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Corresponding Author: Dr. Belal Yousif, PhD

Corresponding Author's Institution: University of Southern Queensland

First Author: Z.N. Azwa Azwa

Order of Authors: Z.N. Azwa Azwa; Belal Yousif, PhD; A.C. Manalo ; W. Karunasena Karunasena

Abstract: The applications of natural fibre/polymer composites in civil engineering are mostly concentrated on non-load bearing indoor components due to its vulnerability to environmental attack. This paper evaluates the characteristics of several natural fibre composites exposed to moisture, thermal, fire, and ultraviolet degradation through an extensive literature review. The effects of chemical additives such as fibre treatments, fire retardants and UV stabilizers are also addressed. Based on the evaluation conducted, optimum fibre content provides strength in a polymer composite but it also becomes an entry point for moisture attack. Several fibre treatments are also being used to improve fibre/matrix interface, thereby increasing moisture durability. However, the treated fibres were found to behave poorly when exposed to weather. The addition of UV stabilizers and fire retardants are suggested to enhance outdoor and fire performance of natural fibre/polymer composite but compromises its strength. Therefore, from the collected data and various experimental results, it was concluded that an optimum blend ratio of chemical additives must be employed to achieve a balance between strength and durability requirements for natural fibre composites.

Dear Editor

I would like to submit a paper entitle of "Degradability of Polymeric Composites Based on Natural Fibres" to the materials and design. This paper address important issues related to the degradation of natural fibres in polymeric composites. I believe the paper has interest to the reader of the journal and will be beneficial for many researchers in the field of materials and design considering the degradation of polymer and bio-materials. I would like to confirm that the paper has not been sent to any journal before and not under review. I hope you can send the paper fore reviewing process.

Dr. B. F. Yousif, PhD,
Faculty of Engineering,
University of Southern Queensland,
Toowoomba, QLD,
Australia.

+6146315331

Belal.Yousif@usq.edu.au

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'Response to Reviewers'

Editor: Thank you for submitting your review paper. There are no technical issues. However, there are areas of the paper that need attention as follows:

1. Include more keywords - you are allowed up to 6 keywords.

The keywords have been updated and highlighted in the revised version as

Keywords: natural fibres; polymer composites; civil applications; characteristics degradation; weathering.

2. Include your personal university telephone number in the contact details in the paper.

In the revised version it has been included as

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3. Make sure all acronyms, including common ones, are defined on first use, remembering the Abstract.

Here are the list of changes in the revised version and highlighted

UV → Ultraviolet (UV)
US → United states (US)
FRPs → natural fibre reinforced polymers.
hemp/UPE → hemp fibre reinforced unsaturated polyester (hemp/UPE)
FRP → fibre reinforced polymer (FRP)
PVC→ polyvinyl chloride (PVC)
SEM → scanning electron microscopy (SEM)
APP → ammonium polyphosphate
PCL → polycaprolactone

4. Do not use all capital letters for the References section heading.
   References

5. Do not use italic font in the references.
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16. The second list of points in the Conclusions can be put in a new section at the end of the paper called 'Future developments', expanding accordingly.
    Section 7 is created:

7. Future Developments

Highlights

- Natural fibres are prone to moisture attack.
- The amount of fibre in a composite shall be limited to its optimum fibre/matrix ratio to limit its moisture susceptibility.
- Fibre treatments are essential to enhance strength and moisture durability of composite.
- Low lignin content in a natural fibre leads to better thermal performance.

A Review on the Degradability of Polymeric Composites Based on Natural Fibres

Z.N. Azwa, B.F. Yousif*, A.C. Manalo and W. Karunasena
Centre of Excellence in Engineered Fibre Composites (CEEFC)
Faculty of Engineering and Surveying, the University Southern Queensland, Toowoomba, 4350 QLD, Australia.
Belal.Yousif.usq.edu.au; Tel: +61 7 4631 5331

ABSTRACT

The applications of natural fibre/polymer composites in civil engineering are mostly concentrated on non-load bearing indoor components due to its vulnerability to environmental attack. This paper evaluates the characteristics of several natural fibre composites exposed to moisture, thermal, fire, and ultraviolet degradation through an extensive literature review. The effects of chemical additives such as fibre treatments, fire retardants and Ultraviolet (UV) stabilizers are also addressed. Based on the evaluation conducted, optimum fibre content provides strength in a polymer composite but it also becomes an entry point for moisture attack. Several fibre treatments are also being used to improve fibre/matrix interface, thereby increasing moisture durability. However, the treated fibres were found to behave poorly when exposed to weather. The addition of UV stabilizers and fire retardants are suggested to enhance outdoor and fire performance of natural fibre/polymer composite but compromises its strength. Therefore, from the collected data and various experimental results, it was concluded that an optimum blend ratio of chemical additives must be employed to achieve a balance between strength and durability requirements for natural fibre composites.

Keywords: natural fibres; polymer composites; civil applications; characteristics degradation; weathering.

1. Introduction

Nowadays, traditional building materials such as concrete and steel are increasingly being replaced by advanced composite materials, e.g. fibre reinforced polymers (FRP) and fibre reinforced cement (FRC). It is expected that fibre/polymer composites will expand their usage in the near future due to the advantages offered by these materials, i.e. high strength, low weight, corrosion resistance, and low maintenance cost [1]. Despite of those advantages, engineers are being challenged to 'go green' in many aspects of the engineering disciplines which includes finding more environmental friendly processes and innovation of biodegradable or recyclable materials. Municipal solid waste (MSW) landfills represent the dominant option for waste disposal in many parts of the world, with 70% of MSW in Australia has been directed to landfills without pre-treatment in 2002 [2]. Fishbein [3] had reported that construction and demolition debris comprises of 10-30% of waste received at landfill sites around the world and from a 2004 publication [4], that number has reached 40% in the united states (US). One of the efforts to meet this challenge is by replacing synthetic materials with natural materials, e.g. reinforcements in polymer composites.

