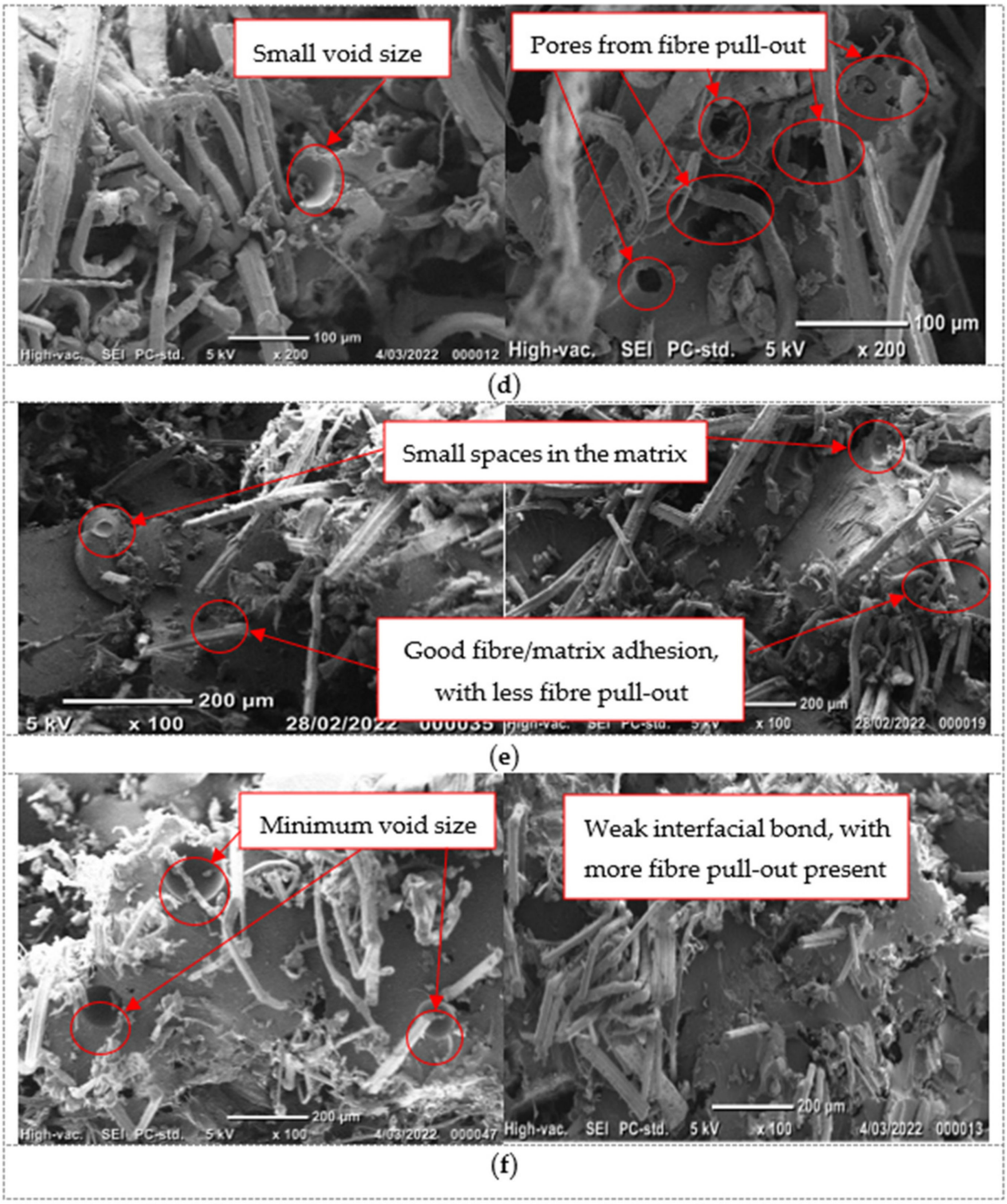


Figure 7. *Cont.*



Group 2: At 60 °C

Figure 7. SEM images for specimens with various percentages of graphene: (**a**) Composite without graphene; (**b**) composite with 0.5%; (**c**) composites with 1% and 1.5% tested at RT; composites (**d**–**f**) with 0%, 0.5%, and (1%, 1.5%), respectively, tested at 60 °C.

4. Discussion

4.1. Influence of Amount of Graphene on Flexural Strength and Stiffness

Adding graphene nanoparticles to the resin matrix changed the flexural behavior of the flax–epoxy composites. For instance, adding 0.5% of graphene to the neat resin increased the flexural strength and modulus by 62% and 47%, respectively, at room temperature (Figure 3a,b). This increase in the flexural strength and modulus can be explained by the inclusion of graphene that filled the available space within the epoxy resin and improved the wettability of natural fibers and polymer matrix by building a bridge between them.

This bridge facilitated the uniform distribution of individual fibers and reduced fiber–fiber interactions and fiber entanglement. The better adhesion between the fibers and resin led to a higher efficiency for transferring internal stresses through the interphase. This finding agrees with the results of the study as suggested by Kamaraj et al. [45], Zhou et al. [46], and Aswathnarayan et al. [47] wherein they observed an enhancement of flexural and tensile strength of plant fiber composites with the inclusion of graphene. They explained that the improvement in the mechanical properties was because of the uniform distribution of filler and improvement of interfacial interaction between the filler and the fibers. It is worth mentioning that graphene particles are stiffer materials than epoxy resin, which increases the stiffness of the matrix but makes it more brittle [48–51]. Increasing the percentage of the graphene to 1.0% and 1.5% slightly decreased the flexural strength by 3% and 4%, respectively, compared with the 0.5% addition. The mode of failure was similar, wherein the composites failed by a compressive crack at the top and a tensile crack at the bottom and with fiber breakage at the cracked zone due to the agglomeration and voids' formation upon increasing the graphene due to the epoxy becoming more viscous, as observed in Figure 7. These defects caused localization and premature failure, as shown by the observed failure where fiber breakage occurred mostly for those fibers passing through the voids (see Figure 7c). As expected, adding more graphene nanoparticles increased the stiffness of the matrix resulting in composites with higher flexural strength and modulus than the specimens without graphene.

4.2. Influence of Amount of Graphene on ILSS

The addition of graphene significantly enhanced the interlaminar properties of the flax fiber–epoxy composites. Adding 0.5% of graphene increased the ILSS by 250% compared with the composites without graphene because of the stronger fiber–matrix interface developed by adding nanoparticles, which allowed stress to transfer easily across the fibers. This was supported by the observed failure behavior, wherein the composites with 0.5% graphene failed by flexural failure (Figure 6b) and not by interlaminar shear. Increasing the graphene to 1.0% and 1.5% slightly reduced the failure stress by 3% and 5%, respectively, compared with the 0.5% addition because of filler agglomeration. These phenomena can be explained by the increased viscosity of epoxy resin because of the increase in the percentage of graphene, which leads to more agglomeration of the filler. This small reduction in ILSS at room temperature is similar to the results reported by Koirala et al. [52], in which carbon nanotube (CNT) sheets reinforced polymer composites showed a gradual reduction in ILSS at room temperature. They explain that this behavior is a result of CNT agglomeration. It should also be mentioned that all the specimens with graphene addition showed flexural failure at room temperature (Figure 6b).

4.3. Influence of Elevated Temperature on Flexural Strength and Stiffness

The flexural strength and stiffness of flax-fiber–epoxy composites with graphene are affected differently at in-service elevated temperatures. At 40 °C, the flexural strength and modulus decrease by around 7–10% and 3–5%, respectively, for all samples, regardless of whether they are filled or not, as shown in Figure 8a,b. There is also no effect of the mode of failure (see Figure 4b). At 40 °C, nevertheless, the increase in the graphene percentage (0.5%, 1.0%, and 1.5%) resulted in higher flexural strength and modulus retention. This means that resin at this temperature started to soften but is still able to hold the fiber and graphene together and transfer stress between them. However, increasing the service temperature to 60 °C reduced the flexural strength and modulus by (20%, 42%, 42%, and 43%) and (15%, 19%, 18%, and 17%) for the specimens with (0%, 0.5%, 1.0%, and 1.5%), respectively. Flexural strength started to be affected by this level of test temperature whereas the flexural modulus remained stable, as the former property was mostly controlled by the interface between the fiber and matrix and the latter property was governed by the properties of the fiber. It can be clearly observed that at this temperature, the resin came close to the T_g, indicating the start of its softening. Moreover, the specimens with graphene showed higher degradation loss in strength under elevated temperature than the specimens with no graphene, which was attributed to the extreme variation in the thermal expansion coefficients of the three phases that developed different internal thermal stresses at the interface of the samples with graphene. This resulted in a lower efficiency of transferring internal stresses through the interface of specimens with graphene than specimens without graphene particles. Unlike the findings observed at 40 °C, increasing the percentage of graphene particles at 60 °C briefly reduced the retention in flexural strength of the tested specimens, confirming the effect of graphene anisotropy on the thermal stresses developed at the interface when increasing the amount of graphene. In other words, the extent of thermal expansion was higher in the hybrid composites with more graphene, leading to further deterioration of the interface. A significant reduction in the flexural properties has been witnessed at 80 °C and 100 °C (see Figure 8a,b). At 80 °C, specimens with no graphene showed 31% and 14% retention in flexural strength and modulus, respectively, whereas specimens with graphene showed almost 22% and 20% retention in flexural strength and modulus, respectively. Furthermore, at 100 °C, specimens with no graphene showed 17% and 11% retention in flexural strength and modulus, respectively. Similarly, specimens with graphene showed only 15% and 14% retention in flexural strength and modulus, respectively, indicating the insignificant effect of graphene on the mechanical performance at high service temperature.

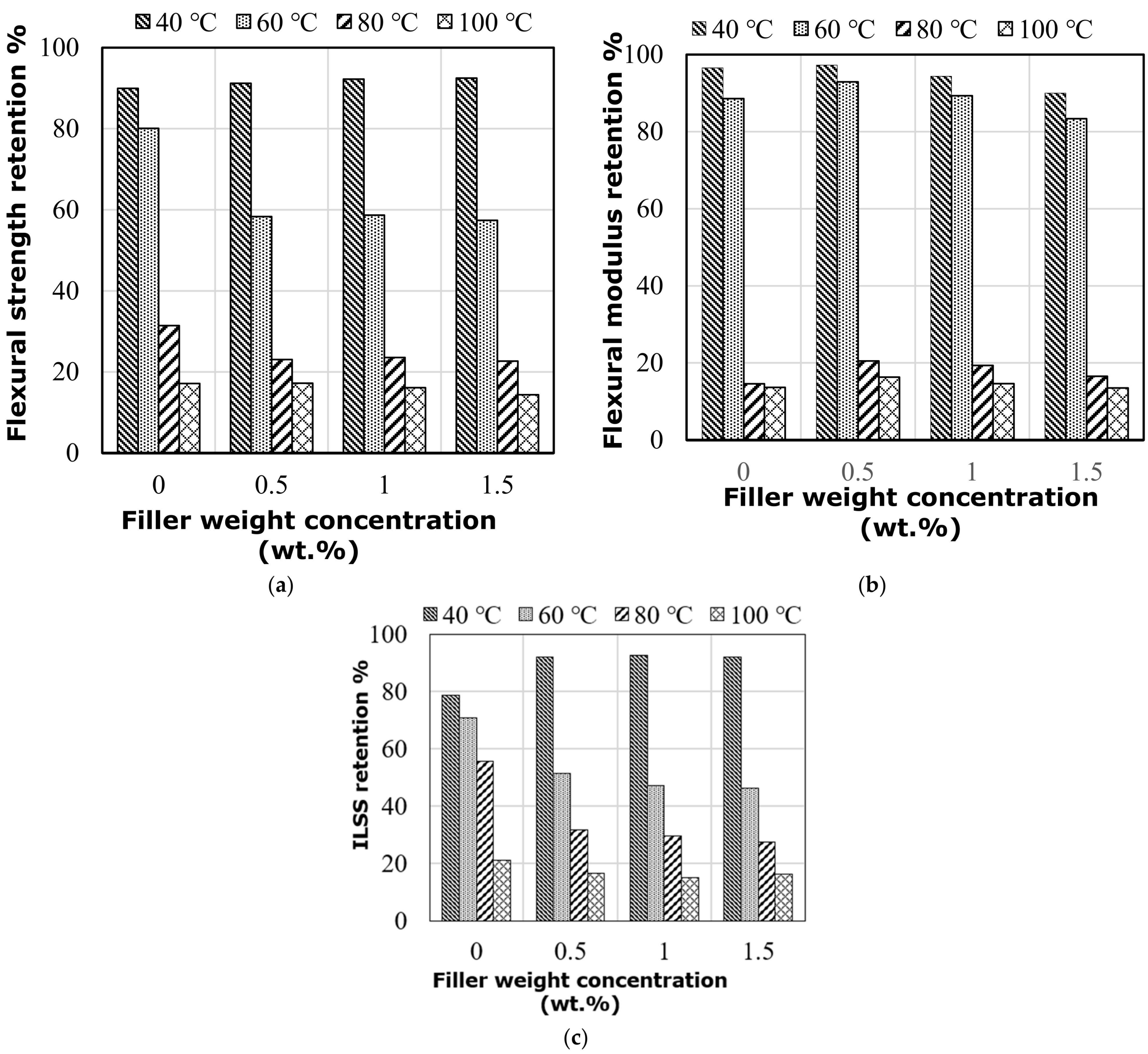


Figure 8. Property retention of the tested specimens at elevated temperature: (**a**) flexural strength retention; (**b**) flexural modulus retention; (**c**) interlaminar shear strength retention.

4.4. Influence of Elevated Temperature on ILSS

The composites with and without graphene particles behaved differently when tested in ILSS at elevated temperature. The ILSS reduction in the specimens with no graphene particles was 22% compared with the 8% reduction in those with graphene particles at 40 °C (see Figure 8c). Due to the graphene inclusion, the latter specimens showed flexural failure instead of the interlaminar failure observed by the former specimens. In contrast, even when showing the same mode of failure at 60 °C, specimens with graphene percentages of 0.5%, 1.0%, and 1.5% revealed 52%, 47%, and 44% retention in the failure load compared with the specimens tested at room temperature. On the other hand, the specimens with no graphene showed 70% retention in the ILSS value. As mentioned earlier, this finding refers to different thermal expansion coefficients between three phases in the hybrid composite, which resulted in various thermal stresses at the interface when tested at elevated temperature leading to a higher reduction in mechanical properties. Moreover, it was obvious that specimens without graphene retained higher ILSS at 80 °C and 100 °C (57% and 20%, respectively) compared with the ones with graphene at the same temperatures (30% and 16%, respectively) because of the absence of graphene at the interface of flax fiber composite, and the extent of thermal expansion was less at the interface. Moreover, with the higher thermal stresses in the latter specimens resulting from the development of different thermal expansion between the layers reinforced with different types of reinforcements, their mode of failure changed from flexural to severe interlaminar shear (Figure 6b), which revealed a significant reduction in ILSS retention compared with the unfilled specimens.

5. Conclusions

This study investigated the effect of graphene nanoparticles on the flexural and interlaminar shear strength (ILSS) properties of flax fiber epoxy composites at in-service elevated temperature. Hybrid composites with graphene ranging from 0, 0.5, 1.0, and 1.5% by weight of epoxy resin were prepared and tested at a temperature of 20 °C to 100 °C with increments of 20 °C. From the test results and observations, the following points are concluded:

An increase in the flexural and ILSS strength of flax fiber–epoxy composites at room temperature was achieved with the addition of graphene nanoparticles. The addition of 0.5% graphene increased the flexural and ILSS strength of tested composites by 62% and 149%, respectively, due to the increase in bond strength at interface between the epoxy resin and flax fibers caused by the contribution of graphene nanoparticles. Increasing the amount of graphene from 0.5% to 1.0% and 1.5%, however, reduced the flexural strength and ILSS strength by 57% and 52%, and 142% and 135%, respectively, attributed to the filler agglomeration as witnessed from the SEM observations.

- The addition of graphene nanoparticles improved the flexural modulus of flax fiber composites by 50%, 53%, and 58%, respectively, for 0.5%, 1.0%, and 1.5% at room temperature. This improvement in the flexural stiffness resulted in the failure mode changing from ductile to a brittle manner due to the greater stiffness of the graphene.
- The addition of graphene nanoparticles has an insignificant influence on the flexural and ILSS strength of flax fiber composites at in-service elevated temperature. The flexural and ILSS strength retention of the composites with 0.5% graphene nanoparticles were 60% and 52%, respectively, at 60 °C, and only 18% at 100 °C. This is a result of the high difference in the thermal expansion of the hybrid composites with graphene, which contributes to the increase in thermal stresses and their effect on the bonding strength of the interface at in-service elevated temperature. In contrast, the composites without graphene retained their flexural strength and ILSS up to 80% and 60%, respectively, at 60 °C, with similar strength retention to the composites with graphene at 100 °C.
- The mode of failure in flexural samples with graphene changed from the fiber breakage at room temperature to fiber pull-out at elevated temperature showing that the

matrix properties governed the failure at in-service elevated temperature. Similar failure behavior can be observed for flexural test specimens without graphene at room temperature. Under ILSS, the stronger fiber–matrix interface by adding graphene nanoparticles changed the failure behavior from interlaminar shear to tensile failure and fiber pull-out at low and moderate temperature, and from fiber pull-out and tensile failure to delamination failure at elevated temperature.

It can be recommended that further studies are required to investigate the inclusion of graphene into natural fiber composites considering the durability and environmental behavior of this type of composite. Various types of filler can be also investigated to study the bonding mechanism between different fillers and fibers.

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CHAPTER 4: PAPER 2 - LONG-TERM WATER ABSORPTION OF HYBRID FLAX FIBRE-REINFORCED EPOXY COMPOSITES WITH GRAPHENE AND ITS INFLUENCE ON MECHANICAL PROPERTIES

4.2. Introduction

In Chapter 3, the addition of graphene nanoparticles was found to significantly improved the mechanical properties of flax fibre composites at room temperature. This hybrid composite is developed for outdoor application where it will be subjected to different harsh environmental conditions. This Chapter investigated the effect of high moisture conditions on the physical and mechanical properties of flax fibre-reinforced epoxy composites with graphene nanoparticles. The flexural and inter-laminar shear properties of composites with 0 %, 0.5 %, 1.0 % and 1.5 % graphene were immersed in water for 1000, 2000, and 3000 hours at room temperature. The results showed that the addition of graphene significantly reduced the moisture absorption and moisture diffusion due to their high aspect ratio. The improvement in the mechanical properties under wet conditions was higher compared to the control samples. However, all hybrid composites exhibited a decrease in their mechanical properties with increasing exposure duration but those with graphene retained higher mechanical properties than those without. The results of this study demonstrated the high barrier properties provided by the graphene to increase the moisture resistance of flax fibre composites, which suggested their possible applications in an outdoor environment. Based on the results of Chapter 3 and Chapter 4, there was an effect of in-service elevated temperature and high moisture on the mechanical performance of hybrid flax composites with graphene, but this effect was investigated as individual weathering cases. Therefore, the combined effect of these environmental factors on the mechanical behaviour of these hybrid composites has been studied and the test results are shown in Chapter 5.

polymers

Article

Long-Term Water Absorption of Hybrid Flax Fibre-Reinforced Epoxy Composites with Graphene and Its Influence on Mechanical Properties

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Abstract: Interest in the use of natural fibres as an alternative for artificial fibres in polymer composite manufacturing is increasing for various engineering applications. Their suitability for use in outdoor environments should be demonstrated due to their perceived hydrophilic behaviour. This study investigated the water absorption behaviour of hybrid flax fibre-reinforced epoxy composites with 0%, 0.5%, 1% and 1.5% graphene by weight that were immersed in water for 1000, 2000, and 3000 h. The flexural and interlaminar shear strength before and after immersion in water was then evaluated. The results showed that graphene nanoparticles improved the mechanical properties of the composites. The moisture absorption process of hybrid natural fibre composites followed the Fickian law, whereas the addition of graphene significantly reduced the moisture absorption and moisture diffusion, especially for hybrid composites with 1.5% graphene. However, the flexural and ILSS properties of the composites with and without graphene decreased with the increase in the exposure duration. The flexural strength of hybrid composites with 0%, 0.5%, 1% and 1.5% graphene decreased by 32%, 11%, 17.5% and 13.4%, respectively, after exposure for 3000 h. For inter-laminar shear strength at the same conditioning of 3000 h, hybrid composites with 0.5%, 1% and 1.5% graphene also decreased by 13.2%, 21% and 17.5%, respectively, compared to the dry composite's strength. The specimens with 0.5% graphene showed the lowest reduction in strength for both the flexural and interlaminar tests, due to good filler dispersion in the matrix, but all of them were still higher than that of flax fibre composites. Scanning electron microscope observations showed a reduction in voids in the composite matrix after the introduction of graphene, resulting in reduced moisture absorption and moisture diffusion.