Fibres such as hemp, kenaf, jute, and bamboo have been studied for their mechanical properties and their potential contributions in composite materials. These natural fibre reinforced composites are finding their way in the construction industry, with a projected increase in demand as high as 60% each year in the US [5] and a predicted growth rate from 10% to 22% per year for the natural fibre industry [6]. Their production consumes, on average, 60% less energy than the manufacture of glass fibres [7]. On the other hand, natural fibres have some issues and disadvantages when used as reinforcements for polymeric composites [8], i.e. degradability, fire resistance, interfacial adhesion, etc. Therefore, an emphasis on those issues may improve the composite quality and open new applications for such attractive materials.

Fig. 1 shows the number of journals published on the degradation of fibre reinforced polymer composites due to moisture, thermal, fire, and ultraviolet (UV) rays for the past 10 years. Although the increment is unsteady, the figure provides a rough indication on the increased interest of researchers on this topic, with natural fibre reinforced polymers being less explored. More importantly, the degradation and the fire resistance of natural fibres are seen as the main limitations of the fibres usage in civil engineering applications. In light of this, there is a need to expand the research on natural fibre/polymer composites with regards of their degradability under different environmental conditions. In this article, a comprehensive review on the degradation of polymeric composites based on synthetic and natural fibres are presented addressing the degradation issues and proposing some ideas to overcome them.

2. Natural Fibre Reinforced Polymer Composites and its Degradation

2.1 The Applications and Drawbacks of Natural Fibre Composites

The application of natural fibres as reinforcement in composite materials is constantly in development. The drawbacks on its mechanical properties are being studied to maximize its full potential as an alternative to synthetic fibres. Civil infrastructure composites have to resist loadings due to tension, compression, impact, fatigue, blast and creep [9]. Presently, natural fibres applications are limited to interior and non-structural applications due to its low mechanical properties and poor moisture resistance [10]. It is being used in the furniture, architectural, and more recently, in automotive industries [11]. Many efforts are currently being undertaken to expand its application, for instance, the development of continuous sisal fibre reinforced composites that allows the design of thin walled elements with high strength in tension and compression. Its applications may include permanent formworks, facades, tanks, pipes, long span roofing elements, strengthening of existing structures, and structural building members [12]. The application of natural fibres is also being studied in geotechnical engineering. It was tested for use in Limited Life Geotextiles (LLG) which is a reinforcing fabric only required to perform its duty for a limited time. LLG can be applied for temporary roads over soft land as well as basal embankment reinforcement [13].

There are some disadvantages associated with the use of natural fibres as reinforcement in polymer composites. These includes the incompatibility between fibres and polymer matrices, tendency to form aggregates during processing, poor moisture resistance, inferior fire resistance, limited processing temperatures, lower durability, variation in quality and price, and difficulty in using established manufacturing process [10, 11]. The incompatibility between natural fibres and polymer matrices leads to low interface strength as compared to glass or carbon fibre composites. The major cause for this drawback is the presence of hydroxyl and other polar groups in natural fibres which makes them hydrophilic in nature. This hydrophilicity results in incompatibility with the hydrophobic polymer matrix [10, 14-16]. Hydrophilicity of natural fibres indicates the high moisture absorption of the fibres which is the main reason of the weak adhesion to hydrophobic matrices and this causes the produced composites to fail in wet conditions through surface roughening by fibre swelling or delamination [10, 11]. Moisture present during manufacturing will lead to poor processability and low mechanical performance of composite [16]. Additionally, the majority of natural fibres have low degradation temperatures (~200°C) which are inadequate for processing with thermoplastics with processing temperatures higher than 200°C [11]. Interfacial treatments can improve this condition either through surface treatments, resins, additives, or coatings [10, 15].

Although it has been highlighted that natural fibres are cheaper than their synthetic counterpart, some processes related to overcome their drawbacks may incur additional cost. Surface modification is necessary and thus need to be optimized in order to compete with glass fibre composites. The cost of natural fibres varies due to crop variability and the difficulty associated with storing, transporting and processing fibres. In order to promote price reduction, new applications using natural fibres must be developed [10]. Furthermore, a detailed understanding of the composition of natural fibres and the different factors that affect its degradation is required.

2.2 Compositions of Natural Fibres and its Effects on Degradation

It is necessary to understand the nature and the compositions of natural fibres to gain a deep understanding on the degradation matters. Natural fibres are subdivided based on its origin, either from plants, animals or minerals. **Fig. 2** shows the types of natural fibres based on their origins. Animal fibres are composed of proteins taken either from hair, silk, or wool [10, 17]. For structural applications, bast fibres provide the best properties. For example, flax fibres are low cost, light weight and have high strength and stiffness [10]. In numerous applications, natural fibres from plants are considered as reinforcements for polymeric composites. Natural fibres from plant can be extracted from the plants' stem or soft sclerenchyma (bast fibres), leaf, seed, fruit, wood or cereal straw.

Natural fibres derived from plant consist mainly of cellulose fibrils embedded in lignin matrix. The structure of a biofibre is shown in **Fig. 3**. Each fibre has a complex layered structure which contains a primary cell wall and three secondary cell walls. The thick middle layer of the secondary cell walls determines the mechanical properties of fibre. It consists of a series of helically wound cellular microfibrils formed from long chain cellulose molecules. Each cell wall is made up of 3 main components which are cellulose, hemicelluloses, and lignin. Lignin-hemicelluloses acts as matrix while microfibrils (made up of cellulose molecules) acts as fibres [10, 17]. Other components include pectins, oil and waxes [17, 18]. Lumen is present in natural fibre, making it a hollow structure unlike synthetic fibres [19].

The most important structural component in many natural fibres is the cellulose, a natural polymer with each repeating unit containing 3 hydroxyl groups. In plants, cellulose is found in the form of slender rod like crystalline microfibrils, aligned along the length of fibre. Cellulose is resistant to hydrlolysis, strong alkali and oxidizing agents but to some extent, is degradable when exposed to chemical and solution treatments. Hemicelluloses are lower molecular weight polysaccharides that function as a cementing matrix between cellulose microfibrils, forming the main structural component of the fibre cell. It is hydrophilic and can be easily hydrolyzed by dilute acids and bases. Lignin is a complex hydrocarbon polymer that gives rigidity to plant and assists on the transportation of water. It is hydrophobic, resists acid hydrolysis and most microorganisms attacks, soluble in hot alkali, readily oxidised, and easily condensable with phenol. Pectin is a collective name for heteropolysaccarides and gives plants flexibility. Waxes consist of different types of alcohols [17, 20]. Wax and oil are substances on fibre surface used to protect fibre [18]. Some examples of chemical compositions of various natural fibres are presented in **Fig. 4**.

Important variables that determine overall properties of fibres are its structure, microfibrillar angle, cell dimensions, defects, and the chemical composition [10, 17, 18]. Microfibrillar angle is the angle between fibre axis and the microfibrils with a diameter of 10-30 nm. Microfibrillar angles are responsible for the mechanical properties of fibres. Smaller angle leads to higher strength and stiffness while larger angles provide higher ductility. Generally, natural fibres with higher mechanical strength possess higher cellulose content, higher degree of polymerization of cellulose, longer cell length and lower microfibrillar angle. Tensile strength and Young's modulus increases as cellulose content and cell length increase [13, 17]. Voids are also present in fibres indicating a certain degree of porosity [18, 26, 27]. Higher degree of voids is found in fibres of plants living in wet habitats. This condition promotes higher moisture absorption of fibre [13].

Reinforcing efficiency of natural fibres is related to the nature of cellulose and its crystallinity [17]. Filaments are bonded into a bundle by lignin and are attached to stem by pectin. Lignin and pectin are weaker polymers than cellulose and must be removed by retting and scotching for effective composite reinforcements [10].

Natural fibre reinforced composites face higher risk of degradation when subjected to outdoor applications as compared to composites with synthetic fibres. This is attributed to the characteristics of natural fibres which are susceptible to biodegradation. Biodegradation of a composite occurs with the degradation of its individual constituents, as well as with the loss of interfacial strength between them. **Fig. 5** shows the cell wall polymers responsible for the properties of lignocellulosics. In reference to **Fig. 4**, we can predict the degradation characteristics of different natural fibres based on their chemical compositions. For example, the tensile strength for jute and hemp are amongst the highest, 400-800 N/mm^2 and 550-900 N/mm^2, respectively [28] which can be correlated to their high cellulose contents. From a study between water hyacinth, reed, sisal and roselle [13], it was observed that water hyacinth and reed, fibres with higher hemicellulose contents, absorb more moisture and experience thermal degradation at a lower temperature as compared to sisal and roselle. Another study on flax, jute and sisal fibres showed that degradation of flax fibres begins at a relatively higher temperature which the author attributed to its low lignin content [24].

Degradation of natural fibre/polymer composite in an outdoor environment is influenced by factors such as moisture, temperature, ultraviolet radiation, and microorganism activities. The following topics discuss in depth on each factor, except for biodegradation by microorganisms.

3. Moisture Durability

Polymer composites are able to absorb moisture in humid atmosphere and/or when immersed in water, especially natural fibre/polymer composites [8, 32]. This in turn effects the fibre–matrix interface leading to poor stress transfer efficiencies. Furthermore, moisture absorption by natural fibres affects their physical, mechanical and thermal properties [21]. It has been reported that the water absorption for biocomposites is typically 0.7–2% after 24 h, 1–5% after a week, and up to 18–22% after several months whereby this behaviour was attributed to the wood fibre chemical compositions in having high hydrophilic content. Natural fibre composites fail in wet conditions through surface roughening by fibre swelling or delamination [10]. Surface morphology of composites undergone moisture absorption is different to that of dry composites in terms of voids, porosity, swelling, sorption in micro-cracks, and disbanding around filler [33].

The fibre component that is responsible for moisture absorption in natural fibres is the hemicelluloses which is the plant cell wall associated with cellulose [13]. It consists of comparatively low molecular weight polysaccharides built up from hexoses, pentoses, and uronic acid residues. Higher content of hemicelluloses causes higher moisture sorption and biodegradation. Natural fibres morphology related to hollow cavities decreases bulk density, results in lightweight, and absorbs more water. Moisture content in fibre influences the degree of crystallinity, crystalline orientation, tensile strength, swelling behaviour, and porosity of fibres. Higher moisture absorption increases the ease of microbial attack (biodegradation). Cellulose fibres are difficult to dissolve due to their high crystallinity, enabling them to retain liquids in the interfibrillar space. The degree of sorption and swelling obtained are determined by the ability of the liquid to interact with the cellulosic fibres [34].

It was observed that the water absorption and desorption pattern at room temperature follows Fickian behaviour where water uptake process is linear in the beginning, then slows and approaches saturation after prolonged time. Fickian diffusion refers to the spreading of water from area of highest to lower concentrations caused by concentration gradient [35] . At higher temperature of immersion, moisture uptake behaviour is accelerated and the moisture saturation time is greatly shortened. This non-Fickian behaviour may be attributed to the difference in sorption behaviour and state of water molecules existing in the composites [21, 34]. The diffusion coefficient characterises the ability of solvent molecules to move among the polymer segments. As the temperature rise in a moisture environment, microcracks on the surface and in the bulk of the material develop leading to peeling and surface dissolution of the composite. This results in the increase of the permeability coefficient [34]. **Fig. 6 (a) and (b)** show typical graphs of Fickian and non-Fickian diffusion, respectively.