Keywords: moisture absorption; flax fibre; natural fibre composite; mechanical properties; graphene nanoparticles; SEM

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1. Introduction

Interest in the use of natural fibres as a replacement for artificial fibres as reinforcements in polymer composites has increased in the last decade due to their advantages, such as being renewable resources and their abundance, recyclability, biodegradability, low density, good mechanical characteristics, light weight and low cost [1,2]. Due to these advantages, natural fibres are now utilised in building and construction, automotive parts and other industrial applications [3–5]. However, natural fibres are found to be highly sensitive to moisture and are incompatible with most polymer matrices [6,7]. These issues are related to their hydrophilic nature, where they tend to absorb a high amount of moisture when immersed in water or exposed to an extremely humid environment. As a result of moisture absorption, natural fibres used as reinforcement swell and cause micro-cracks in the polymer matrix, which directly affect most composite properties [8,9]. Therefore, the water absorption of natural fibre composites should be evaluated for their wide use in different engineering applications [10].

The sensitivity of natural fibre-reinforced polymer (NFRP) composites to humid environmental conditions has been highlighted by several researchers [11–13]. These researchers concluded that the exposure of composites to an aggressive environment for a long period of time caused their mechanical properties to be reduced. The variation in the mechanical strength reduction depends on the type of fibre used as reinforcement, the filler used as an additive and the resin used as a matrix. A number of critical parameters govern the moisture diffusion behaviour of the NFRP composites [14–16] including the diffusion of water molecules through micro-cracks in the polymer matrix composites. Other mechanisms are the capillary transport of water molecules along interfacial bonding between the fibre and the polymer matrix and the water diffusion in the micro-cracks of the polymer matrix caused by fibre swelling. It should be highlighted that the swelling of natural fibres constrains their use as effective internal reinforcement for polymeric composites in outdoor applications as it reduces the long-term service of these composites under wet conditions by weakening the fibre/matrix interface. An understanding of the diffusion behaviour of NFRP composites is therefore necessary.

There are a number of factors contributing to the water absorption of plant fibre, including the porosity and internal structure of the fibre [17,18]. On the other hand, the cellulose content in the plant fibre reduces water absorption and makes the fibre structure more hydrophilic. Among all available plant fibres, flax fibre has one of the highest cellulose contents, reaching approximately 72% [19,20], as shown in Table 1, and a low micro fibril angle of 2 to 8 degrees. The higher degree of cellulose content in flax fibres is responsible for the strength of the fibres, while the latter property controls the stiffness. Both contribute to the mechanical properties of the fibre and the performance of the produced composites [21]. The cellulose contains hydroxyl groups, which interact with water molecules to form a hydrogen bond. Due to this hydrophilic character, flax fibres become less compatible with hydrophobic polymer matrices [16]. Although this inherent incompatibility has been treated with physical and chemical techniques such as alkali, peroxide and silane treatment, NFRP composites still suffer from this issue. More efficient techniques should be explored to enhance the bonding of natural fibres and the polymer matrix and to improve their moisture absorption properties.

Table 1. Internal structure of flax fibres.

Cellulose	Hemi-Cellulose	Pectin	Lignin	Wax	Moisture Ratio
62–72%	18.6–20.6%	2.3%	2–5%	1.5–1.7%	8–12%

Recently, nanomaterials such as titanium dioxide (TiO_2), carbon nanotubes (CNTs) and multiwalled nanotubes (MWNT) as secondary reinforcement have been drawing the attention of researchers due to their excellent properties when incorporated into polymer matrices. Their engagement improves the physical, mechanical and thermal properties of neat resin and polymer composites. [22] reported that the hybridization of natural fibre (5, 10 and 20 wt%) with 2% and 5% of montmorillonite (MMT) in styrene-butadiene-styrene triblock copolymer matrix composites showed significant improvement in the tensile strength, tensile modulus, and elongation at break for composites filled with 2% MMT and reinforced with 5% by weight of natural fibre. In addition, the water absorption behaviour of the composites filled with 2% MMT and reinforced with 5% by weight of fibres decreased by approximately 15% after 400 h of immersion in water. A study by Nayak et al. [23] observed improved mechanical properties of glass fibre-reinforced epoxy hybrid composites with the inclusion of 0.1%, 0.3% and 0.7% of TiO_2 and immersed in water for 625 h. The flexural strength retention and ILSS strength retention were improved by 19% and 18%, respectively, for hybrid composites with 0.1% of TiO_2, while also reducing the moisture absorption by 9%. On the other hand, the hybrid composites with 0.7% of TiO_2 showed a maximum improvement in modulus retention of 22% compared to the glass fibre composites. They attributed the improvement in mechanical properties and water absorption behaviour to the addition of nano TiO_2. The effective aspect ratio of TiO_2 particles improves the interface adhesion by creating additional sites of mechanical crosslinking, thereby improving the properties. Moreover, Kushwaha et al. (2014) found that the inclusion of 0.15% by weight of carbon nanotubes to bamboo fibre-reinforced epoxy composites improved the mechanical and moisture absorption properties by 6.7%, 2.7%, 5.8%, 31%, 85% and 11.8%, respectively, for tensile strength, tensile modulus, flexural strength, flexural modulus, impact strength and moisture absorption after 1600 h of conditioning in water compared to a composite without carbon nanotubes. The improvement in the mechanical properties and reduced water absorption with the addition of carbon nanotubes is due to increasing the bonding strength at the interface, which leads to a high-performance composite. These researchers concluded that the addition of nanofiller to the polymer matrix plays a significant role in minimizing water absorption by reducing free volume spaces in terms of the amount, size and distribution of these spaces, depending on the uniform dispersion of the nano-filler in the polymer matrix. They also mentioned that the effect of adding nano-filler improved the interface area by making strong covalent bonds between this filler and the polymer matrix, thus attempting to restrict the ability of water molecules to move freely in the interface area. In addition to that, the barrier properties of nano-filler can contribute to the formation of a zigzag path that slows the amount of water diffusion through the composite matrix.

The mechanical performance of NFRP composites in dry conditions is considered acceptable, but the information on the behaviour of these composites under long-term wet environmental conditions is limited. Thus, further investigation is required to fully understand the effects of graphene nanoparticles on the durability performance of natural fibre composites in a humid service environment as this performance is considered a critical factor for safety standards for using this material for outdoor applications. This study investigated, for the first time, the effects of graphene nanoparticles on the water absorption behaviour of natural flax fibre composites to extend their use in long-term wet conditions and to understand the critical parameters governing moisture diffusion behaviour.

The experimental works focused on the water absorption behaviour of flax-natural fibre composites with graphene at different percentages by weight (0%, 0.5%, 1% and 1.5%) and immersed in water for 1000, 2000 and 3000 h. The effects of these parameters on the flexural and inter-laminar properties before and after conditioning were evaluated. The results of this study will provide a better understanding of the behaviour of flax-natural fibre composites filled with graphene nanoparticles under wet conditions, which is crucial for their wide acceptance and use in external mechanical and structural engineering applications.

2. Experimental Program

2.1. Materials

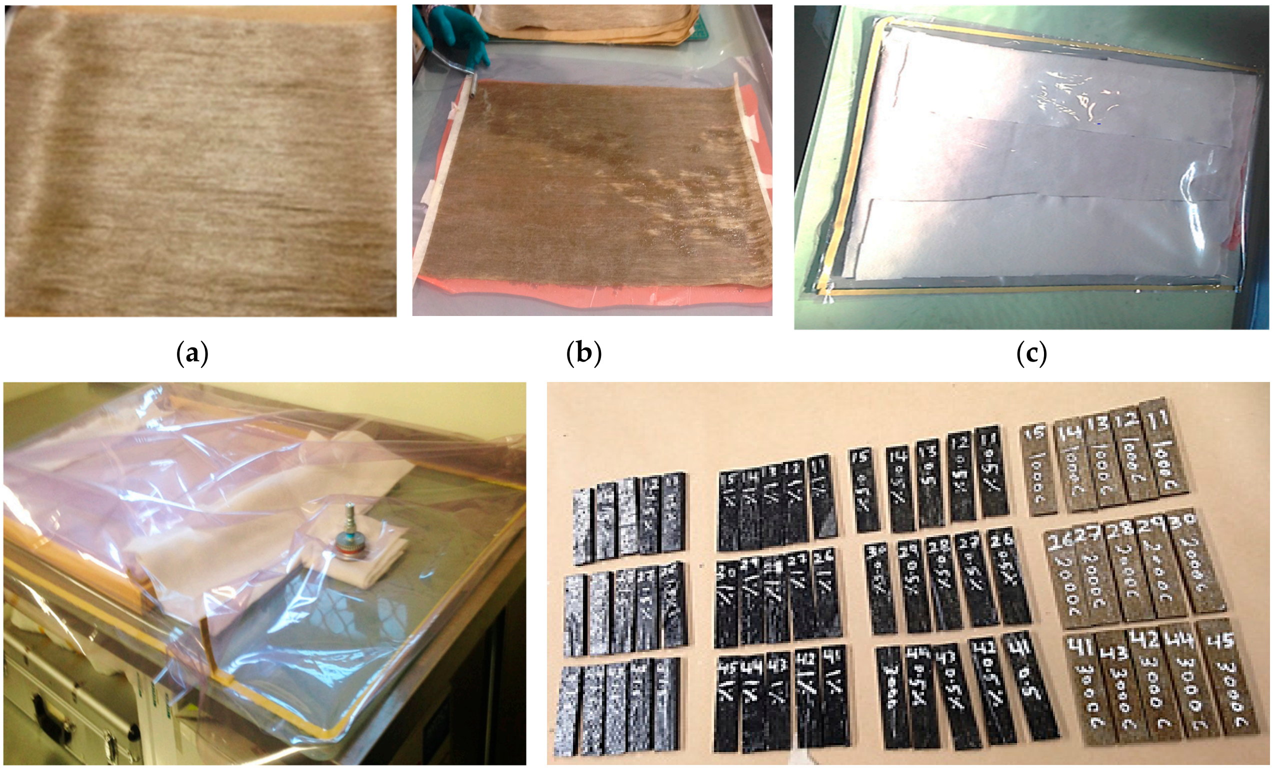
Epoxy resin (R246TX) and hardener (H160) (ATL Composites, Queensland, Australia) were mixed and used as a matrix to manufacture the composites. The resin-to-hardener ratio used was 1:4 by weight, as recommended by the supplier. Graphene nanoparticles with an average surface area of 300 m^2/g were supplied by Sigma-Aldrich, Bayswater, Australia. The unidirectional flax fibres with a thickness of 0.36 mm were supplied by Colan Composite Reinforcement, Huntingwood, Australia. Table 1 shows the internal structure of flax fibres. The properties of the neat epoxy resin, natural fibres and graphene listed in Table 2 are based on the available literature and as described by the manufacturer.

Table 2. Properties of epoxy resin, natural fibres and graphene.

Material	Density (g/cm^3)	Elastic Modulus (GPa)	Tensile Strength (MPa)
Graphene	0.03	340	130×10^6
Flax fibres	1.40	70.0	1400
Epoxy resin	1.12–1.17	3.4	130

2.2. Specimen Fabrication

Figure 1 shows the manufacturing process of the fibre-reinforced epoxy composites. Unidirectional flax fibres were cut into dimensions of 600 mm in length and 400 mm in width (see Figure 1a). A total of six layers were manufactured to obtain a nominal plate thickness of 4 mm. Prior to adding the resin, the flax fibre sheets were placed in an oven at 40 °C for 30 min to remove moisture as per the manufacturer's recommendations as it would affect the wettability and bond between the resin and fibres. Epoxy resin was mixed for five minutes and poured onto the fibre sheets until saturated using the hand layup technique. The flax fibre layers were then placed on top of each other to build the composites with a fibre volume ratio (V_f) of 25%. The V_f was calculated by weight. A metal roller was used to ensure that the resin was evenly distributed throughout the fibre sheets and to remove any air bubbles while wetting the fibres (see Figure 1b).



(**a**) (**b**) (**c**)

(**d**) (**e**)

Figure 1. (**a**) Flax fibre sheet; (**b**) wetting fibres; (**c**) closing vacuum bagging; (**d**) vacuum bagging system; (**e**) test specimens.

Different percentages of graphene nanoparticles by weight (0.5%, 1.0% and 1.5%) were mixed with the epoxy resin before adding the hardener to produce the hybrid composites [24]. It is worth mentioning that 1.5% graphene content was selected due to the high viscose epoxy mixture for higher graphene content. Thus, hard mixing of the mixture was performed using the normal shear mixer beyond 1.5% of graphene, which contributes significantly to form agglomeration. Moreover, it was found by trials and previous research [1,2] that there is no significant enhancement in the mechanical properties beyond 1.5%.

A homogeneous mixture was obtained by using an electric shear mixer for five minutes as per the recommendations of the graphene supplier. After wetting, the sheets were inserted into a vacuum bag sealed with yellow sealant tape to create an airtight seal (see Figure 1c). A constant pressure of 92 kPa was then applied, and the samples were initially left for 24 h to cure (see Figure 1d). Subsequently, the manufactured plates were demoulded and post-cured for 3 h at 120 °C as recommended by the supplier. The composite plates were then cut according to specimen dimensions using a waterjet to produce the test samples (see Figure 1e).

2.3. Water Absorption Test

The water absorption and water diffusion coefficient of flax fibre composites and hybrid nanocomposites were measured following ASTM D570 [25]. Initially, all samples were weighed in a dry condition after coating their edges with a thin layer of resin to ensure the entry of moisture is only through the top and bottom surfaces of the composites, as was also implemented by [26]. The samples were then immersed in tap water for 1000, 2000 and 3000 h. After 24 h of immersion, the samples were taken out of the water, dried with tissue paper, and immediately weighed with a digital scale of 0.001 mg accuracy. Once the samples were weighed, they were immediately re-immersed in water. At regular intervals, the weighting process was repeated over 126 days of immersion in water. Moisture absorption was then calculated as the weight difference between dry and wet samples, and the moisture content percentage (M_t%) was calculated using Equation (1).

$$M_t(\%) = \left(\frac{W_t - W_0}{W_0}\right) \times 100 \tag{1}$$

where W_0 and W_t are the weight of the dry and wet samples after time t, respectively.

On the other hand, Equation (2) was used to calculate the diffusion coefficient (D) assuming that the moisture diffusion behaviour of composites follows the Fickian diffusion behaviour as shown in Figure 2.

$$D = \pi\left(\frac{Kh}{4Mm}\right)^2 \tag{2}$$

where h, K and Mm are the sample thickness, the initial slope of the plot of $M(t)$ against $t^{1/2}$ and the maximum increase in weight, respectively.

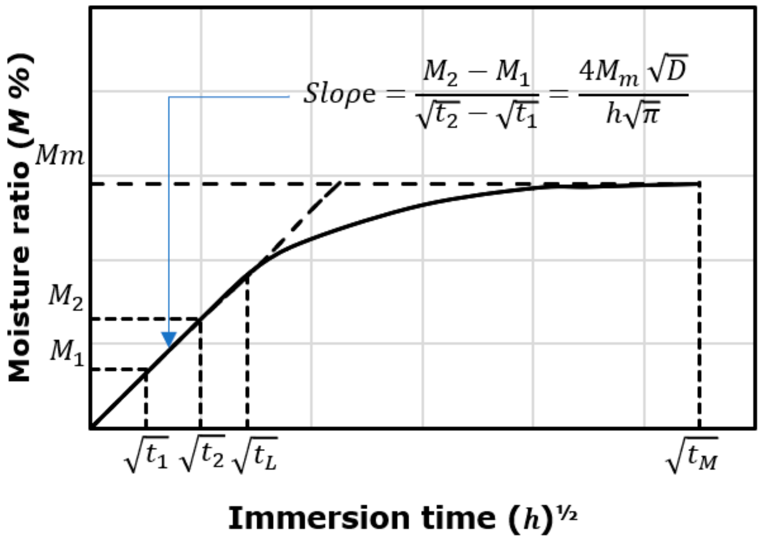
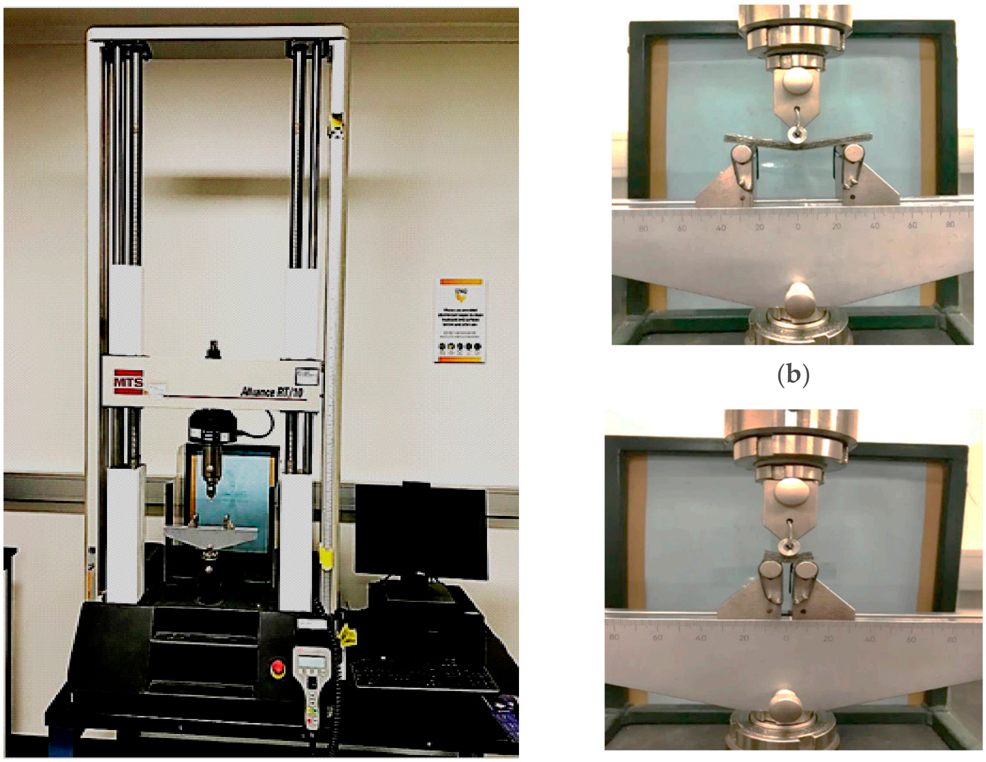


Figure 2. Diagram of calculating moisture content with square root of immersion time.