In a polymer composite, the transport of water can be facilitated by three mechanisms which are by diffusion inside the matrix, by imperfections within the matrix (microspace, pores or cracks) or by capillarity along the fibre/matrix interface [29, 36]. Moisture diffusion into a polymer depends on its molecular and microstructural aspects which include polarity, the extent of crystallinity of thermoplastics and the presence of residual hardeners or other water attractive species [34, 37]. Diffusion process of moisture absorption was studied in [37] by studying the pattern of electrical conductivity of the composite. The composite studied started showing conductivity after it absorbed approximately 50% of maximum moisture.

Water absorbed in polymers consists of free water and bound water [16]. Free water are water molecules that are able to move independently through voids while bound water are dispersed water molecules that are bounded to the polar groups of the polymers. **Fig. 7** shows the conditions of moisture in a polymer matrix. When a natural fibre/polymer composite is exposed to moisture, water penetrates and attaches onto hydrophilic groups of fibre, establishing intermolecular hydrogen bonding with fibres and reduces interfacial adhesion of fibre-matrix. Degradation process occurs when swelling of cellulose fibres develop stress at interface regions leading to microcracking mechanism in the matrix around swollen fibres and this promotes capillarity and transport via micro cracks. Free water decreases and bound water increases as water is absorbed excessively. Water soluble substances start leaching from fibres and eventually lead to ultimate debonding between fibre and matrix as reported on the hemp fibre reinforced unsaturated polyester (hemp/UPE) composites [21]. Debonding between fibre and matrix is initiated by the development of osmotic pressure pockets at the surface of fibres due to the leaching of water soluble substances from the fibre surface [34]. This process is summarised in **Fig. 8**. After long period, biological activities such as fungi growth degrade natural fibres [16]. Damaging effect by water can be reduced by fibre treatments as reported on kenaf fibres in [38]. However, moisture containing other constituents will alter the absorption behaviour of natural fibres. For example, in salt water, salt precipitates on fibre surface forms a protective layer that reduces rate of moisture absorption while in diesel and engine oil, chemical attacks enhances its degradability [38].The characteristics of natural fibre composites immersed in water are influenced by the nature of the fibre and matrix materials, by the relative humidity and manufacturing technique, which determines factors such as porosity and volume fraction of fibres [21]. The manner in which composite materials absorb water depends upon several factors such as temperature, fibre volume fraction, orientation of reinforcement, permeability nature of fibre, area of exposed surfaces, diffusivity, reaction between water and matrix and surface protection [34].

It can be summarised that natural fibre/polymer composites are sensitive to moisture and in time, moisture exposure will cause them to lose their functionality. This aspect should be considered in producing a composite that can be used in a high humidity environment. One of them is the selection of appropriate fibre to ensure that it possess the right characteristics for high moisture resistance. At high temperature, the damages caused by moisture is known to accelerate thus for composites exposed to this condition, added protections are vital.

3.1 Effect of Fibre Content on Moisture Absorption

From the literature, it has been reported that the fibre volume fraction influences the amount of moisture absorption and may enhance or worsen the matrix properties. For instance, sisal fibre/cement composites showed that drying shrinkage increases with presence of sisal fibres as reported in [12]. The drying shrinkage of cement matrix is related to the magnitude of its porosity and to the size, shape, and continuity of the capillary system in the hydrated cement paste, i.e. natural fibres enhanced matrix porosity. Porous nature of fibre at micro-structure level created more moisture path into the matrices leading to higher drying shrinkage [12].

On the other hand, absorption amount increased in poly-lactic acid (PLA) and poly-butylene succinate (PBS) composites as bamboo fibres content increased which lowered the strength of the PLA and PBS despite of the fact that PLA and PBS can only absorb about 1% of water. In another work, the increase of bamboo fibre content caused the absorption rate to quicken because of its strong hydrophilicity of bamboo fibres [39]. The degradation in mechanical properties of hemp fibre/UPE composite specimens increased with increase in percentage moisture uptake, and was more significant at elevated environmental temperature. Moreover, the diffusion coefficient values increases steadily with the increase in fibre volume fraction due to higher cellulose content as reported on hemp fibre/UPE and sisal fibre reinforced polypropylene (sisal fibre/PP) composites [21, 34]. With regard of the mechanical properties of the composites under moisture absorption, the results on sisal and roselle fibres reinforced hybrid composite revealed that the percentage reduction in tensile and flexural strength of the composites increased with fibre content and length when the composites have been tested under wet conditions [33].

In terms of the age of fibres used, its effect on resulting composites strength was studied in [40]. It has been found that the adhesion property of the natural fibres is superior with matured fibre due to the fact that the aged fibre has less moisture absorption, possibly because they were kept in air tight containers. In spite of the fact that fibres have better strength, composites with aged fibres show better mechanical properties under wet conditions.

Fibres are added to polymers to create a composite that is stronger and less prone to cracks. However, the addition of cellulosic fibres in a polymer composite makes it more susceptible to absorb moisture. As the volume of fibres increase, the rate of moisture absorption also increases. Therefore, for a natural fibre composite to be used outdoor, fibre content should be limited only to attain its intended strength. This is to minimise moisture absorption and increase the durability of composites.

3.2 Effect of Surface Treatment on Moisture Absorption

Poor adhesion between fibres and polymer matrix generates void spaces around the fibres in natural fibres composites which leads to a higher water uptake [41]. Fibre modification through alkalization process can reduce the moisture absorption. Potassium hydroxide (KOH) or sodium hydroxide (NaOH) is commonly used to decrease the hydrogen bonding capacity of cellulose and eliminate open hydroxyl groups that tend to bond with water molecules. It also dissolves hemicelluloses (most hydrophilic) thus reducing the ability of fibre to absorb moisture [10]. These coupling agents build up chemical and hydrogen bonds which reduce fibre/matrix debonding caused by moisture thus improving the fibre/matrix adhesion and consequently, the moisture resistance of the composites. The decreased rate of water absorption and the extent of decrease varies and depends on the nature of the chemical treatment [34].