2.4. Mechanical Testing

The mechanical properties of the controlled and conditioned hybrid composites were evaluated under bending and interlaminar shear. Both tests were performed using the 10 kN MTS machine under a 3-point test setup at a loading rate of 1.3 mm/min (see Figure 3a) but with different span-to-depth ratios. The flexural test samples were 80 mm long, 16 mm wide and 4 mm thick and were tested over a 64 mm support span producing a span-to-depth ratio of 16, as suggested by [27] and shown in Figure 3b. On the other hand, the inter-laminar shear strength (ILSS) test shown in Figure 3c was implemented using 24 mm long by 16 mm wide and 4 mm thick test specimens, and with a support span of 20 mm producing a span-to-depth ratio of 5 as suggested by ASTM D2344 [28].



(**a**) (**b**) (**c**)

Figure 3. Mechanical tests of hybrid composites: (**a**) MTS machine; (**b**) flexural test and (**c**) interlaminar test.

2.5. SEM Observations

The scanning electron microscope (SEM) JEOL JXA 840A (Jeol, Tokyo, Japan) was used to examine the damage features, fracture surface and fibre–matrix interface of the dry and wet samples with and without graphene after prolonged immersion in water and tested at room temperature. The graphene distribution within the composite matrix was also evaluated by SEM, after carefully preparing the samples with dimensions of 10 mm by 10 mm from the tested specimens.

3. Results and Discussion

3.1. Dynamic Mechanical Analysis (DMA)

The thermo-mechanical properties of the polymer have been evaluated by using a DMA device, a Q800 type (Mettler-Toledo Ltd, Melbourne, Australia) of thermal analysis instrument, to determine the glass transition temperature of dry and wet samples based on [29]. DMA test samples were cut with dimensions of 50 mm × 8 mm × 4 mm. After clamping the specimens in a dual-cantilever system, DMA tests were performed using a multi-frequency strain mode, with a temperature increase rate of 5 °C/min to scan the temperature from room temperature to 120 °C.

Figure 4 shows the dynamic mechanical analysis (DMA) curves of hybrid composites with different graphene loadings after immersion in water for 3000 h. The temperature at the highest peak value of the storage modulus was considered to be the glass transition temperature (Tg) of the sample. The DMA results in Table 3 showed that exposure of these composites to water caused a lower storage modulus as well as the glass transition temperature (Tg) values compared with dry samples, as was also reported by Saha et al. [30] for thermo-mechanical properties of flax-hemp/epoxy hybrid composites. The main reason for lower values of the Tg is the plasticization of the epoxy matrix caused by water absorption, which normally acts as a plasticizer [31]. Similarly, Al Rifai et al. [32] observed lower glass transition values induced by the plasticization effect for the long-term durability of basalt fibre-reinforced polymer bars. Moreover, the trend of Tg results in this study is in agreement with other studies reported in the literature such as [33]. On the other hand, it can be noted from Figure 4 that the wet composites with 1% and 1.5% graphene showed a higher storage modulus than the dry samples. Qin et al. [34] highlighted that this phenomenon can be explained by the better orientation of the molecular chain for wet samples as of the presence of moisture. Thus, higher-oriented chains result in better shear resistance, and higher potential energy in the wet specimens revealed higher storage energy than the dry samples. This study also showed that adding nanofillers enhanced the molecular chain, resulting in an obvious enhancement in the storage modulus. Further studies are recommended to investigate this aspect.

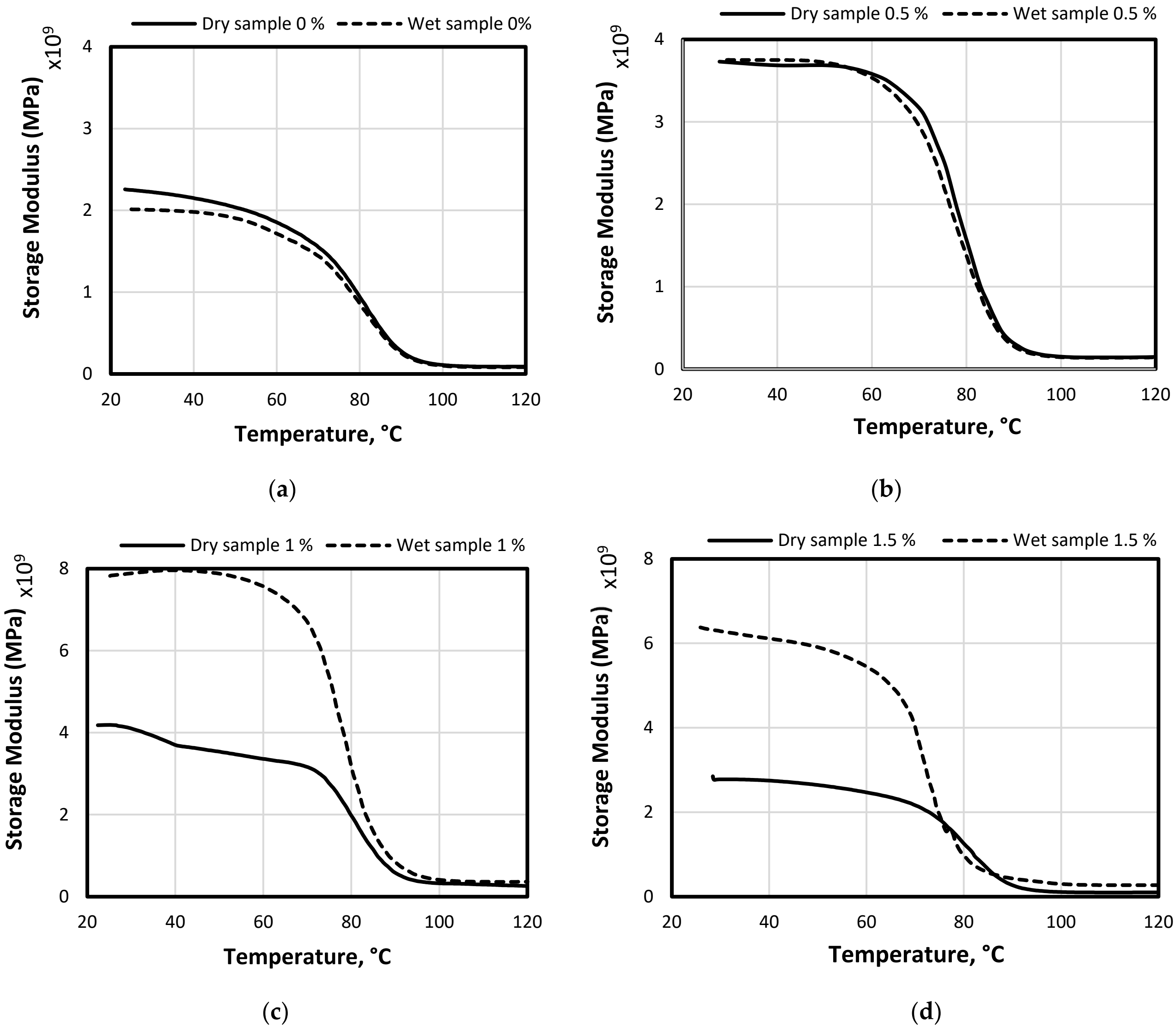


Figure 4. Storage modulus of dry and wet samples: (**a**) Samples with 0%; (**b**) samples with 0.5%; (**c**) samples with 1%; (**d**) samples with 1.5%.

Table 3. Glass transition temperature of dry and wet samples.

Sample	Glass Transition Temperature		
	Dry Condition	Wet Condition	% Drop in Tg
0%	72.0 °C	71.3 °C	0.97
0.5%	76.9 °C	74.4 °C	3.25
1.0%	79.3 °C	71.0 °C	10.47
1.5%	80.3 °C	71.6 °C	10.60

The effect of the plasticization on Tg can be explained by the weak interactions between the epoxy resin and graphene nanoparticles. This means that the weak filler/matrix interaction causes the glass transition temperature to drop as pointed out by [35]. With the increase in the filler content, agglomeration of the filler occurs due to the increase in viscosity, which leads to weak bonding by forming micropores between the graphene nanoparticles, allowing the entry of water molecules between these nanoparticles. In this case, the filler agglomerate is joined by weak Van der Waals forces. This can lead to a weakening of the bonding strength of the hybrid composites resulting in a significant drop in Tg values as shown in the samples with 1% and 1.5%.

3.2. Moisture Absorption Behaviour of Hybrid Flax Fibre Composites

Figure 5 shows the relationship between the percentage weight gain and the square root of the immersion time for flax/epoxy hybrid composites with different levels of graphene by the weight of the matrix at room temperature. It was found that the moisture absorption process of these specimens follows Fickian law, which can be described as linear at the initial stage of the water absorption curve and then slows down until it approaches the saturation level after a long period of time. The results show that adding graphene nanoparticles to the epoxy matrix results in lower moisture absorption of hybrid flax fibre-reinforced epoxy composites than those specimens without graphene for the three different immersion durations. This is attributed to the presence of graphene nanoparticles, which act as barriers against moisture in the epoxy matrix. The results also showed that the initial moisture absorption rate and the maximum moisture content values decrease as the amount of graphene nanoparticles increases. This is due to the effective aspect ratio of graphene, which created the tortuosity path and improved the bonding strength at the interface. This is supported by the reduction in moisture diffusion coefficients as shown in Table 4. The moisture absorption behaviour results obtained in this study are in agreement with the results reported by [36] for luffa/epoxy composites with graphene. However, the samples with 1% graphene recorded higher water absorption than those with 0.5% graphene. This is owing to more voids being formed in the modified matrix in the former samples, as revealed by the SEM image in Figure 10b. Moreover, Figure 11b shows the presence of small cracks in the interface between the fibre and matrix, which contributes to the penetration of water through the bulk matrix during the immersion process. Zhang and Mi [37] have attributed the development of these inevitable cracks and voids within the composite matrix to the manufacturing and solidification process.

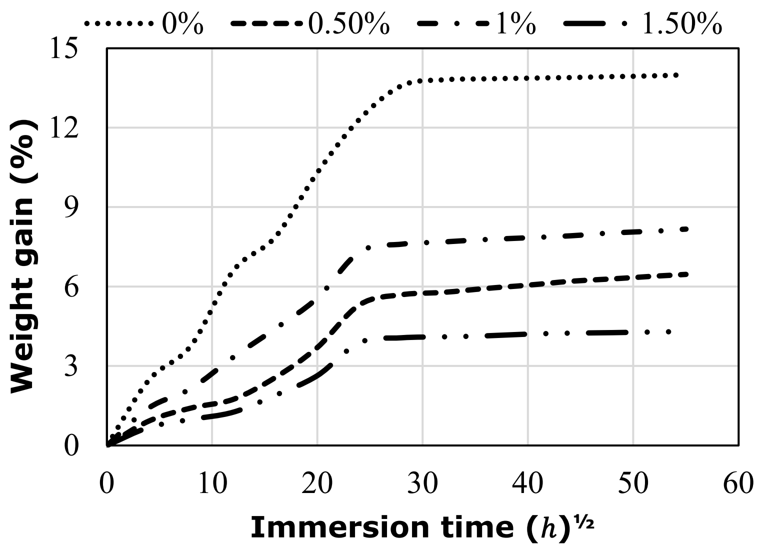


Figure 5. Moisture absorption behaviour of hybrid composites with various graphene weights.

Table 4. Average values of M_t% and $D \times 10^{-9}$ mm^2/s for flax/epoxy hybrid composites.

Condition	Physical Measure	Composite Materials with Filler Ratios			
		0%	**0.5%**	**1%**	**1.5%**
Immersion for 1000 h	*Mt*%	13.4	4.2	6.6	3.6
	D	4.8	2.8	3.5	1.4
Immersion for 2000 h	*Mt*%	13.6	4.4	6.8	3.8
	D	4.9	3.6	4.2	2.5
Immersion for 3000 h	*Mt*%	13.7	4.6	7.0	4.0
	D	6.0	4.5	5.4	4.4

For three different immersion durations, flax fibre epoxy composite samples show poor moisture resistance due to the hydrophilic nature of flax fibre, which is attributed to the hydroxyl groups on its surface. This also explains the higher saturation level of the control specimens than that of the hybrid samples. This phenomenon can be explained by considering the moisture absorption properties of flax fibre. Given the high cellulose content in flax fibre (approximately 72%), the composite absorbs a high amount of water which causes the fibre to swell. This swelling in the flax fibre creates micro-cracks in the epoxy matrix composite. As such, the micro-cracks provided an active capillary mechanism for the water molecules to penetrate into the composite interface through these micro-channels. This inevitably results in swelling stress, which causes deterioration of the natural fibre-based composite properties by separating the flax fibre from the epoxy resin matrix as observed from the SEM. Plasticization due to water absorption is also another factor affecting the performance of the composite fibre/matrix interface, which reduces the bonding strength between them.

Even though flax fibre epoxy composites tend to absorb high amounts of water, graphene nanoparticles seem to limit this tendency by reducing the voids and filling micro-channels, which slows down the diffusion of water molecules into the composite matrix. As a result, the hybrid composites show lower water absorption than those without graphene because the graphene nanoparticles have moisture resistance due to their hydrophobic nature. These nanoparticles attached to the fibre surface act as external protective materials that contribute to reducing the water absorption rate and improving the adhesion of the fibre/resin matrix interface by increasing the surface roughness of the fibre. In the shortest water immersion period (1000 h), the addition of 0.5% graphene nanoparticles decreased both the moisture diffusion coefficient and moisture absorption of flax fibre composites by 41.2% and 68.7%, respectively. In contrast, when these samples were immersed for

3000 h, the moisture diffusion coefficient and moisture absorption content were significantly enhanced by 23.7% and 66.4%, respectively, compared to that of the control samples. It was noted that the increased moisture content and diffusion coefficient with increasing exposure time are due to the internal plasticization of the matrix as evidenced by the reduction in Tg found by dynamic mechanical analysis (DMA) as shown in Table 3. From Table 4, it can be noted that the percentage of moisture absorption increased slightly with an increasing exposure duration for all composites. The moisture absorption results of this study are in agreement with the experimental results from Chaharmahali et al. [38] for hybrid bagasse fibre-reinforced polypropylene composites with graphene. Nevertheless, at any given duration of water immersion, the moisture diffusion coefficient, as well as the moisture absorption content, can be reduced by adding graphene nanoparticles. Chaharmahali et al. [38] also mentioned that the trend of water absorption in bagasse fibre composites decreased with the presence of graphene. These reductions also emphasize the importance of graphene nanoparticles. Graphene nanoparticles have demonstrated their ability to reduce moisture absorption and the diffusion rate by hindering interface plasticization and protecting fibres from swelling through the following mechanisms: (i) A tortuous path is formed by graphene particles, which acts as a longer path to the diffusion of water in the composite matrix, and (ii) providing additional sites for mechanical interlocking between the fibres and the resin through the effective aspect ratio of these nanoparticles attached to a fibre surface, which can improve the bonding performance. Both contribute to the reduction in moisture absorption and the diffusion rate.

3.3. Flexural Behaviour of Hybrid Flax Fibre Composites

3.3.1. Effect on Flexural Strength

Figure 6 shows the flexural strength (FS) and strength retention of hybrid flax fibre-reinforced epoxy composites with different graphene percentages in dry and wet conditions. In dry conditions, the FS of the flax fibre composites increased with the addition of graphene. This improvement is due to the graphene providing a better stress transfer mechanism at the interface between the epoxy matrix and the flax fibres. Another simple explanation is attributed to the high surface area of graphene providing an effective chemical interaction with the matrix resin, thus increasing the strength. It should be noted that the average FS value increased, with the highest value recorded for the composite samples with 0.5% due to the good dispersion of nanoparticles. Ashok et al. (2020) and Ashok & Kalaichelvan [36] also stated that the improvement in the flexural, impact and tensile strength of the luffa fibre composite with nano-filler is attributed to the enhancement of the fibre/matrix interface adhesion after nano-filler hybridization, causing an effective load transfer mechanism from the epoxy matrix to the luffa fibres and thus increasing mechanical properties. However, adding more graphene than 0.5% to the epoxy matrix results in lower flexural strength due to the agglomeration of graphene nanoparticles caused by the increase in viscosity of the epoxy resin as shown from the SEM observations (see Figure 11b,c). As such, similar behaviour in increasing viscosity with a high amount of graphene has been confirmed by other studies [39]. The same trend of flexural strength results has been observed by Nayak et al. [23] for the glass fibre-reinforced epoxy composites with nano TiO_2 particles, which showed a reduction in flexural strength due to the agglomeration effect.

The absorbed water reduced the flexural strength of hybrid composites, as also shown in Figure 6. The FS also decreases with exposure duration. This reduction in flexural strength is associated with an increase in the moisture absorption rate, which results in the plasticization of the epoxy matrix and fibre microstructure, thus impairing the adhesion of the fibres to the epoxy matrix at the interface. This observation is also supported by Table 1, which showed an increase in moisture absorption values with increasing exposure time. Regardless of the exposure duration, the flexural strength of all samples with different graphene percentages decreased after immersion in water when compared to their dry strength, indicating that the properties of the fibre/matrix interface, which govern the flexural strength, are affected by moisture absorption and diffusion. As can be observed in

Figure 6, the FS of composites with 0.5% graphene and immersed in water for 1000, 2000 and 3000 h decreased by 3.0%, 7.3% and 13.4%, respectively, compared to the dry composite strength, but is higher than the wet strength of the other specimens. This can be explained by the uniform dispersion of graphene nanoparticles. This uniform dispersion of graphene nanoparticles throughout the matrix limits the available voids in this matrix for water molecules and reduces the diffusion of these water molecules at the composite interface by filling the micro-channels, resulting in higher wet strength. The retention of FS at different immersion durations proves that the addition of graphene increased the bonding strength at the fibre/matrix interface, and reduced moisture absorption, resulting in an increase in the strength of the hybrid composites. However, the composites with 1% graphene exhibited lower FS than those with 0.5% and 1.5%, regardless of the exposure duration, due to higher moisture absorption as a result of the increased number of voids formed in the modified matrix during the fabrication process as well as the presence of small cracks in the sample interface, as witnessed in the SEM (Figure 12b). The slightly lower strength of the wet samples with 1.5% graphene compared with the dry specimens is due to the lower moisture absorption rate. A possible justification for this observation could be the fibre swelling induced by moisture absorption causing pressure on the surrounding matrix. This swelling effect bridged the gap between the fibre and the matrix, thus providing increased adhesion of the fibres to the matrix, resulting in a slight reduction in FS. Muñoz and García-Manrique [16] also observed the positive effect of fibre swelling on the short-term flexural and tensile properties of bio-epoxy composites reinforced with flax fibres. Another possible justification may be due to the additional reduction in free volume in the matrix with this number of graphene particles. The influence of graphene content on flexural strength retention is illustrated in Figure 6b. Generally, flexural strength retention is improved by increasing the amount of graphene for all conditions, compared with specimens without graphene (see Figure 6b). Hybrid composites with 1.5% graphene retained 98%, 95% and 92% of the dry strength for 1000, 2000 and 3000 h, respectively, which was the highest improvement in flexural strength retention. This improvement is due to the reduced moisture absorption within the composite matrix as the graphene particles fill the free spaces in the matrix.

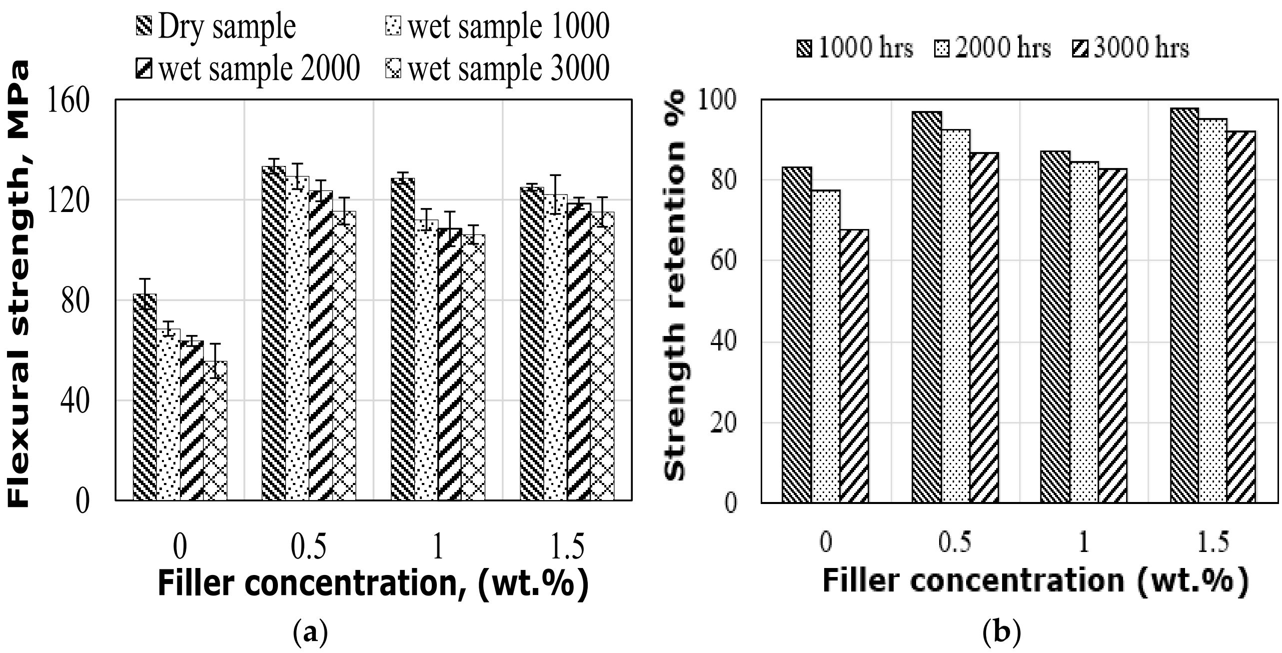


Figure 6. (**a**) FS under dry and wet environments; (**b**) FS retention.

Figure 7 shows the failure mode of hybrid flax fibre-reinforced epoxy composites with graphene at different weight percentages under flexure in wet conditions. From Figure 7a, it can be noted that weak fibre/matrix adhesion at the composite interface without graphene led to flexural crack propagation along the sample interface, which resulted in lower flexural strength. In contrast, the failure mode in flexural test samples with graphene under the same conditions changed from a crack along the fibre/matrix interface to a crack along the thickness of the sample. This indicates the excellent adhesion between the filler/fibre and the matrix, which delays crack initiation and propagation and causes increased flexural strength, as shown in Figure 7b.

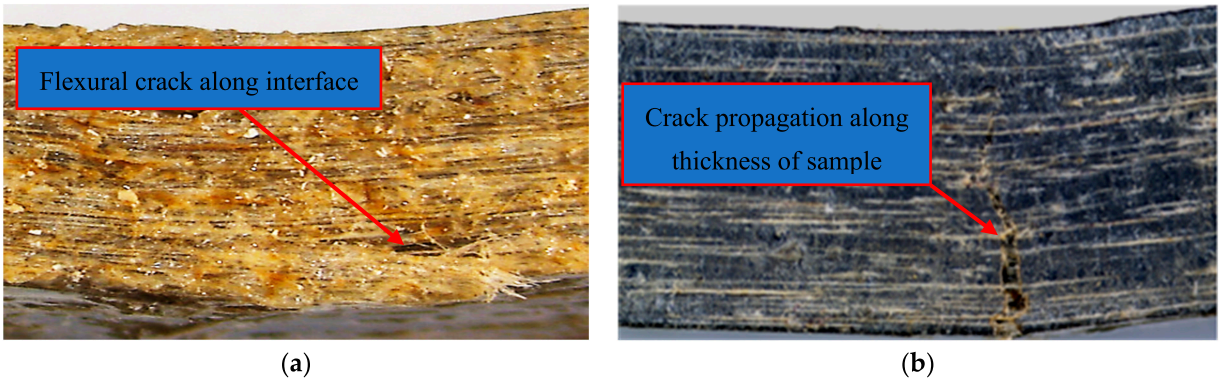


Figure 7. Failure of hybrid composites under flexure in wet conditions: (**a**) Unfilled composites and (**b**) filled composites.

3.3.2. Effect on Flexural Modulus

Figure 8 shows the flexural modulus (FM) and modulus retention of flax fibre-reinforced hybrid epoxy composites with graphene at different weight percentages (0%, 0.5%, 1% and 1.5%). In a dry environment, an expected increase in the flexural modulus with increasing graphene was noted because of the high modulus of graphene nanoparticles. Wang and Drzal [40] also mentioned that graphene particles are stiffer materials than epoxy resin, which increases the stiffness of the matrix but makes it more brittle. For wet composites, a reduction in the FM was observed with increasing exposure duration, regardless of the amount of graphene. This reduction in wet modulus can be explained by the amount of moisture absorption, which resulted in plasticization at the interface between the flax fibre and the epoxy matrix. The penetration of water molecules into the composite matrix acts as a plasticizer that facilitates the weakening of the bonding at the interface between the fibres and the synthetic matrix, resulting in a lower modulus. The specimens with 1.5% graphene showed the highest values of flexural modulus at 9.1, 8.7 and 8.4 GPa for 1000, 2000 and 3000 h, respectively, which are 45.7%, 52.3% and 55.8% higher than the other composites without graphene. The reduced moisture absorption in specimens with 1.5% graphene is attributed to the presence of a larger number of graphene particles, which increases the stiffness of the matrix. This increase in matrix stiffness in turn limits the fibre extension in the matrix and thus prevents microcracks in the matrix as supported by the SEM image in Figure 12c. However, a remarkable reduction in FM was observed in wet-modulus specimens with 1% graphene, regardless of exposure time, which was attributed to higher moisture absorption causing the flax fibres to swell. This swelling caused micro-cracks to develop at the interface of the composites (see Figure 12b), which resulted in moisture being absorbed throughout the composite matrix, thus reducing the FM. The increase in exposure duration up to 3000 h results in further deterioration at the interface of the hybrid composite, with 1% graphene resulting in an increased strength loss, as evidenced by the modulus retention shown in Figure 8b. The low modulus retention of wet samples with 1% graphene can be directly attributed to the formation of microcracks in the epoxy matrix and gaps between the fibre and matrix due to the swelling of fibre caused by moisture absorption, which reduced the adhesion at the interface (see Figure 12b). In comparison with dry specimens, the FM of the wet samples with 1.5% graphene decreased by 8.9%, 12.8% and 16.3%, respectively, for 1000, 2000 and 3000 h of water immersion. It can be assumed that moisture absorption affected the flax fibre, and hence, FM is considered to be more sensitive to the fibre properties [15]. Another reason for this modulus reduction is due to the degradation of the fibre/matrix adhesion. Regardless of the exposure duration and amount of graphene, all specimens exhibited higher flexural modulus than the samples without graphene. This further confirms that graphene nanoparticles can decrease the free volume in the epoxy matrix and increase the contact area and chemical interactions with the epoxy matrix due to their higher surface area, resulting in reduced moisture absorption and distribution. It can be concluded from these observations that the inclusion of graphene nanoparticles in the epoxy matrix helped reduce moisture absorption and diffusion at the interface of natural fibre composites. as well as improve the bonding strength, thus increasing the performance of these composites. Figure 8b indicates the influence of graphene addition on FM retention under different immersion durations. Hybrid composites exhibited higher modulus retention at 0.5% and 1.5% graphene than those without graphene in all conditions. However, specimens with 1% graphene retained only 64%, 58% and 51% of their dry modulus for 1000, 2000 and 3000 h, respectively, which is lower than the modulus retention of the control composite tested under the same conditions. This reduction in modulus retention is attributed to higher moisture absorption of these samples.

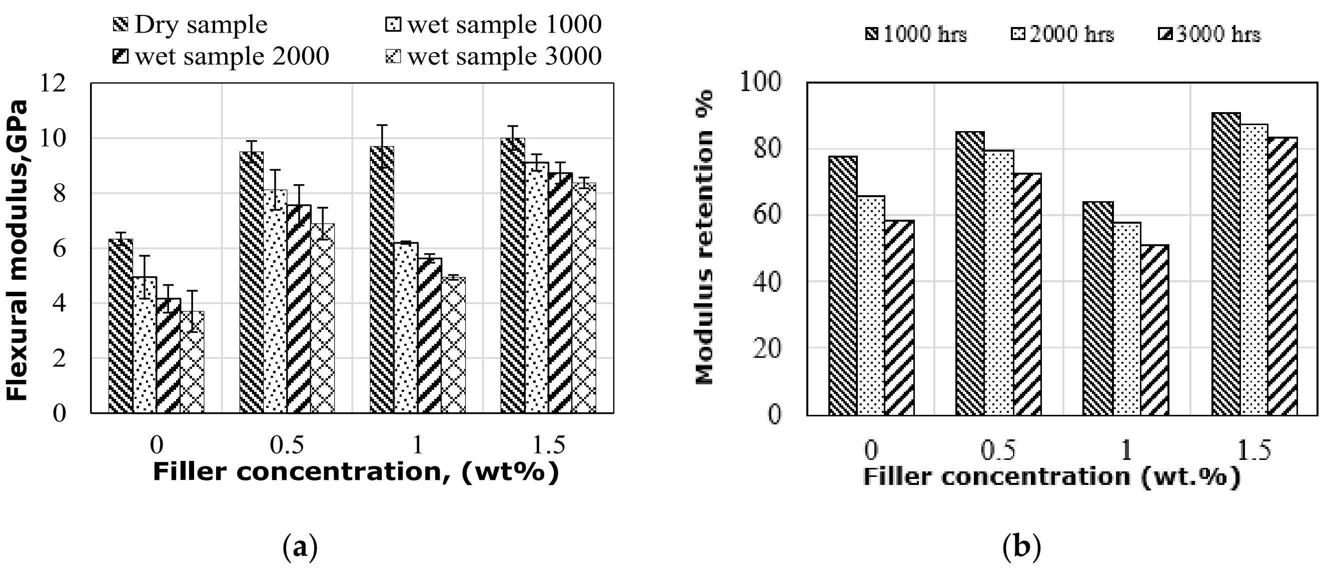
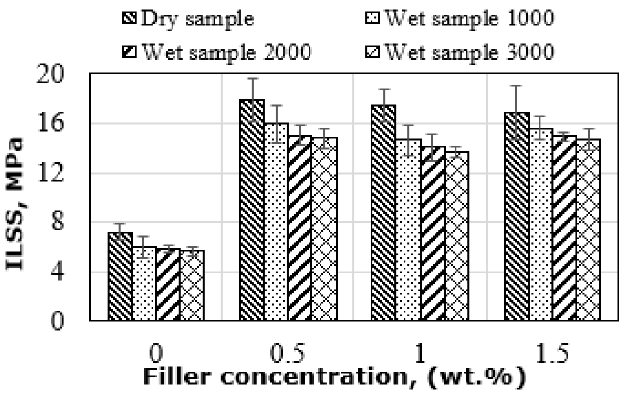


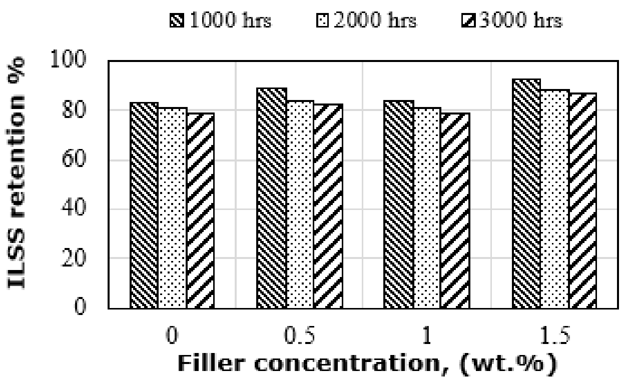
Figure 8. (**a**) FM under dry and wet environments and (**b**) FM retention.

3.4. ILSS Behaviour of Hybrid Flax Fibre Composites

Figure 9 shows the inter-laminar shear strength (ILSS) of the dry and wet hybrid composites. Regardless of the exposure duration, similar ILSS behaviour can be observed for wet specimens with different amounts of graphene. Wet composites with 0.5% graphene failed at the highest ILSS strength of 15.9 MPa for 1000 h, which is 11% lower than the dry composites. This is the same mechanism observed in flexural strength, where there is a good filler distribution in the matrix. However, the highest reduction in wet ILSS strength was observed for specimens with 1% graphene, which was 20%, 23% and 25% lower than that of the dry ILSS strength for 1000, 2000 and 3000 h, respectively, as a result of the plasticization effect at the flax fibre/epoxy matrix interface from higher moisture absorption, which has been demonstrated at lower Tg values. This effect could be more pronounced by the agglomeration of graphene nanoparticles as the epoxy becomes more viscous after increasing the amount of graphene (see Figure 12b), thus the interfacial stress concentration causes crack initiation and propagation, as also observed by Kong et al. [41]. This observation could be the significantly reduced effective surface area at 1% graphene loading, which suffers from non-uniform dispersion of the graphene or poor distribution during mixing. Loste, Loste et al. [42] and Neitzel et al. [43] mentioned that nanoparticles naturally show a strong aggregation tendency, which is attributed to the strong attraction between the particles. This aggregation causes a lower effective aspect ratio of these particles, which reduces the interaction between the fibre and the matrix, thus reducing adhesion at the fibre/matrix interface. Flax fibre swelling is another reason to reduce the strength of these samples by causing microcracks at the interface of these specimens and thus increasing the moisture content as discussed beforehand. The SEM observations in Figure 12 support these justifications. However, increasing the amount of graphene by weight to 1.5% in the epoxy matrix showed a reduction in water permeability through the hybrid flax composite interface, which can be attributed to the barrier mechanism generated by these nanoparticles, showing slightly lower ILSS strength. For comparison purposes, the ILSS strength of the wet samples regardless of the exposure duration and graphene content is lower than that of the dry composites because of the deterioration of the flax fibre/epoxy matrix interface adhesion as a result of the moisture-induced plasticization effect. Alaaeddin et al. [44] have also attributed the low mechanical properties of natural fibre composites filled with nanofillers immersed in water to the formation of hydrogen bonds through chemical interactions of water molecules with hydroxyl groups of cellulose, thus impairing the interfacial adhesion of the reinforcements to the matrix. The ILSS retention results presented in Figure 9b show that the addition of graphene can significantly contribute to the retained strength of 89%, 84% and 82% for 0.5% graphene, 84%, 81% and 79% for 1% graphene, and 92%, 88% and 87% for 1.5% graphene at 1000, 2000 and 3000 h, respectively. The control composites retained 83%, 80% and 78%, respectively, under the same conditions. The maximum improvement in ILSS retention was observed for specimens with 1.5% in all conditions due to the low amount of moisture absorption.



(a)



(b)

Figure 9. (**a**) ILSS strength under dry and wet environments and (**b**) ILSS strength retention.

Figure 10 shows the inter-laminar shear failure of hybrid flax-reinforced epoxy-based composites. As shown in Figure 10a, specimens without the graphene addition failed due to the inter-laminar shear between the layers of the fibres along the interface due to weakness at the fibre/matrix interface. The specimens with graphene, however, show the same failure behaviour before and after exposure to water. Tensile failure rather than inter-laminar shear mode was observed in hybrid flax composites regardless of the graphene weight ratio, which was attributed to the stronger fibre/matrix interface developed by adding nanoparticles (see Figure 10b). This may also be due to the epoxy matrix becoming stronger and stiffer than the flax fibres due to the addition of graphene.

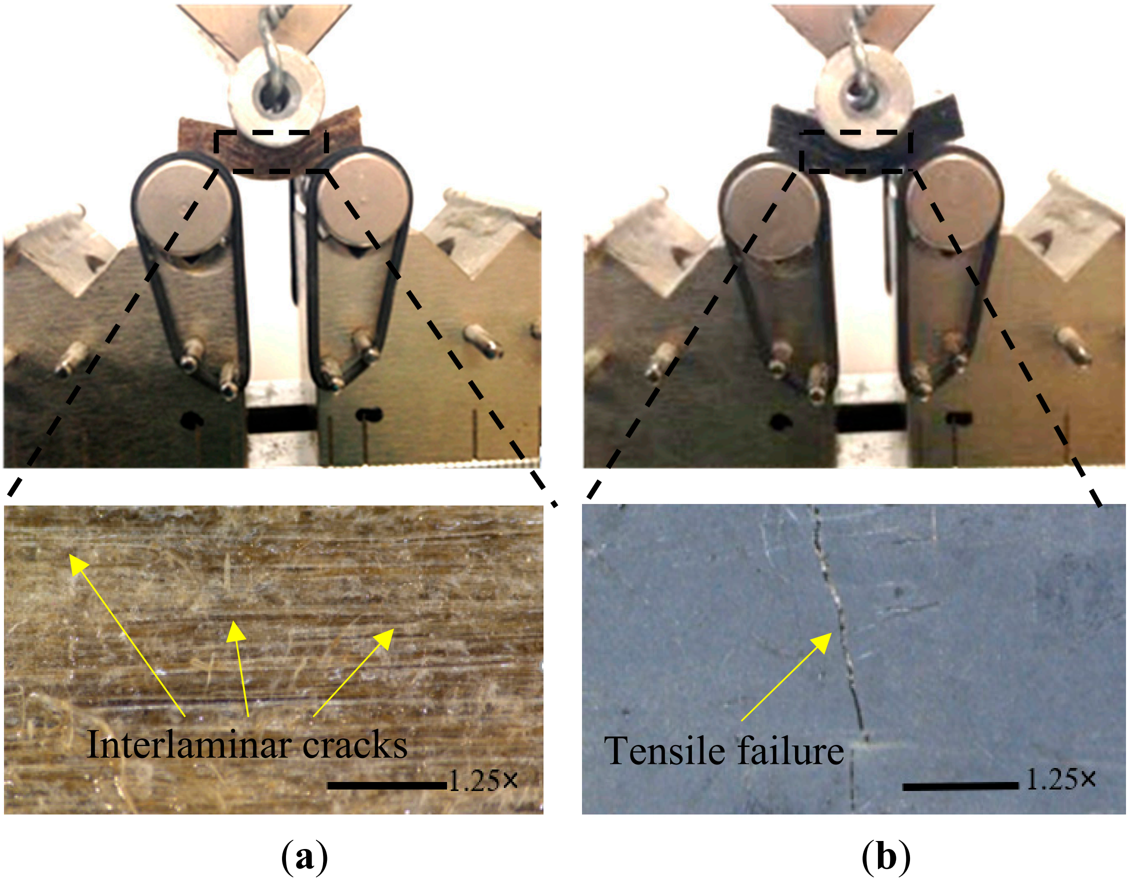
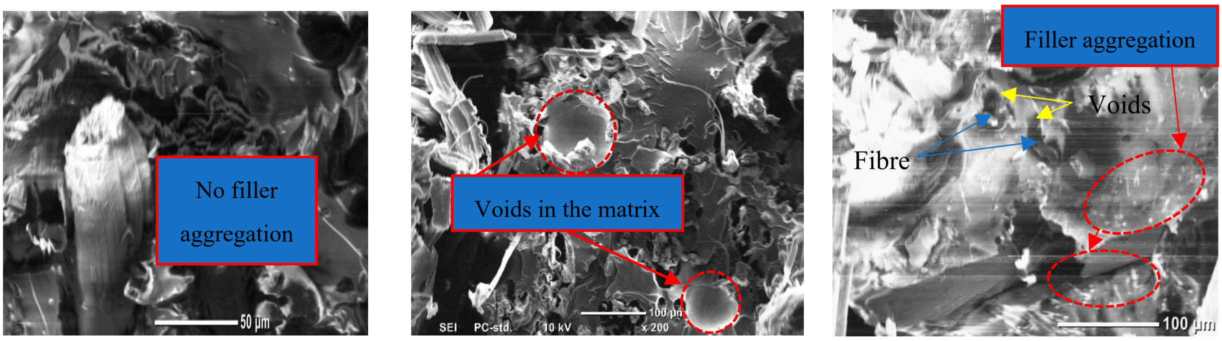


Figure 10. ILSS failure of hybrid composites under wet conditions: (**a**) Composite without graphene and (**b**) composite with graphene.