Silane treatment is used to stabilize polymer composites reinforced with natural fibres by treating the fibres to resist against water leaching. Silicon is accumulated in the cell lumina and bordered pits of fibres thus plugging these typical penetration pathways for water. Treatment in bulk is more effective than surface coating because the later only decreases the water sorption rate but does not reduce the amount of water to be absorbed because the cell walls are not filled with polymeric silane. Bulking treatment, on the other hand, may reduce the cell wall nano-pore size and deactivate or mask the hydroxyl functionalities thereby decreasing water sorption [14].

Maleic anhydride polypropylene (MAPP) coupling agent was introduced to a bamboo fibre reinforced polymer. Moisture uptake by the composite due to immersion in water decreased. This can be attributed to the increase in interfacial adhesion where less water accumulation in the interfacial voids and prevents water from entering bamboo fibre [42]. The water absorption for PLA/bamboo fibre composite increased greatly during the first 20 hours of immersion and then levelled-off. With the addition of bio-based coupling agent, lysine-based diisocyanate (LDI), the absorption amount and time to reach the plateau were smaller and longer than without LDI, indicating that the addition of LDI makes the absorption of water difficult. This is a result of improvement in interfacial adhesion between the polymer matrix and bamboo fibres due to the coupling effect of LDI and the reaction of LDI with the hydroxyl groups of polymers and bamboo fibres which causes less hydrophilicity [39].

Moisture decreases bond strength by bonding with fibre's hydroxyl group thus lessen bond with matrix. Water evaporates, leaving voids in cured composites. For better bond, fibres must be dried before matrix is introduced. For short to medium term protection, polymer coatings can be applied to reduce moisture absorption [10]. Short jute fiber/PLA composite was coated with 0.1 mm thick polypropylene plastic adhesive tape and subjected to hygrothermal environment [43]. In this it has been observed that at the end of the tests, fewer microcracks have occurred in the coated sample with lower moisture absorption rate. Temporarily, coating has effectively served as an isolating barrier of moisture diffusion but the film is still inevitably permeable. With increasing time, water molecules penetrated the film and were absorbed by PLA matrix and natural fibre, causing debonding, microcracks and delamination in the coated sample.

Fibre treatments improve moisture durability by reducing fibre hydrophilicity, improving fibre/matrix bonding and/or plugging water penetration pathways in fibre. These treatments are done in bulk, which are applied throughout the whole composite material and are more effective and longer lasting than surface isolation through coating. A combination of these protection systems will give a better moisture resistance as coating provides front line defence against moisture penetration while fibre treatments ensure long-term durability. A maintenance schedule is required to monitor coating effectiveness during composite's service life, as with steel coating for corrosion protection.

3.3 Effect of Degradation Due to Moisture on Mechanical Properties of Composites

Study performed in [13] has shown that the maximum tensile strength and elongations for wet yarns from natural fibres are higher than dry ones. This is because, moisture in fibre influences degree of crystalinity and the crystalline orientation of fibres whereby it results in higher amounts and better orientation of crystalline cellulose in fibres. Elongation is also found to be higher as absorbed water molecules act as lubricant. Fibres could slide over one another during stretching which results in extra extension and elongation. However, natural fibre reinforced composites faces adverse effects when exposed to moisture. It causes decrease in mechanical properties, provides the necessary condition for biodegradation, and changes their dimensions [16, 29, 37, 44]. Decrease in mechanical properties is due to poor stress transfer caused by degradation of the fibre–matrix interface [29].

The moisture absorption properties of natural fibre composites depend on its filler component. In [37], it has been found that high-density polyethylene (HDPE) films submersed in distilled water at room temperature experience no weight gain after one year thus moisture only penetrate into composites through rice hulls. The factors that affect the fibre distribution will finally affect the moisture absorption ability. This includes fibre concentration, size, and shape. In contrast, Hu et al. [43] states that the aging of biopolymer composites is a chemical and physical interaction process where water molecules were adsorbed physically by both the matrix and fibres, and were absorbed chemically by polymer molecules. Irreversible weight gain after aging observed in [43] in jute fibre/PLA composites subjected to hygrothermal environment can be attributed to the chemical reaction between water and PLA that results in water molecules being permanently absorbed by PLA and transformed into hydrolytic products. This hydrolysis process of PLA resulted in molecular chain breakage and caused decrease in strength.

A study by Joseph et al. [34] reveals that the tensile properties of sisal/PP composites decreased with increased water uptake, time of immersion and fibre loading. Plasticisation effect of water weakens the fibre/matrix bonding, resulting in interfacial failure. The behaviour was strongly dependent on chemical treatment and fibre orientation, whereby longitudinally oriented composites (anisotropic) provide maximum strength and reinforcement along the direction of fibre alignment as compared with randomly oriented composites.

The tensile strength and modulus of bamboo fibre reinforced polymer were considerably degraded after aging in water at 25°C and further reduced with increased in soaking time. The decreased in mechanical properties is due to dissolution of polymer matrix, debonding of fibre/matrix interface, and degradation of fibres during aging in water. The composite experienced different swelling and shrinkage of fibres, causing uncoupling at the interface. As moisture level increases, the modulus of polymers is reduced, presumably through a plasticizing process [42]. Commercial decking boards made from approximately 1:1 of rice hull and HDPE absorbed 4.5% moisture after 2000 hour exposure to 93% relative humidity (RH) and 40°C under simulated extreme climatic exposure conditions. It was found that moisture content was the major factor causing deformation; swelling and bowing of the boards [44].