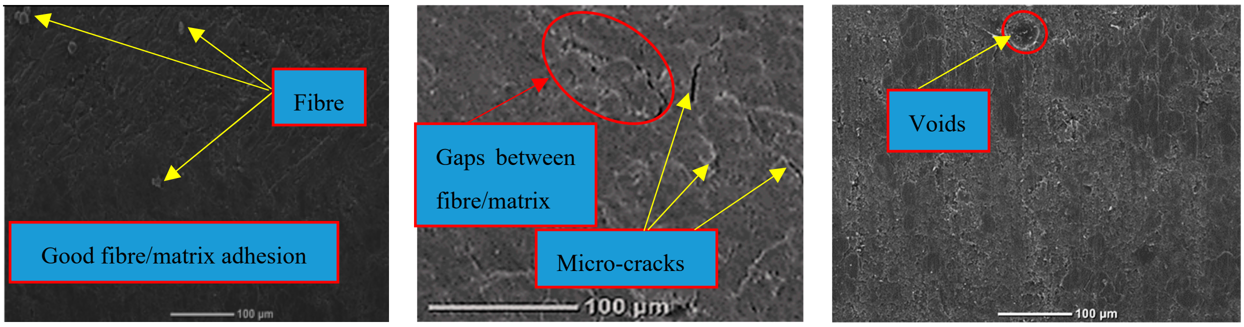
3.5. SEM Image Observations and Analysis

Figures 11 and 12 show SEM images of the microstructure of hybrid composites under wet and dry conditions at room temperature. These images (up to ×500 magnification) show the internal structure of the hybrid composites in terms of the dispersion of graphene particles in the matrix. Regardless of exposure time, adding 0.5% graphene nanoparticles to the epoxy matrix in dry composites improved the fibre–matrix interface resulting in more fibre fractures rather than fibre pull-out (see Figure 11a). However, adding more graphene results in aggregation due to its high surface area and van der Waals forces between nanoparticles, and agglomeration because of the increased viscosity of the epoxy resin. This then causes an increase in the number of void formations in the hybrid composites (see Figure 11b,c). This aggregation/agglomeration results in an imperfect adhesion of the fibre/matrix interface by creating gaps between the flax fibre and the synthetic matrix, which reduces mechanical performance, as observed by Ashok & Kalaichelvan [36] for luffa fibre-reinforced epoxy composites with graphene. In contrast, after immersion in water, the wet specimens with 0.5% graphene exhibited excellent bonding strength between the flax fibre/filler and the resin matrix caused by the uniform dispersion of graphene nanoparticles, which reduced the number of voids in the matrix as revealed in Figure 12a. Figure 12b shows that the deterioration in fibre/matrix interfacial adhesion and matrix cracking in the wet composites at 1% were characterised by the appearance of a gap between the flax fibre and the epoxy matrix induced by the plasticization of the matrix. This indicates weak adhesion of the fibre to the matrix at the interface. For specimens with 1.5%, no fibre pull-out can be observed due to fibre swelling induced by moisture absorption causing pressure on the surrounding matrix, and the effective aspect ratio of graphene also increased the adhesion of the resin to the fibre despite the occurrence of filler agglomeration. This also explains the lowest moisture absorption in these specimens.



(**a**) (**b**) (**c**)

Figure 11. SEM images of dry hybrid composites at different graphene weight ratios: (**a**) Filled with 0.5%; (**b**) filled with 1% and (**c**) filled with 1.5%.



(**a**) (**b**) (**c**)

Figure 12. SEM images of wet hybrid composites at different graphene weight ratios: (**a**) Filled with 0.5%; (**b**) filled with 1% and (**c**) filled with 1.5%.

4. Conclusions

This study investigated the effect of moisture on the flexural and inter-laminar shear properties of hybrid flax-fibre-reinforced epoxy composites. Hybrid composites with graphene content of 0, 0.5, 1.0 and 1.5% by weight of the epoxy resin were prepared and immersed in water for 1000, 2000 and 3000 h at room temperature. From the test results and observations, the following conclusions can be made:

- The addition of graphene nanoparticles decreased the moisture absorption and moisture diffusion coefficient of flax-fibre-reinforced epoxy composites due to the graphene providing a barrier and a tortuous path to the matrix. Hybrid composites with 1.5% graphene exhibited the lowest moisture absorption rates and diffusion coefficients, which were 73%, 72%, and 71% and 71%, 49% and 26% lower, respectively, for 1000, 2000 and 3000 h than the ones without graphene.
- Graphene nanoparticles have a beneficial effect on the flexural and inter-laminar properties of flax fibre epoxy composites under wet conditions. This effect is mainly due to the improvement in the interfacial adhesion of the flax fibre to the epoxy matrix, and the increase in the stiffness and strength of the epoxy matrix is due to the addition of high-stiffness graphene.
- The moisture absorption affected FS and ILSS regardless of the graphene weight ratio, where a continuous decreasing trend was observed with increasing exposure durations. This is due to the matrix properties governing these two properties at room temperature.

- Longer-exposure duration deteriorates the interface of the hybrid composites more than shorter exposure times due to the increased ingress of water affecting its mechanical strength. Immersing the specimen with 0.5% graphene in water for 3000 h showed 10.7% and 7.3% higher reduction in flexural and ILSS strength, respectively, as compared to the same sample immersed in water for 1000 h.
- Regardless of the graphene weight ratio, the flexural modulus is the most significantly affected mechanical property by moisture absorption as this property is governed by fibre properties. Increasing the immersion time increased the water absorbed by the flax fibres and further reduced the flexural modulus as the absorbed water caused continuous deterioration of the flax fibre.
- Wet conditioning changed the failure behaviour of hybrid flax fibre composites. The laminates without graphene failed due to weak interfacial adhesion between the fibre and the matrix as evidenced by the crack propagation behaviour along the interface, whereas the hybrid composites with graphene failed by the flexural crack showing strong bonding strength at the interface. Under ILSS, the composites without graphene failed in inter-laminar shear mode originating either from the middle or ends of the samples, but those with graphene showed flexural failure due to the stronger fibre/matrix interface.

The overall findings from this work highlighted the benefits of graphene in decreasing the moisture absorption of flax fibre epoxy composites and enhancing their strength retention, which will enable this type of natural fibre composite for use in wet environments. Further studies can, however, be conducted to investigate the moisture absorption of hybrid flax fibre epoxy composites longer than the exposure time considered in this study.

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CHAPTER 5: PAPER 3 - DURABILITY OF HYBRID FLAX FIBRE-REINFORCED EPOXY COMPOSITES WITH GRAPHENE IN HYGROTHERMAL ENVIRONMENT

5.3. Introduction

Chapters 3 and 4 demonstrated that the performance of flax fibre-reinforced epoxy composites under in-service elevated temperature and high moisture can be enhanced by the addition of graphene nanoparticles. In is important to note however that temperature and moisture co-exists in outdoor environment which can affect the long-term behaviour of fibre composites. This chapter investigated the combined effect of temperature and moisture on the physical and mechanical properties of flax fibre-reinforced epoxy composites. Hybrid composites with graphene at different weight ratios were prepared and tested under flexural and inter-laminar shear properties after conditioning in the environmental chamber at 98 % relative humidity for 1000, 2000, and 3000 hours and at different exposure temperatures of 20 °C, 40 °C, and 60 °C. An analytical expression was then developed using the Arrhenius model to predict the service life of these hybrid composites.

The results of the study showed that graphene nanoparticles can be effective reinforcements for natural fibre composites in hygrothermal environment and will have great potential in improving their durability properties. The addition of nanoscale graphene to the epoxy matrix achieved a good balance between the mechanical strength and hygrothermal resistance of natural fibre composites. Arrhenius model predicted that 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. The main findings from this research are further summarized in Chapter 6 including a number of recommendations for future research studies to progress the development and production of natural fibre-reinforced polymer composites suitable for outdoor applications.

DURABILITY OF HYBRID FLAX FIBRE-REINFORCED EPOXY COMPOSITES WITH GRAPHENE IN HYGROTHERMAL ENVIRONMENT

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Abstract

Natural fibre composites are highly sensitive to the hygrothermal environment (humidity and in-service elevated 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 inter-laminar 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. 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.

Keywords: Durability; Natural fibre composites; Flax fibre; graphene nanoparticles; mechanical strength; SEM.

1. Introduction

In recent years, plant fibres have become an effective reinforcements for polymeric composite materials. These natural fibre 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. 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 [4]. Balla et al. [5] 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 [5]. Moreover, Khotbehsara et al. [6] 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. Le Duigou et al. [7] and Wang et al. [8] 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. [9] and Wang et al. [10] 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. [11] and

Shaohua et al. [12], 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 [13]. 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 [8, 14-22]. 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. [8] 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. [15] 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.[23] 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 [14, 24]. 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 [25]. 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 in-service 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 in-service 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 [26] and beneficial effects in retaining their mechanical properties under in-service elevated temperature [27]. 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. [6] revealed that epoxy-based matrix system filled with fire retardant and fly-ash subjected to relative humidity of 98% at in-service 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. [28] 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. 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 [29]. Firdosh et al.[30] 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. [31] 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.[32] highlighted the usefulness and time-effectiveness of accelerated experimental tests to study the long-term durability of such composite materials. Brebu [29] 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. [33] 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. [11], a common method used to accelerate the water absorption process and degradation mechanism is by hygrothermal aging, which involves the absorption of water at in-service 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. [31] and Manalo et al.[28]. 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.[34] 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 [35]. Silva et al.[36] 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. [33] 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 as this performance is an important factor for their design and use in outdoor engineering applications.

This study aimed at 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.

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 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.

Table 1: Properties of flax fibres, graphene, and epoxy resin.

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 [37]
Flax fibre	1400	70.0	1.40	[38]
Graphene	130×10^6	340	0.03	[39]

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 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 [27]. 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.

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

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

2.3 Hygrothermal ageing and absorption testing

Aging was performed under combined humidity and temperature in which samples were conditioned in an environmental chamber (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. [12]. 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. [40] and Cadu et al. [41].

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 [42], 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 0.001mg. 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 equation (1).

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

a) Environmental chamber
b) Flexural Test
c) Interlaminar Test

Fig.2: Aging and mechanical tests for hybrid composites

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 performed in a 3-point bending test using a universal testing machine with a mechanical test speed of 1.3 mm/min and a capacity of 10 kN, as shown in Fig.2 (b and c). The flexural and interlaminar properties of the hybrid composites were evaluated following the ASTM D790[43] and ASTM D2344 [44], 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.

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 840A (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 behaviour 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 [5, 45] consisting of hydroxyl groups that form hydrogen bonds with water molecules. After 3000 hours of conditiong 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. 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.[46]. 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 [26]. Moreover, graphene nanoparticles reduce the sizes of free voids within the epoxy matrix as reported in other studies [47, 48]. 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 in-service 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 [18]. These sorption results justify the lower strength values recorded for hybrid composites conditioned in humidity at in-service 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 fibres as supported by previous investigations [26, 49, 50]. 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 [26]. Prolongo et al.[51] 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.

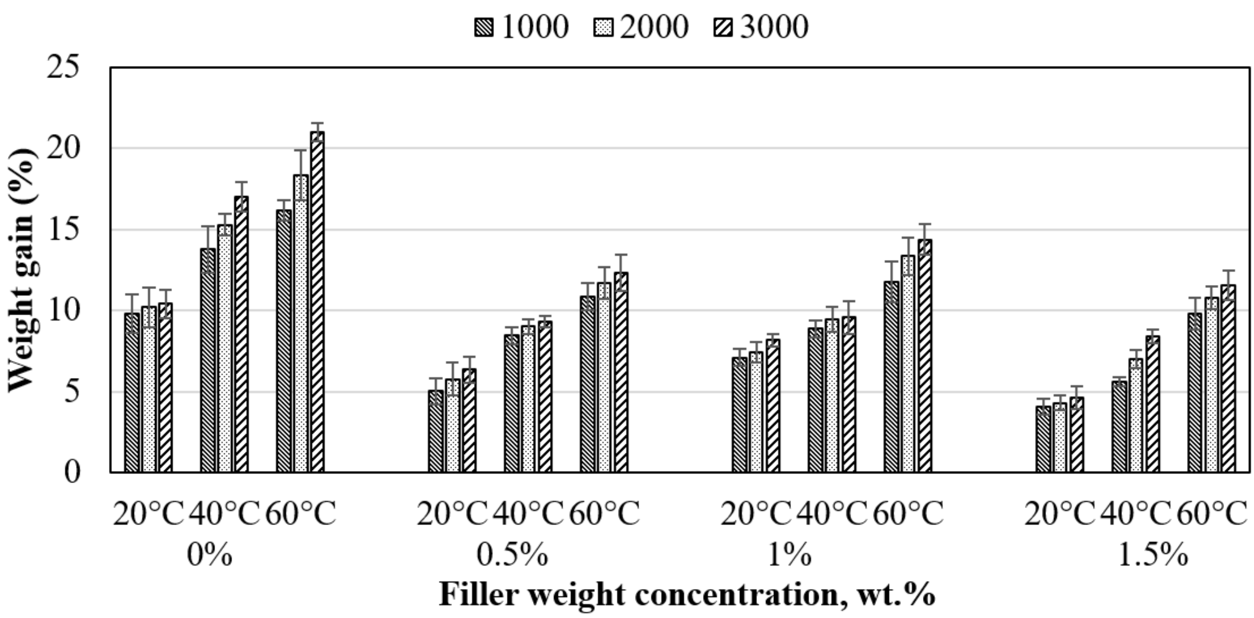


Fig. 3: Moisture absorption of hybrid composites at different temperatures

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 in-service 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. 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 c and (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 [52, 53].

The FS retention of conditioned hybrid composites with and without 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 with 0.5 %, 1 %, and 1.5 % graphene retained at least 97.5 %, 94.1 %, and 90.3 % of their initial FS, respectively, at the same conditioning temperature and exposure durations. 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 samples with 0.5 %, 1 %, and 1.5 % graphene, where 84.8 %, 80.4 %, and 77.3 % 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} [54], and the flax fibre with a negative thermal expansion coefficient is -8×10^{-6}/°C in its longitudinal direction as reported in the literature [55, 56], while the thermal expansion coefficient of epoxy matrix is 64–68 $\times 10^{-6}$ K^{-1} [54]. 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 in-service 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 (92.1%) 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 in-service 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 c left. It is worth noting that since the hygrothermal conditioning at in-service 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 [6, 27].

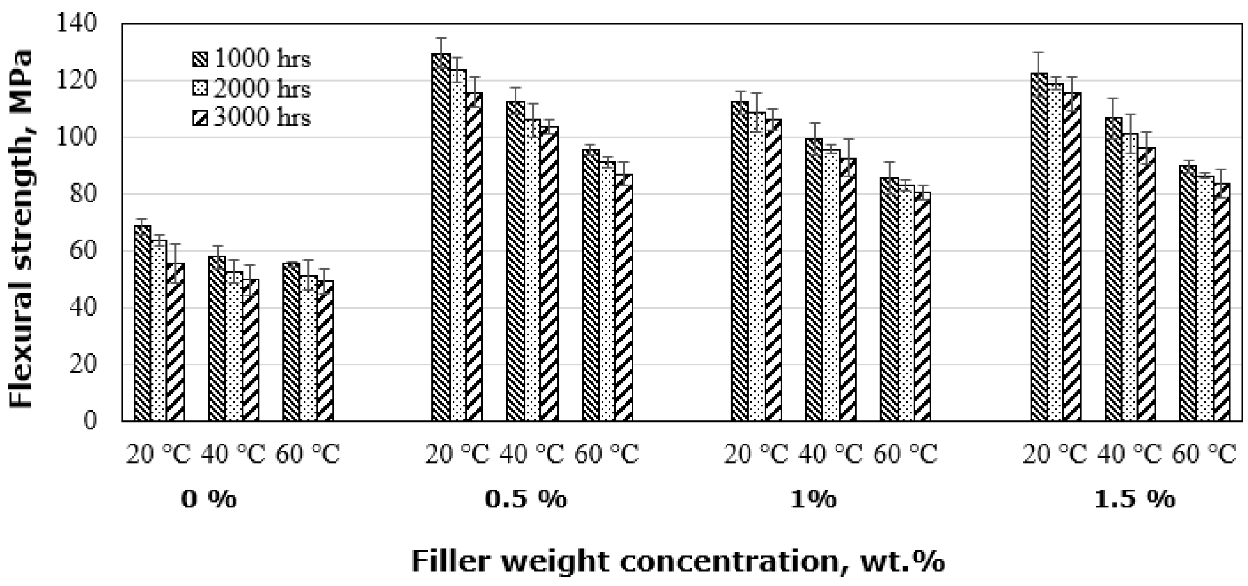


Fig. 4: Flexural strength of hybrid composites under hygrothermal conditioning

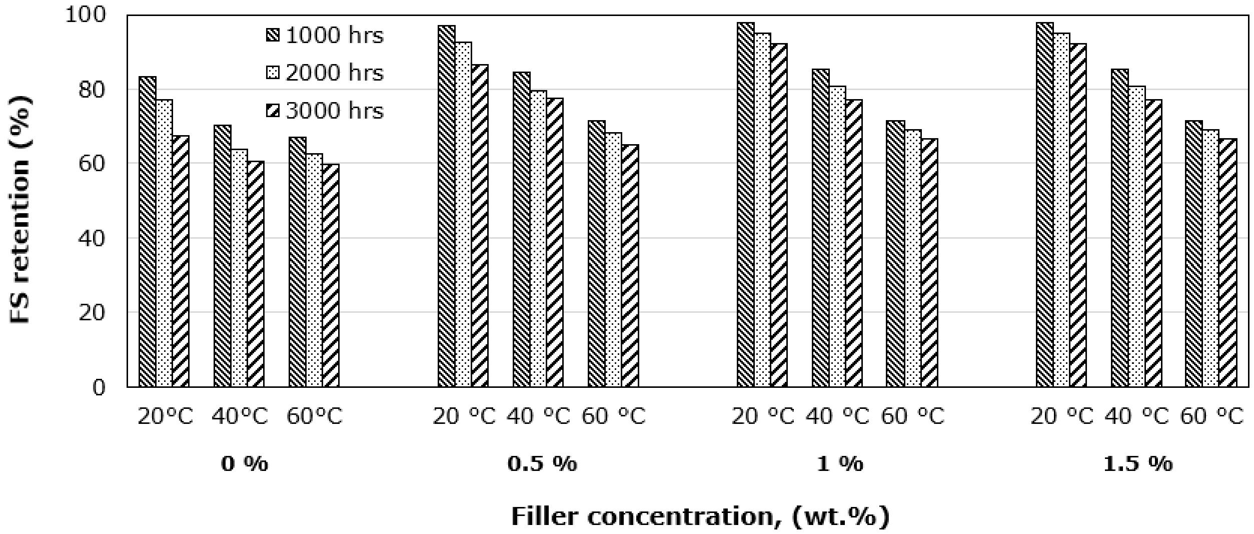


Fig.5: Flexural strength retention of hybrid composites under hygrothermal conditioning

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 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 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.[26], 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 [57, 58], 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 microcracks in the composite structure. The SEM image in Fig. 10 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 [59]. Reddy et al.[60] 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.

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), 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 (see Fig.10 c). Thus, it caused more interface deterioration and decreased modulus retention. As shown in Fig. 7, the higher modulus 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 with 0.5 % and 1.5 % graphene retained at least 88.3 %, 83.4 %, and 78.1% for 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 58 %, 54.1 %, and 52.4 % of the 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.

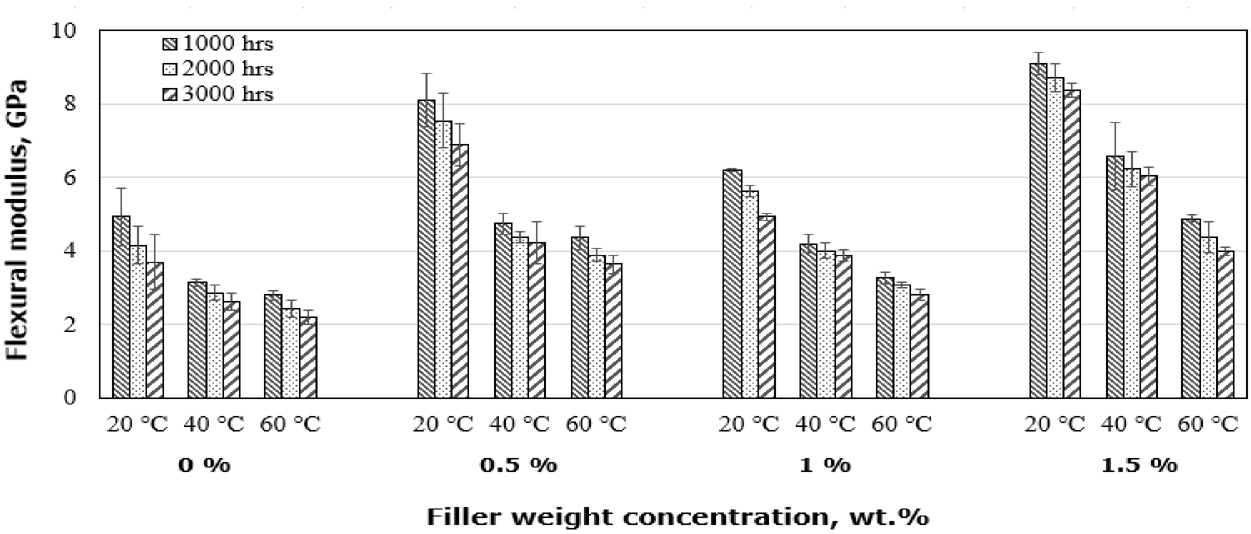


Fig. 6: Flexural modulus of hybrid composites under hygrothermal conditioning

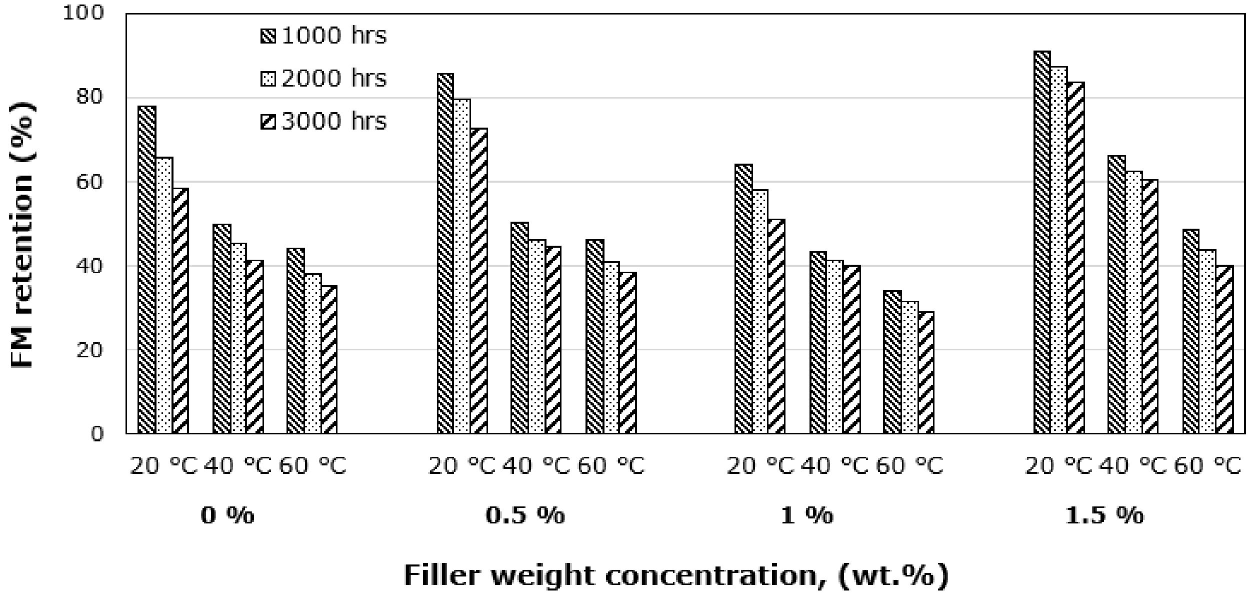


Fig. 7: Flexural modulus retention of hybrid composites under hygrothermal conditioning

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 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. [53]. 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 [61]. 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 [62] 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 (c and d). This aggregation reduces active surface area of graphene particles to interact with the epoxy matrix and thereby decreasing the ILSS. Because graphene nanoparticles with higher surface area provide higher load-transfer efficiency when their degree of dispersion is appropriate [51]. 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 in-service 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 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 of conditioned hybrid samples filled with 0.5 %, 1 %, and 1.5 % graphene decreased to 72 %, 74 %, and 78 %, 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.

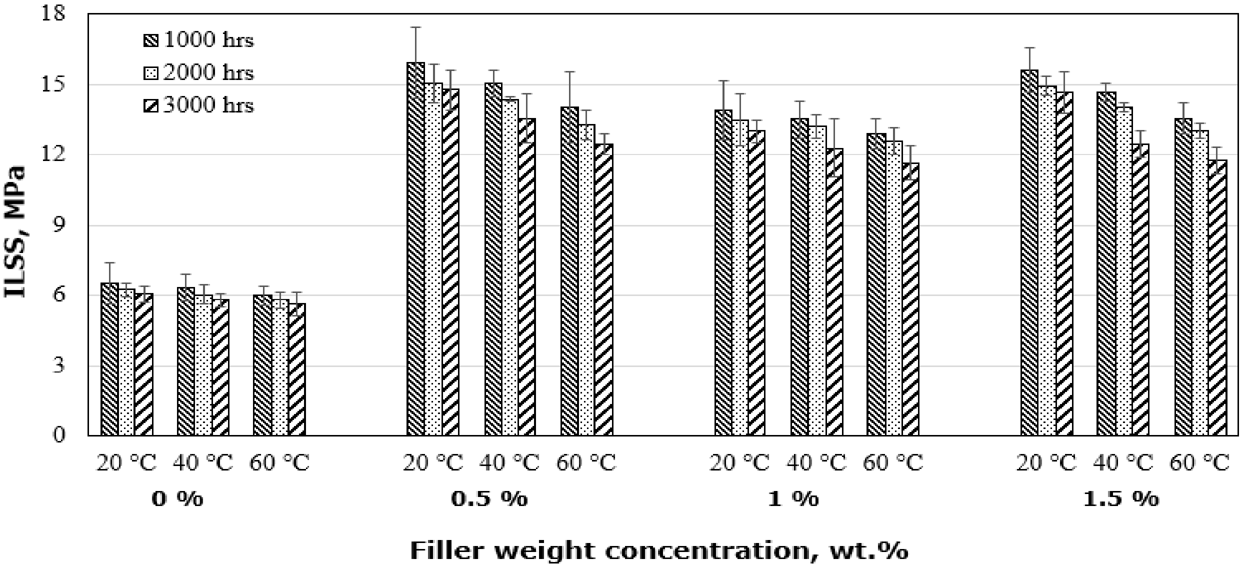


Fig. 8: Interlaminar shear strength of hybrid composites under hygrothermal conditioning

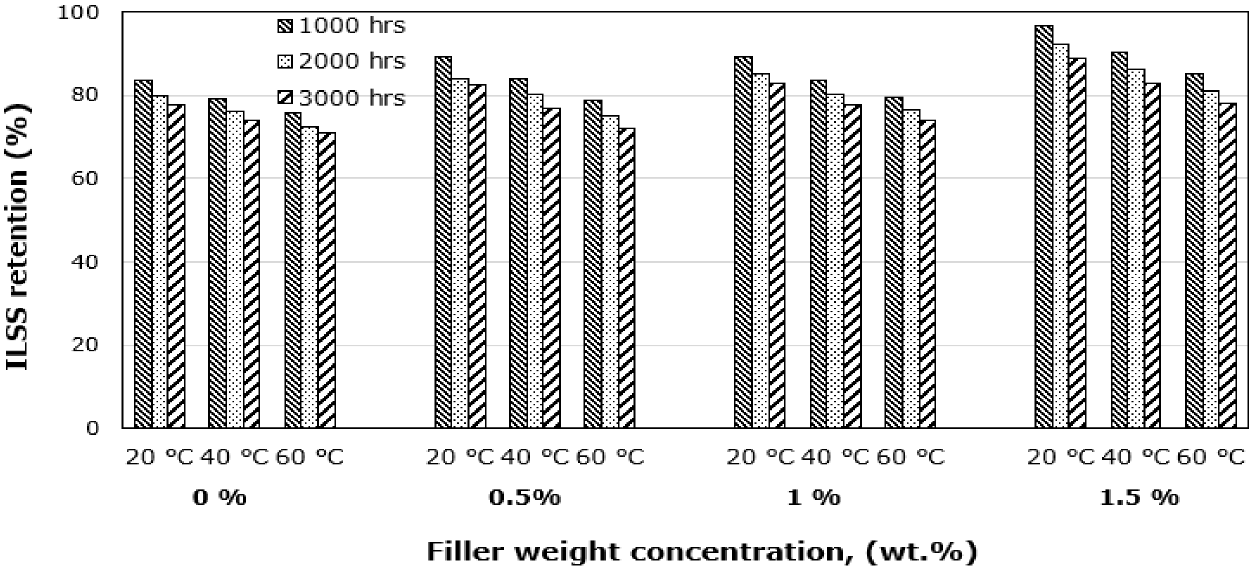
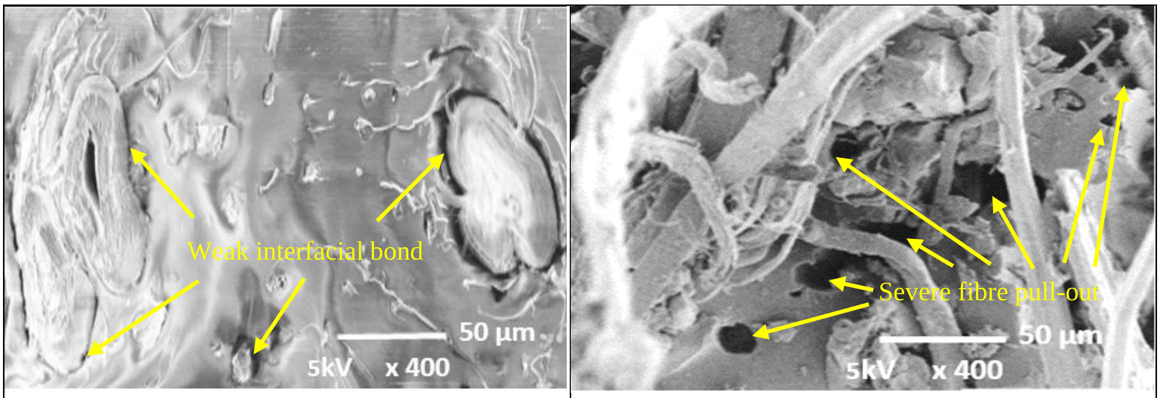


Fig. 9: ILSS retention of hybrid composites under hygrothermal conditioning

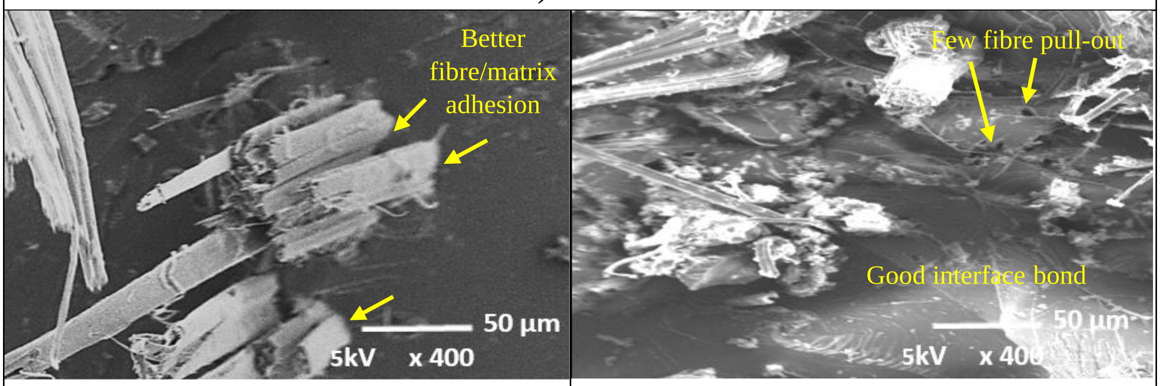
3.4 SEM and FTIR analysis on fracture surface

3.4.1 SEM analysis

Fig.10 shows the SEM results of hybrid composites with various graphene weights under mechanical tests 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. The SEM images in Fig. 10 indicate the strong influence of interfacial adhesion of the composite materials on their strength. As shown in Fig. 10 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. 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 b right). Fig.10 b left shows a complete adhesion of the flax fibre to the epoxy matrix, which explains less moisture absorption content. The SEM micrograph in the Fig. 10 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 (c and 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 c 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 c 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 c (right). Micro-cracks developed in the interface of specimens with 1 % graphene caused by swelling of the fibre were shown in Fig. 10 c (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 d right), with lower fibre/matrix debonding present (Fig. 10 d left in the bottom image), indicating adequate interfacial bond as shown in Fig. 10 d (left in the above image). 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.[63] 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.[64] 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.[65] 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.



a) 0 %



b) 0.5%

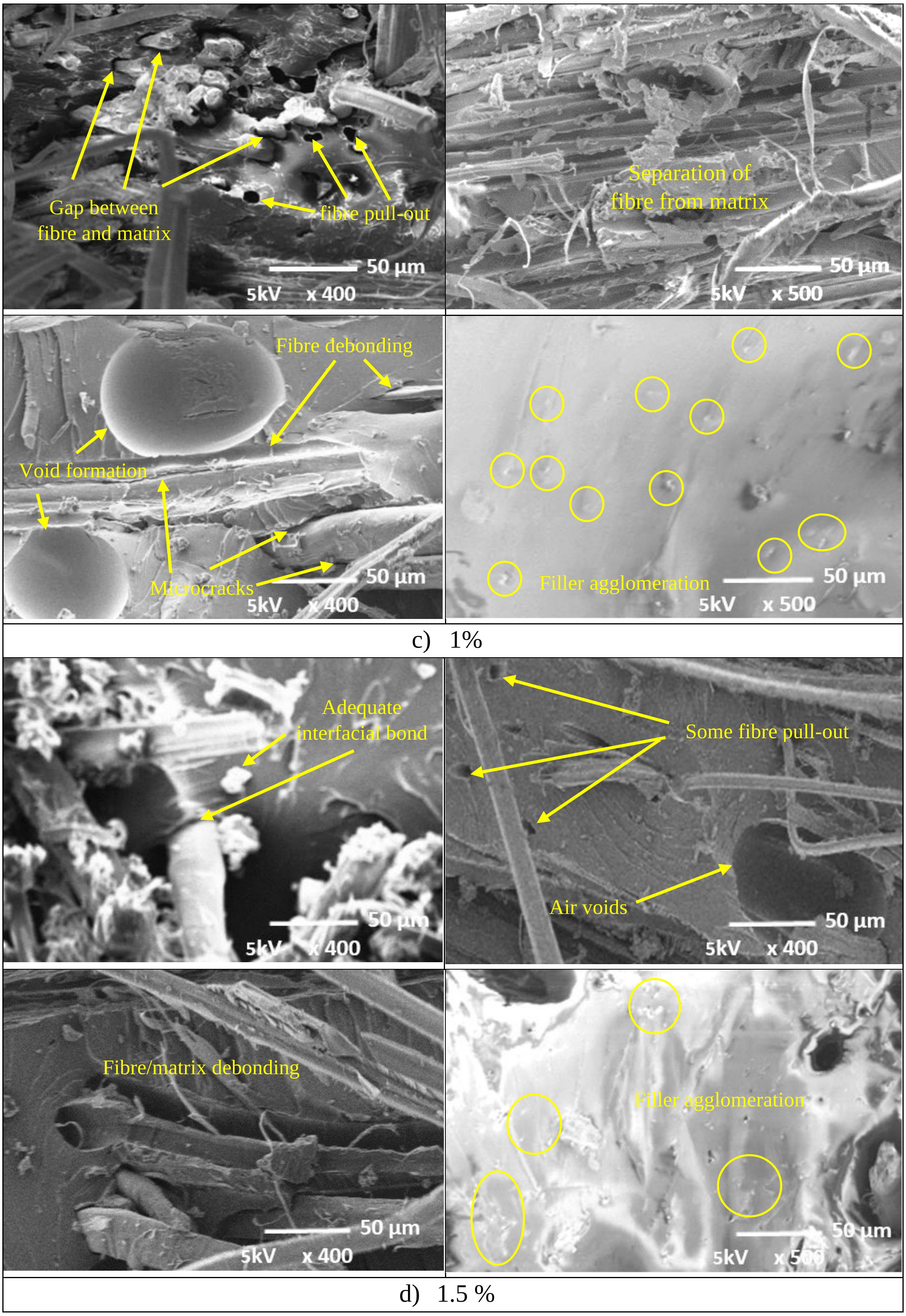
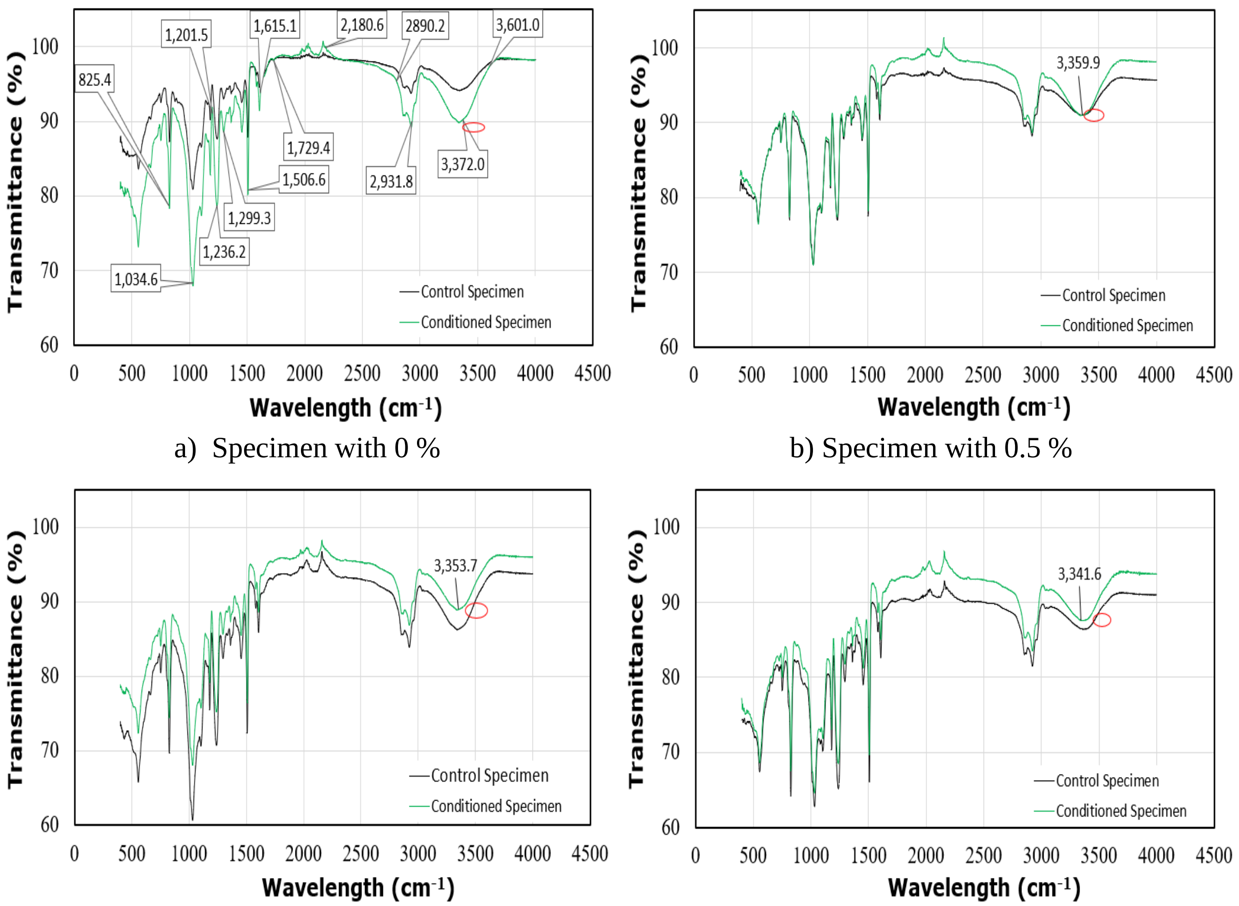


Fig.10: SEM micrographs of hybrid composite surfaces after hygrothermal exposure.