Studies were done on the effect of moisture on bamboo composites. Bamboo absorbs moisture when it is exposed to humid conditions or immersed in water due to its structure and composition. Moisture absorption depends on species and treatment conditions [16]. Water absorption is the main shortcoming when used as reinforcement or permanent shutter form with concrete because untreated bamboo faces dimensional variation due to water absorption. This causes micro and macro crack in cured concrete. Bamboo as reinforcing bar suffers dimension change due to moisture and temperature variations which influence bond with concrete severely. Water-repellent treatment is necessary to ensure strength of bonding [45].

Effect of moisture absorption on bamboo strip vinyl ester composite was studied in [16]. Ground tissue occupies large proportion of volume in bamboo strip. This honeycomb structure with numerous capillary spaces is ideal sites for holding water. Bamboo strips undergo anisotropic dimensional expansion as they absorb moisture. Softening effect on strip is indicated by consistent increase in breaking strain and decrease in modulus of elasticity. Increase in tensile strength is due to the availability of free water molecules, providing plasticizing effect which is advantageous to strength of cellulose fibres. This result is comparable to a study on Duralin fibre wherein water uptake is seen to be advantageous for some natural fibres at 66% relative humidity due to fibre plasticising effect as a result of the presence of free water [21].

Higher fibre volume composites immersed in water generally have greater decrement in tensile and flexural properties compared to dry samples. However, it is interesting to note that for certain amount of natural fibres, the ultimate tensile stress of wet samples is higher than that for dry samples. This may be due to fibre swelling causing gaps between the fibre and the polymer–matrix to be filled, leading to an increase in the mechanical properties of the composites [21].

Based on these studies, it can be said that generally, water absorption by fibres in a natural fibre composites causes degradation in their mechanical properties. An optimum fibre/polymer content ratio is required to achieve optimum composite strength [18, 42, 46]. This strength will deteriorate when exposed to moisture attack which is influenced partly by the fibre volume, length and characteristics. To preserve the strength of a natural fibre/polymer composite, it is essential to protect it from excessive moisture exposure.

4. Thermal Resistance

A critical technical barrier for widespread use of fibre reinforced polymer (FRP) in structural engineering application is the degree of fire resistance of the material. Additionally, there is limited amount of information regarding FRP behaviour in fire. At lower temperature of 100-200°C, FRP soften, creep and distort (degradation of mechanical property) causing buckling for load bearing structure. It is a requirement for FRP strengthened concrete structure to meet minimum strength requirement of un-strengthened concrete structure in fire. Any strength contribution from FRP is ignored in a fire situation [9]. At 300-500°C, polymer matrix decomposes, releasing heat and toxic volatiles [9]. Decomposition of burning polymers includes the production of combustible gases, non-combustible gases, liquids, solids (usually char), and entrained solid particles (smoke). These outcomes may produce hazards such as the evolution of toxic gases, loss of physical integrity, and melting and dripping thereby providing other ignition sources [47]. Polyvinyl chloride (PVC) is a self-extinguishing material, but it should be avoided due to the toxicity of the generated gases. Polyolefins and HDPE burn and drip when in contact with fire thus results in instant loss of integrity. The addition of fibres improves this behaviour and integrity of composites [48].

For natural fibres, flammability is in part due to differences in chemical composition. Higher cellulose content results in higher flammability while higher lignin content results in greater char formation [10, 31]. The present of silica or ash provides better fire resistance. In terms of the fibre microstructure, high crystallinity and lower polymerization improve fire resistance. Phenolic-based synthetic composites have low flammability, less smoke, low flame spread, high ignition delay, low peak heat release rate, and high oxygen index. Char during fire exposure protects the core of material, thereby increasing structural integrity. This is the best matrix for natural fibre [10]. Flax fibres have low lignin content and are considered the best for thermal resistance among natural fibres studied. During thermal decomposition of lignin, relatively weak bonds break at lower temperature whereas the cleavage of stronger bonds in the aromatic rings takes place at higher temperature. With lower lignin content, degradation begins at higher temperature, but fibres do not have the oxidation resistance given by the aromatic rings in the lignin [24].

The burning process is comprised of heating, decomposition, ignition, combustion and propagation. Flame retardancy can be achieved by interfering with any of these stages that can terminate the process before actual ignition occurs [49]. To improve fire resistance of natural fibre composites, a few methods can be used. Fire barriers that can be applied are ceramics, intumescents, silicone, phenolics, ablatives, glass mats, and chemical additives. Intumescent system (coatings/additives) are most promising fire barrier treatments as they foam and expand when heated, forming a cellular, charred surface that protects underlying material from heat flux/flame. The best potential for flame retardant of natural FRP is by combining char-forming cellulosic material with intumescent system [10]. It is possible to minimize generation of combustion by increasing polymer stability or char formation. This will reduce visible smoke, decrease flammability and limit volume of combustion products formed [24]. Other methods for improving fire resistance of composites include fire retardant coating of the composites at the finishing stage and impregnation or modification of lignocellulosic particles or fibres with fire retardants before the manufacturing process [31].

Polymer by itself when exposed to high temperature behaves poorly and becomes very hazardous. Fibre is introduced to improve this condition but in the case of natural fibres, the improvement is limited due to the characteristics of the fibres which are more flammable than synthetic fibres. Many methods can be introduced to increase the durability of composites against thermal degradation. Method selection may be influenced by cost and the degree of resistance.

4.1 Thermal Degradation of Natural Fibre Composites

There are a few methods chosen by researchers to study the behaviour of natural fibre composites in a fire situation. In this section, cone calorimeter and the thermogravimetric analysis method to measure the thermal degradation of natural fibres are discussed.