3.3.2 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 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 [66], 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 [67, 68], and the characteristic absorption band at 2180 cm^{-1} is associated with CO [69]. 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 [70]. 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 [71]. The sharp absorption band found at 1300- 1200 cm^{-1} is due to the C-O stretching vibration in the ester group [72]. The apparent bands around the 1237 and 1035 cm^{-1} region are associated with the asymmetric and symmetric stretching vibration of C–O–Φ [73]. The spectral absorption band located in the region of about 827 cm^{-1} corresponds to the C–H bending in the benzene ring [67]. 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 [74-76]. 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.[77] 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.



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

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.

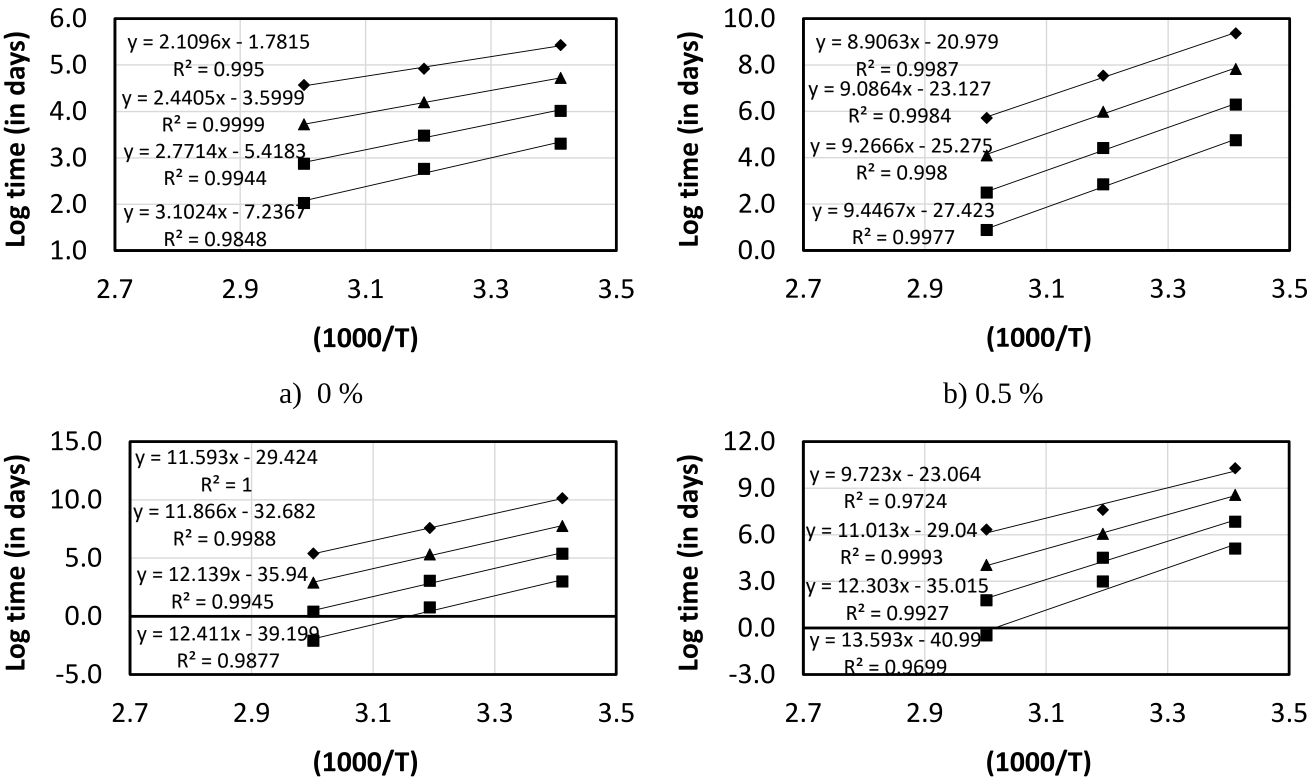
$$K = A \exp [-E_a / RT] \text{ -------------------------- Eq.2}$$

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 Equation 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.

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

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 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 Equation (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. [36] and Manalo et al.[40], 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.



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

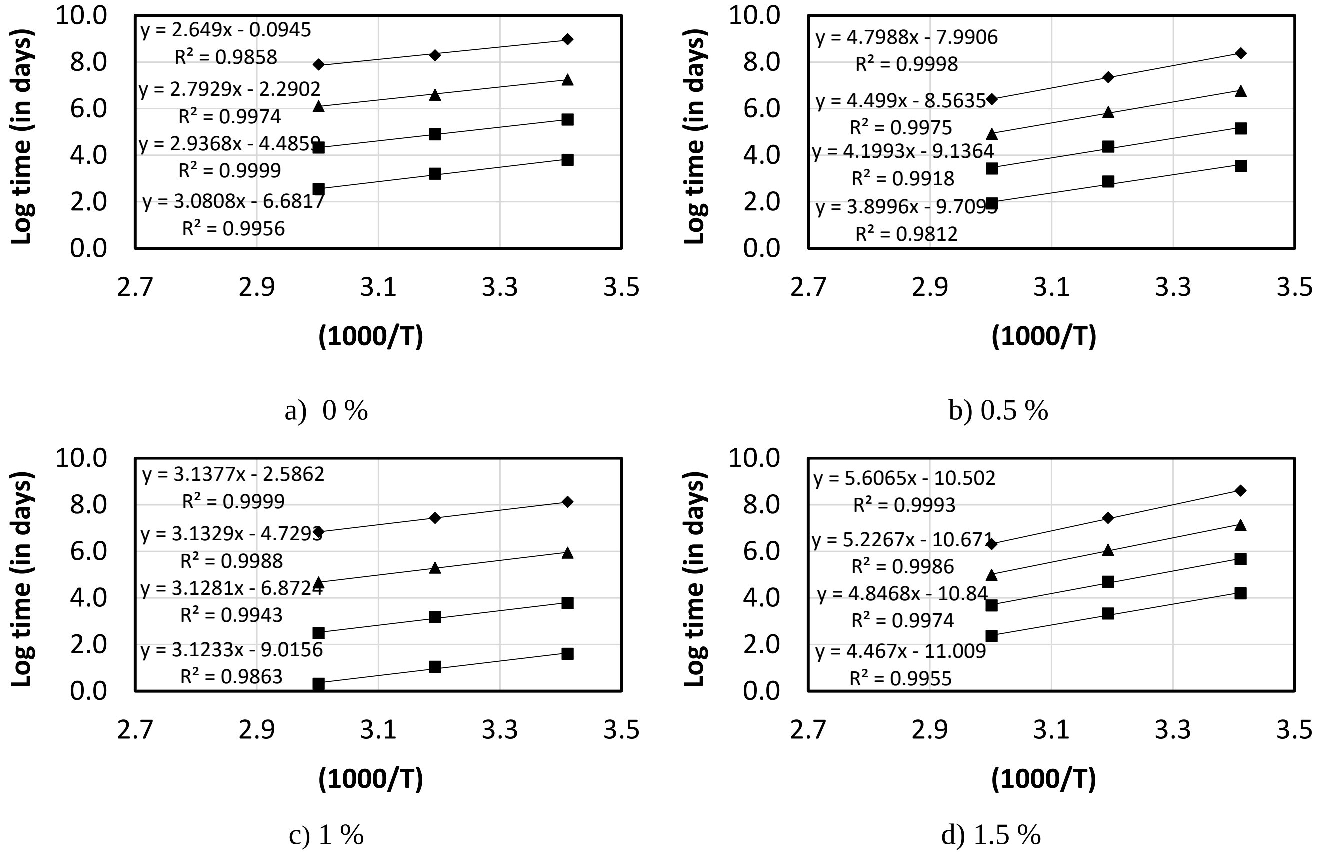


Fig.13: Arrhenius plot for ILSS retention of hybrid composites with various levels of graphene

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 [78]. 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.

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

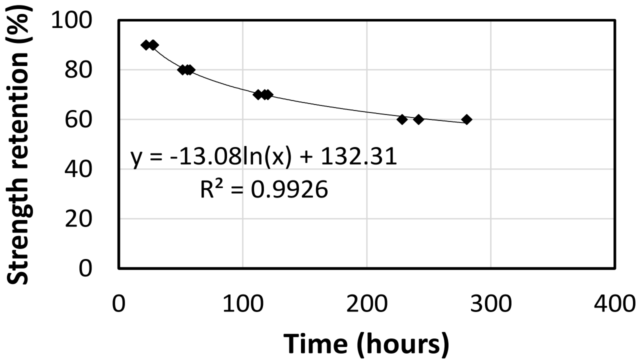
Table 3. Time-shift factor and Ea/R values of hybrid composites at different temperatures

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

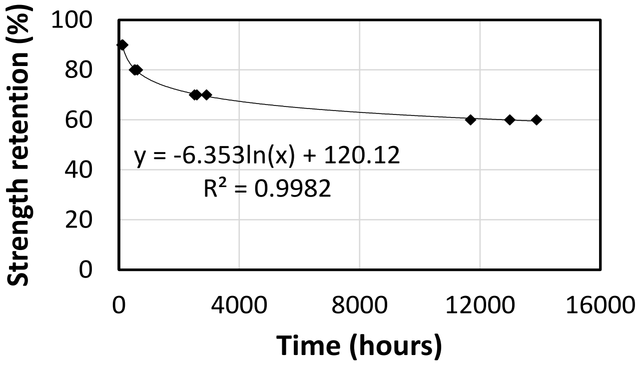
The TSF can then be used to shift the strength retention plots obtained from accelerated aging tests in laboratory conditions to a longer-term degradation plot. The reference temperature in this study was set at room temperature (20 °C) and the time safety factor was considered to be 1.0 at this temperature since degradation rates are measured very low when such composite materials are exposed to this level of temperature [79]. 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 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 have a clear degradation mechanism resulting from the accelerated tests.

4.3 Development of master curves

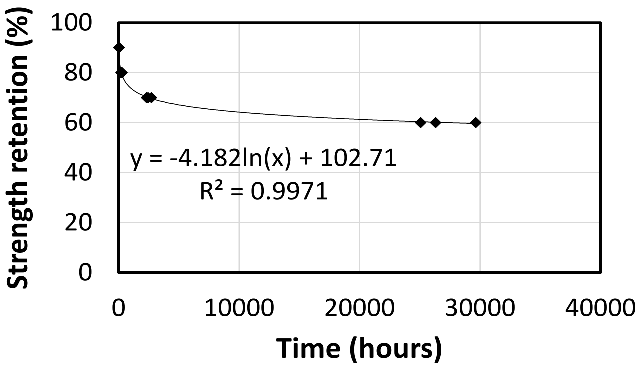
The master curves were developed using accelerated aging tests for this study along with the concept of Arrhenius model. These curves can provide all the data required for every retention level as suggested by Ali et al.[80], corresponding to its TSF obtained from Equation 4. The master curves at conditioning 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.



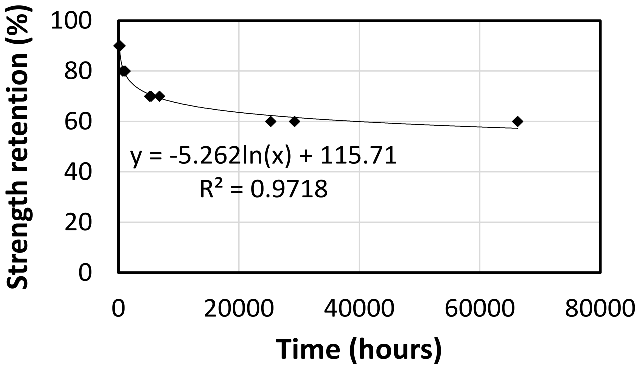
a) 0 %



b) 0.5 %

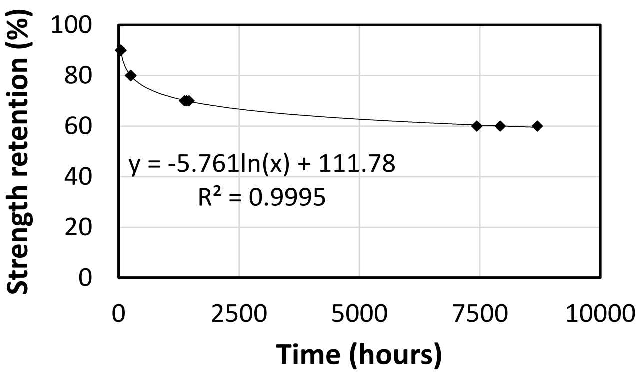


c) 1 %

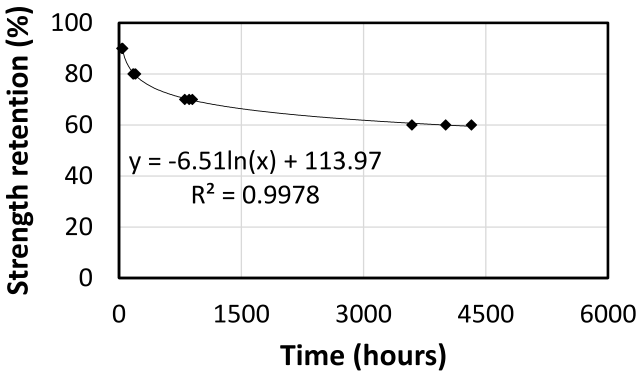


d) 1.5 %

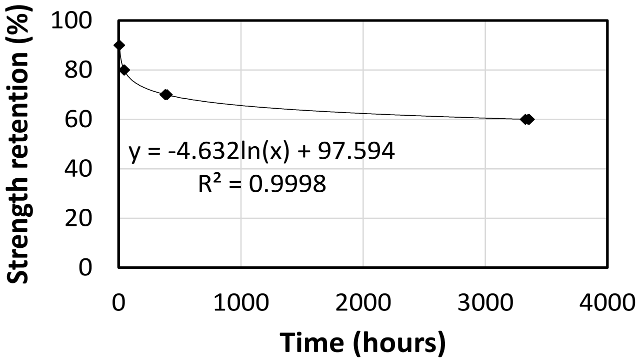
Fig. 14: Master cures for FS retention of hybrid composites at 20 °C



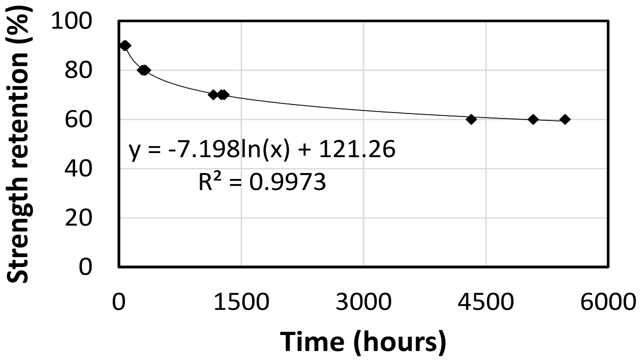
a) 0 %



b) 0.5 %



c) 1 %

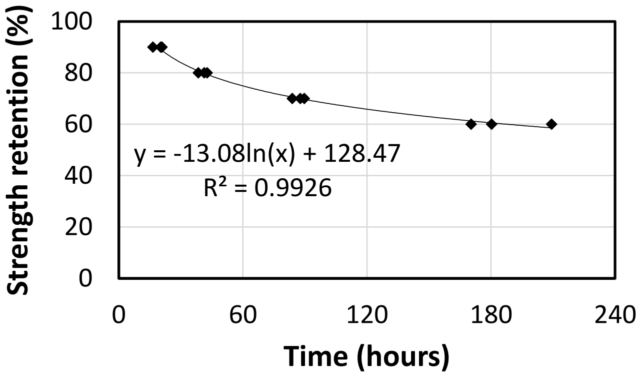


d) 1.5 %

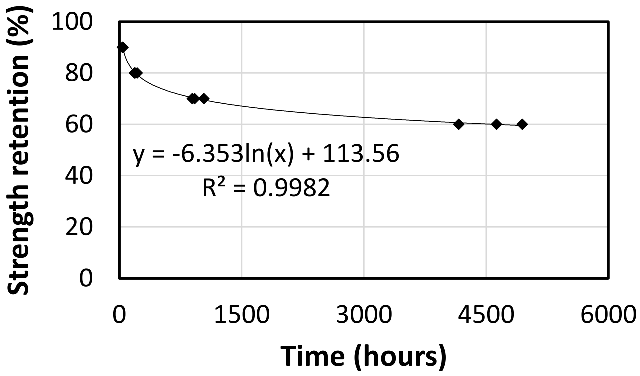
Fig. 15: Master cures for ILSS retention of hybrid composites at 20 °C

4.4 Long-term durability prediction using master curves

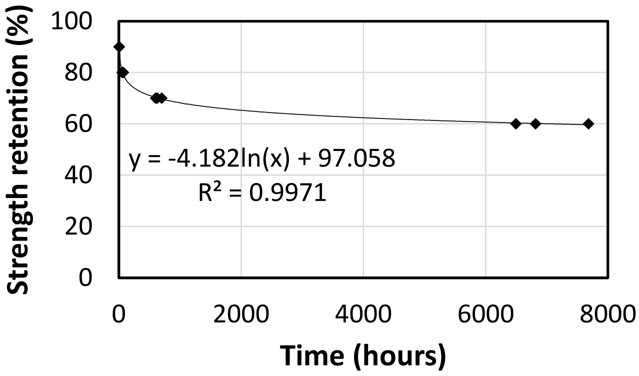
The best way to predict the long-term durability of hybrid composites is to use the master curves developed in this study based on the accelerated aging data as suggested by Chen et al.[81]. The time in years to attain specific mechanical strength retention levels for hybrid composites with graphene 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 [6]. 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.