4.1.1 Cone calorimeter

Cone calorimeter is widely used for assessing flammability of polymer materials by exposing samples to a specific radiant flux. It can be used to measure heat release rate (HRR), total heat released (THR), mass loss rate (MLR), time to ignition (TTI), smoke emission (SEA – specific extinction area), and average carbon monoxide (CO) and carbon dioxide (CO_2). Lower HRR indicates smaller contribution to a fire [47, 50]. Subhra et al. [51] had adopted a comparative study of loss of mechanical properties of composites during thermal aging by heating composite sample at 50°C for 30 days in an oven. The loss of tensile strength was measured periodically and it was found that the loss increased with heating time. The magnitude of reduction depends on the moisture content, heating medium, exposure period, and fibre species. Single flame fire or flame propagation tests were performed by Garcia et al. [48] to study the burning speed of composites. Flame was applied for 5 s and the time to burn 45 mm length specimens was determined. Limiting Oxygen Index (LOI) test measures the minimum concentration of oxygen that is required to support flaming combustion of a material in a flowing mixture of oxygen and nitrogen and calculated using equation 1 [50].

$$\text{LOI, \%} = [\text{volume of oxygen/volume of nitrogen + volume of oxygen}] \times 100 \qquad (1)$$

Oxygen concentration reported is its volume percent in a mixture of oxygen and nitrogen [52]. LOI test does not predict how a material will perform in a fire, but is able to compare between materials whereby higher OI suggests better fire performance. The LOI of natural fibre is higher than that of polymer, suggesting that natural fibres may be easier to extinguish in a fire than polymers due to the higher concentration of oxygen required to sustain burning [47, 50]. Smoke density in the process of burning of sample was measured by the change of light intensity in a chamber. It is useful for measuring and observing the relative amounts of smoke obscuration produced by burning or decomposition of material [52].

4.1.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is used to study the thermal stability of natural fibres. A typical TGA curve for composite thermal degradability shows a sample subjected to heat will slowly suffer weight drop, then the weight will drop sharply over a narrow range and finally turns back to zero slope as the reactant is exhausted. The shape of the TGA curve is determined by the kinetic parameters of the pyrolysis such as reaction order, frequency factor and activation energy while the values obtained depend upon atmosphere, sample mass, sample shape, flow rate, heating rate and the mathematical treatment used to evaluate the data. Theoretically, when a reaction occurs in a differential thermal analysis (DTA), the change in heat content and in thermal properties of the sample is indicated by a deflection or peak. If the reaction proceeds at a rate varying with temperature (indication of activation energy), the position of the peak varies with the heating rate if other experimental conditions are maintained fixed. This variation in peak temperature could be used to determine the energy of activation for reaction of different reaction orders [53]. In short, thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves are used to determine the weight loss and to identify the decomposition of material at a certain temperature, respectively [31]. A typical thermogravimetric graph for the decomposition process of natural fibres is shown in **Fig. 9**.

Thermal decomposition processes of different lignocellulosic fibres have very similar TG and DTG curves due to their similar characteristics. Approximately 60% of the thermal decomposition of most natural fibres occurred within a temperature range between 215 and 310°C with an apparent activation energy of 160-170 kJ/mol [23]. Thermal degradation behaviour can be evaluated through the decomposition temperature (T_d). For studied fibres in [13], the T_d is at 290-490°C. Based on [29], the degradation process of natural fibres includes dehydration combined with emission of volatile components initiating at a temperature of about 260°C, and rapid weight loss due to oxidative decomposition corresponding to the formation of char as the temperature increased. Early decomposition shows less thermal stability [13]. Three main stages of weight loss of natural fibres during fire as highlighted by a few researches are presented in Table 1.

Thermal degradation of composites can also be studied through TGA. The parameters obtained can be used during processing for determining the degree of degradation of materials when they are processed [53]. The main decomposition range of various natural fibres studied in [23] overlaps with the processing temperatures of some thermoplastics. Temperature plays a significant role in the dimensional stability of natural fibre composites where it causes direct thermal expansion or contraction and by affecting the rate and the amount of moisture adsorption which will lead to fibre swelling [44]. To some extent, thermal degradation of polyethylene/cellulose composites during processing undergoes oxidation process which results in enhanced adhesion between polymer and cellulose fibres [54].

TGA curves were plotted by Lee et al. [39] to analyse the thermal degradation of PLA/bamboo fibre composite and PBS/bamboo fibre composite and its components. The thermal degradation of biopolymers, PLA and PBS shows a single stage and occurred at 376 and 405°C, respectively while for bamboo fibre is as shown in Table 1. The composites for both polymers with bamboo fibre have lower degradation temperature than the pure polymers [39]. For a given heating rate of a biopolymer composite, the temperature at the maximum degradation rate is slightly shifted to higher values as sisal fibre content increases. This may be due to the decreasing in starch content in the composite [53]. With increased weathering time, TGA curves are shifted to lower temperatures, showing a decrease in thermal stability for both pure polypropylene (PP) and its composites. The decrease in thermal stability of PP could be due to the reduction of molecular weight of PP. For the composites, TGA transitions were shifted to slightly lower temperatures after 1000 hour weathering. This could be the result of PP chain scission along with degradation of both the fibre and the fibre–matrix interfacial bonding [29].

With the addition of FRs (ammonium polyphosphate and silica), the thermal decomposition steps were altered as follows [50]:

Stage 1: Decomposition is accelerated, generation of volatile compounds (ammonia and H_2O), a phosphorus rich layer and more char residual, which could protect the polymer matrix against heat.

Stage 2: Char layer show heat insulation properties and inhibits the heat and mass transfer between surface and melting polymer, resulting in the increase of fire resistance of the composites, so the second decomposition is shifted to higher temperature.