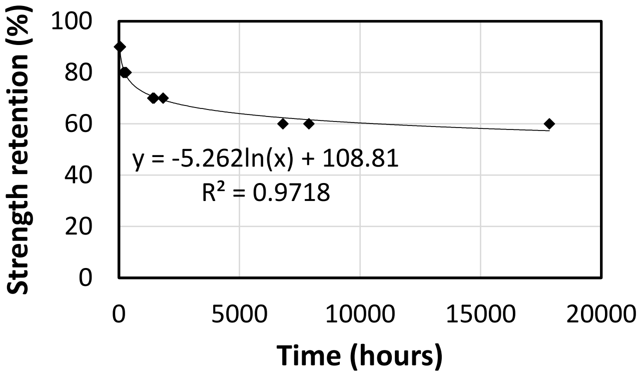
a) 0 %



b) 0.5 %

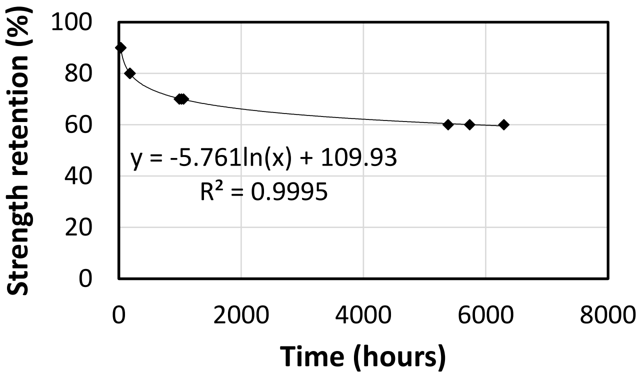


c) 1 %

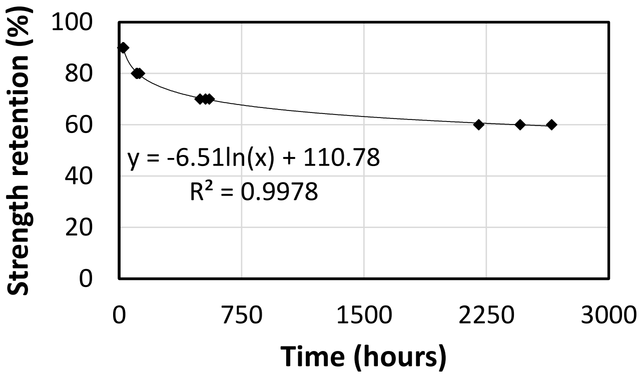


d) 1.5 %

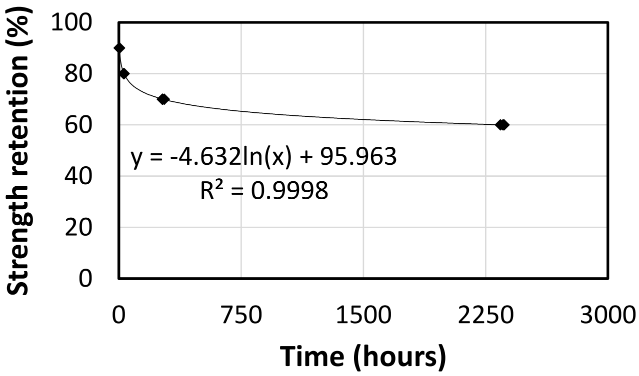
Fig. 16: Master cures for FS retention of hybrid composites at 30 °C



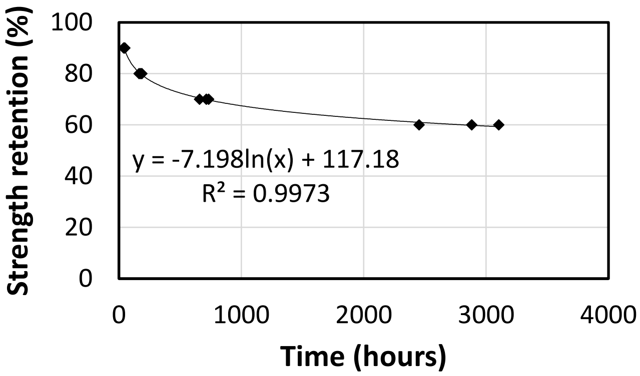
a) 0 %



b) 0.5 %



c) 1 %

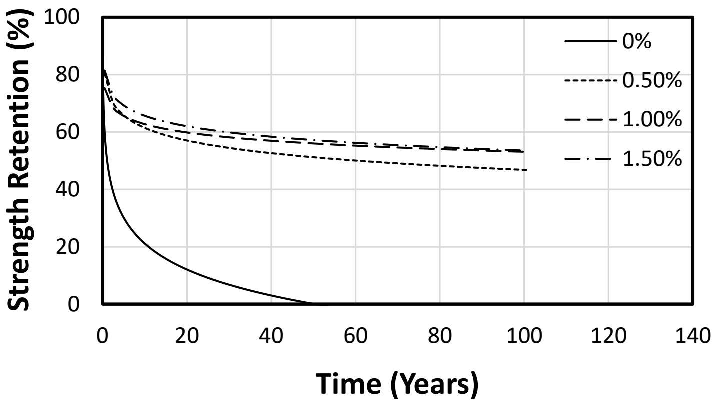


d) 1.5 %

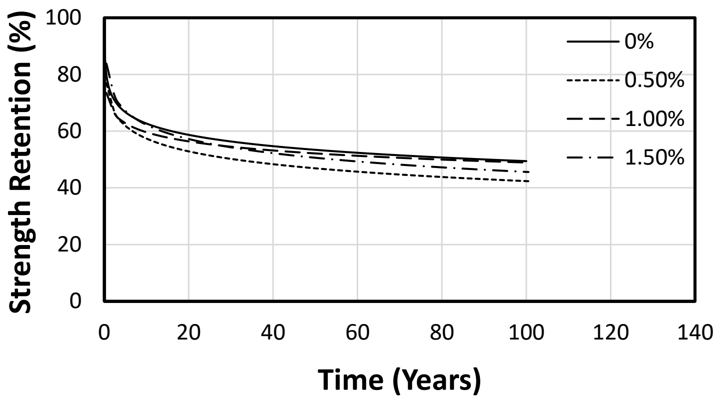
Fig. 17: Master cures for ILSS retention of hybrid composites at 30 °C

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% to 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 [82]. 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. [76] for particulate filled epoxy polymers and they found that flexural samples showed lower strength 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 [83] 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 the natural fibre composites after 100 years which shows a strength retention of 40% to 50% regardless the graphene filler content. However, graphene filler played a major role to increase the ILSS of the flax fibre composites (up to 2.5 times, as shown in Fig. 8).



a) Flexural



b) Interlaminar

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

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 decreases with the increase of graphene percentage. However, the moisture absorption rate increased with the increase of exposure duration and conditioning temperature.

- Graphene nanoparticles significantly improved the mechanical properties of hybrid composites allowing them to retain a noticeable portion of their strength after the hygrothermal conditioning. The strength retention however becomes lower as the conditioning temperature and exposure duration increased.
- 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.
- The hybrid composites showed no change in the chemical structure after hygrothermal conditioning as evidenced by FTIR analysis. The high-intensity peaks of the stretching vibration of hydroxyl (OH) groups observed indicates the presence of moisture in the matrix, but no other changes in the functional groups.
- Master curves along with time-shift factors were developed using the Arrhenius model to establish a correlation between the mechanical strength retention of hybrid composites and their equivalent service life. 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.

- Structural members from natural fibre composites with long-spans are not recommended to be used in the applications subjected to flexural loads due to high moisture capacity of the natural fibre leading to loss the compression-tension action through the thickness of the composite specimen. Whereas it is acceptable for use in short span members as demonstrated with its high ILSS retention.

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.

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CHAPTER 6: DISCUSSION AND CONCLUSIONS

This chapter concludes the research study conducted within the framework of a project titled "Mechanical and Durability Performance of Hybrid Composites Incorporated Flax Fibres and Graphene". In particular, this chapter summarizes the main findings of this research work and outlines a number of recommendations of possible areas for future studies.

6.1 Conclusions

Natural fibre-reinforced polymer (NFRP) composites provide a potential alternative option to synthetic fibre-based polymer composites in various industrial applications. The main limitations of NFRP composites when used for outdoor applications are their limited thermal stability and moisture sensitivity. These challenges can potentially be overcome by reinforcing these natural fibre composites with nanomaterials. Therefore, this thesis focused on the long-term durability properties of hybrid flax fibre-reinforced epoxy composites with graphene under the effect of different environmental conditions, in particular the effects of moisture, thermal, and hygrothermal environments. The individual conclusions gathered from the chapters of this research contributed to the understanding of how the hybrid effect plays a role in the long-term performance of natural fibre composites under these harsh environments and their associated service life issues. The significant findings from this research work are summarised as below:

6.1.1 State-of-the-art review on the long-term behaviour of flax fibre composites with fillers

The main challenge associated with the use of NFRP composites under different environmental conditions is their low thermal degradation property and moisture resistance. These challenges can be addressed by modifying the composites by introducing nanoparticles with high thermal resistance and low moisture adsorption. Based on the extensive review of literature, the following conclusions can be drawn.

- The sensitivity of natural plant fibres to absorb moisture due to their hydrophilic nature makes their composites more susceptible to deterioration when exposed to this type of environment. This reveals the importance of studying the moisture-related degradation of NFRP composites and thus their degradability in moisture environments can be improved by using a sufficient amount of nanoscale fillers such as graphene nanoparticles.
- NFRP composites has low thermal stability, and its properties will degrade when used in outdoor applications. Understanding the sensitivity of natural fibre properties to such thermal environments is critical and their thermal performance with the addition of graphene requires a detailed investigation.
- The resistance of hybrid natural fibre composites with graphene nanoparticles under the combined effect of humidity and in-service elevated temperature is unknown. Investigating the short and long-term properties of natural fibre composites can provide a better insight into the suitability of use of hybrid composites in outdoor applications.

The literature review highlighted that the inclusion of nanoscale graphene to flax fibre composites successfully enhanced their initial mechanical characteristics at room temperature. However, the mechanical degradation changes of hybrid composites are mainly dependent on the effect of each type of exposure environment and exposure duration on the interfacial bond adhesion, and the properties of both the fibre and the matrix. Therefore, a better understanding of the mechanical and long-term properties of NFRP hybrid composites with graphene against these aggressive environments is critical for their safe design and use in outdoor applications. These objectives have been addressed throughout this study.

6.1.2 Effect of in-service elevated temperature *on the behaviour of flax fibre composites with graphene*

The reinforcing effect of graphene weight ratios on the mechanical properties of flax fibre composites under in-service elevated temperature was investigated. Hybrid composites with graphene ranging from 0%, 0.5%, 1%, and 1.5 % by weight of the matrix were prepared and tested at in-service elevated temperatures of 20 °C, 40 °C, 60 °C, 80 °C and 100 °C. The significant findings of this research work are summarised as follows:

- The addition of graphene has a positive effect on the flexural and ILSS of flax fibre composites at room temperature. Composites with a hybrid ratio of 0.5 % graphene exhibited the maximum flexural and ILSS, with increments of 62 % and 149 %, respectively. This significant enhancement was achieved due to the improvement in the interfacial bond between the resin and fibres as well as the additional stiffness came from the graphene nanoparticles addition as it had a good in the matrix. Beyond which, there is no major enhancement in the flexural strength and ILSS due to the filler agglomeration.
- Composites with 0.5 % graphene performed the best under in-service elevated temperature with the flexural and ILSS retention were 60 % and 52 %, respectively, at 60 °C and only 18 % at a temperature higher than 60 °C. This is because of the difference between the thermal expansion coefficients of flax fibres, epoxy resin and graphene.
- The addition of graphene changed the failure behaviour in flexure from fibre fracture to fibre pull-out. Hybrid composites under ILSS load failed in tensile failure and fibre pull-out rather and this failure mode changed from fibre pull-out and tensile failure to the delamination behaviour at in-service elevated temperature.

The findings of this study highlighted that the addition of graphene improved the mechanical properties of hybrid flax fibre-reinforced epoxy composites with graphene at room temperature, but this improvement is insignificant at in-service elevated temperature. Another interesting factor to be explored is moisture absorption which aids in the deterioration of both the properties of the fibre and the polymer matrix and thus affects their composite durability especially for conditioning in high humidity environments.

6.1.3 Effect of moisture absorption on the behaviour of flax fibre composites with graphene

In this study, the mechanical degradation of hybrid flax fibre-reinforced epoxy composites under moisture environment was investigated. Flax fibre composites with hybrid ratios of 0 %, 0.5 %, 1.0 %, and 1.5 % graphene by weight of the epoxy matrix were prepared and immersed in water for 1000, 2000, and 3000 hours at room temperature. The significant outcomes of this study are summarised below.

- The addition of graphene nanoparticles achieved a good balance between moisture resistance and mechanical strength improvements with flax fibre composites due to their superior intrinsic properties of high strength and hydrophobic nature. The positive hybrid effect of graphene increased the flexural modulus of flax fibre composites due to its stiffer nanoparticles.
- The contribution of graphene to the flexural and ILSS under wet conditions decreases with increasing exposure duration. In contrast to this, the effect of moisture absorption on flexural modulus is more pronounced than other mechanical properties because it is highly dependent on the fibre properties.
- The interfacial strength of flax fibre composites with and without graphene under wet conditions is strongly dependent on the type of failure mode. Hybrid composites under flexure has strong interfacial bond adhesion whilst those without graphene demonstrate weak bonding strength of the fibre with the polymer matrix. Under ILSS loading, the failure mode of flax fibre composites occurred at the middle and ends of samples with the most common failure pattern being inter-laminar delamination due to low interfacial bond strength.

The results of this study revealed that the positive influence of denser graphene network formation at higher contents outweighed the negative influence of graphene agglomeration in hybrid composites under wet conditions. However, longer exposure duration and filler agglomeration significantly affected the contribution of graphene and its positive hybrid effect on the mechanical improvements of flax fibre composites. In the actual environment, the applications of hybrid flax fibre-reinforced epoxy composites in outdoor use are often subjected to moisture and in-service elevated temperature at the same time, which affects their durability properties. To ensure their safe use in outdoor environments, the combined effect of humidity and in-service elevated temperature on the long-term performance of hybrid flax fibre-reinforced epoxy composites was experimentally and analytically studied.

6.1.4 Effect of hygrothermal condition on the behaviour of flax fibre composites with graphene

The effect of graphene weigh ratio from 0 % to 1.5 % on the durability behaviour of flax fibre composites after hygrothermal conditioning was evaluated under flexural and ILSS tests. Hybrid composites were conditioned in 98 % constant relative humidity for 1000, 2000, and 3000 hours at exposure temperatures of 20 °C, 40 °C, and 60 °C. From the test results of this study, the following points are concluded:

- The reduction of the moisture absorption behaviour of hybrid composites can be achieved through the hybrid effect of graphene. Hybrid flax fibre composites showed a high strength retention with low moisture absorption. However, the degradation of composites was more pronounced by temperature than exposure duration.
- The flexural and ILSS properties of the hybrid composites show similar trends with exposure duration, and both decrease significantly in moisture conditioning at 60 °C for 3000 hours. In contrast, flax fibre composites continue to absorb moisture and undergo fibre swelling and matrix plasticization under the combined effect of humidity and in-service elevated temperature, which causes their mechanical properties to drop significantly under all conditions due to poor fibre/matrix interface adhesion.
- The effect of humidity and in-service elevated temperature on flexural modulus was more obvious than on flexural strength due to fibre properties controlling this property.

However, the hybrid modulus retention was higher than that estimated from flax fibre composites because of the positive hybrid effect of graphene on moisture absorption.

- The addition of graphene to flax fibre composites did not change in their chemical structure under hygrothermal environment, and the high-intensity peaks at 3600- 3200 cm-1 are likely related to the stretching vibration of hydroxyl (OH) groups. The presence of these OH groups indicates that hybrid composite matrix contains moisture.
- The analytical prediction based on the Arrhenius model was able to reliably predict the long-term flexural and ILSS properties of hybrid flax fibre-reinforced epoxy composites after hygrothermal exposure. The mechanical strength retention of hybrid composites was in the range of 40 to 50 % of their original flexural and ILSS after 100 years of service at an average annual temperature for Australia (30 °C).

The results of this study demonstrated that the hygrothermal resistance of flax fibre composites improves when they are hybridized with graphene, and this hybrid influence is strongly associated with its dispersion within the polymer matrix. A significant positive hybrid influence is present in all hybrid composites with the maximum hybrid effect (the maximum flexural and ILSS properties) being achieved for the samples with 0.5 % graphene. The developed model showed that flax fibre-reinforced hybrid epoxy composites can retain sufficient strength even at outdoor applications their service life.

6.2 New opportunities and future research

The effectiveness of adding nanoscale graphene in enhancing the long-term durability of hybrid flax fibre-reinforced epoxy composites as presented in this research study demonstrates the high potential to develop their use in outdoor applications. Based on the results obtained from the studies presented in this thesis, opportunities and new research areas can be explored to understand the effects of environmental parameters on the long-term durability of newly produced hybrid composites.

- The effect of the most important environmental factors on the mechanical performance of hybrid flax fibre-reinforced epoxy composites with graphene including moisture, heat and hygrothermal environments has been studied in this research work. Further research is required to evaluate the influence of other environmental factors such as ultraviolet (UV) radiation to provide a comprehensive understanding of the performance of these hybrid composites.
- This thesis focused on studying the effect of graphene on the thermal performance and moisture absorption behaviour of flax fibre composites as well as the mechanical properties after hygrothermal conditioning. There is an opportunity in using other functional fillers such as halloysite nanotubes (HNT), carbon nanotubes (CNTs) and silicon carbide nanoparticles (n-SiC) to investigate their effect on the long-term durability of natural fibre composites that can potentially increase their use in outdoor environments beyond what was achieved in this study.
- The contribution of graphene to the mechanical performance of flax fibre composites exposed to hygrothermal environments for a maximum exposure duration of 3000 hours was investigated. In the future, their performance beyond this duration should be investigated to highlight the importance of understanding issues related to degradation mechanisms.
- This thesis focused on the effect of in-service elevated temperature on the mechanical behaviour of hybrid composites with graphene. Further studies should investigate the fire behaviour of these hybrid composites that can overcome their restrictions and extend their potential engineering applications.
- This thesis investigated the effect of tap water solution on the long-term properties of hybrid composites with graphene only, where their long-term behaviour when exposed to varying chemical solutions such as alkaline solution and saline solution should be

studied to find out how the hybrid effect of graphene nanoparticles contributes to this behaviour.

- Natural fibre composites used in this study are not 100 % bio composites because they were prepared using synthetic epoxy resin reinforced with flax fibres and nanoscale fillers. There is an opportunity to manufacture bio composites with 100 % plant-based resins used as a matrix and natural fibres with nano fillers as reinforcements. These produced composites should be investigated against various environmental conditions to evaluate their long-term durability and to see if the use of synthetic polymer matrices or fibre surface treatments is justified.
- The main challenge of using graphene nanoparticles in polymer reinforcement or composite materials is the agglomeration and restacking due to Van der Waals attraction between its nanoparticles, leading to higher filler-filler interaction than the matrix-filler interaction. Therefore, further studies are needed to investigate the dispersion of graphene in natural fibre composites using some techniques in the manufacturing process like in-situ polymerization, solution blending and melt blending to obtain a better dispersion of graphene in the polymer matrix.
- Developing analytical models can correctly predict the long-term behaviour of hybrid composites and provide accurate information that cannot be achieved experimentally. Further studies and analysis are required to generate more experimental data to expand the use of this analytical model for hybrid composites.

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