The main problem for quantitative analysis in TG experiments is the overlap of peaks (particularly in the case of composites) of DTG curves as shown in **Fig. 10**. For example, study on sisal fibre reinforced polycaprolactone/starch (PCL/S) composite in [55] shows at least four peaks were obtained whereby a large first peak (191-230°C) represents loss of low molecular weight components; the second peak (Tmax = 311°C), may be assigned to starch plus the contribution by overlapping of the first peak of the sisal fibre (hemicellulose); the third shoulder at T_{max} = 354°C is attributed to the second peak of sisal fibre (attributed to cellulose); and the fourth and main peak corresponds to the degradation of PCL. This partial overlap of decomposition curves of biodegradable matrix and sisal fibre are attributed to the components of each compound which are starch and cellulose derivatives from the matrix and, lignin, hemicellulose and cellulose from the fibre [53].

It is important to identify the type of information required in order to choose the suitable test methods. TGA is widely used by most researchers to study on the thermal degradation of natural fibre composites. Early decomposition, observed by lower temperature of start of degradation, implies less thermal stability and this can be used to compare thermal performance of various composites.

4.2 Effect of Surface Treatment on Thermal Degradation

The biocomposites studied in [39] were mixed with a bio-based coupling agent, LDI. Although lower than the pure polymers, the thermal degradation temperature was increased by increasing LDI content. The increase of molecular weight by cross-linking reaction between matrix and bamboo fibre, or molecular chain-extension of the matrix itself, could have influenced the increase of thermal degradation temperature.

A study on Jute/HDPE composites treated with a coupling agent, maleic anhydride (MAPE) shows higher temperature of the first degradative process than of the composites without coupling agent and percentage of weight loss in both degradation processes was also lower than in the untreated composites. MAPE in the composites ensures better thermal stability as compatibilised composites present more interfacial interaction due to reaction between acid groups of the maleic anhydride groups and hydrophilic groups on the fibre surfaces. This larger interaction promotes greater interaction between the degradation processes of the two components, whereby degradation of one component may be accelerating the degradation of the other component [11].

A study on the thermal stability of unbleached and bleached composites were undertaken by Beg et al. [29]. It was found that unbleached fibre composites started to decompose earlier than bleached fibre composites. Residual lignin and hemicellulose contents decreased with bleaching thus supports the increase in thermal stability. However, unbleached fibre composites have greater amount of residue due to higher amount of lignin, contributing to char formation, insulating against further thermal degradation.

From the studies above, it can be concluded that surface treatment improves thermal performance of natural fibre/polymer composites. It is important to note that higher content of lignin in untreated fibres produce more char. The optimum degree of lignin removal can be further studied in order to evaluate the positive contribution of lignin in forming chars as well as its negative impact to low temperature degradation.

4.3 Effects of Fire Retardants

The most widely used method to acquire flame retardancy is the incorporation of fire retardants (FRs). Depending on the nature of the additives, they can act chemically or physically in the solid, liquid or gas phase [49], although most are particles or powders [47]. To improve fire performance of natural fibre/polymer composites, FRs can be added to the plastic melt during processing [47]. FRs for biocomposites should be temperature resistant to avoid decomposition during processing [41] and should not contain any halogen because these compounds produce toxic gases like those formed during polyvinyl chloride (PVC) combustion [48]. Halogen-based and phosphorus-based compounds prove effective in suppressing the flame behaviour of synthetic polymers to the expense of negative environmental impact and health concerns [41]. Anatomy based system on its own is not fire resistance but show synergistic effects with halogenated compounds. The use of organic fire retardants can produce high toxic products after thermal decomposition and combustion. Nanocomposites constitute a new development in flame retardancy but is very expensive thus are not suitable in commodity products like construction elements [47]. A small amount of nanoclay can significantly improve the flame retarding properties of wood fibre reinforced HDPE nanocomposites [50].

To produce safe composites, fire retardants should be selected among phosphorus (this contradicts [41]) and inorganic systems like borates, stannates or hydroxides [47]. For environmental and health safety reasons, an increasing attention on inorganic compounds such as metallic hydroxide additives are being considered as FRs [49]. Stark et al. [47] states that the most effective additives in producing flame retardants are compounds containing bromine, chlorine, or phosphorous, or two or more of these elements. Other elements which have exhibited some flame retardant effects includes antimony, boron, nitrogen, silicon, dicyanodiamide, ammonium, and zinc which are often used with phosphorous or halogenated compounds [47, 49].

Additive-type flame retardants improve fire performance through the following mechanisms [47]:

1. Redirect decomposition and combustion reactions toward the evolution of non-combustible gases, or heavy gases that interfere with the interchange of combustion gases and air;
2. Redirect the decomposition and combustion reaction toward reducing the heat of combustion;
3. Maintain the physical integrity of the material; and
4. Increase the specific heat or thermal conductivity.

However, it must be noted that fire retardant worsened the outdoor durability [48] thus an optimum blend ratio shall be employed to achieve a balance between strength and fire safety of composites. Addition of fire retardants and other additives like antioxidants affect the interfacial adhesion, orientation and dispersion of fillers in the polymer matrix [41]. Some FRs and their mechanism of flame retardancies are summarised in Table 2.

The addition of 9% FR in [48] showed no formation of bubbles during burning and the rate of flame spread is much slower than specimens without FR. Only the external surface of the specimens was burnt, while the internal zone was not altered. A blend of sodium metasilicate and zinc borate in solid form was used as fire retardants by Shubhra et al. [51] in hybrid biocomposites reinforced with rice husks and sawdust. The TG curves for composites with FRs have higher temperature curves than the samples without fire retardants. This improved fire retardancy was attributed to the thermal shielding and diffusion barrier effects yielded by the effective silica layer formed during the combustion process together with the addition of flame retardant agents that slow the propagation of the burning reaction. The high silica content in rice husks may also contribute synergistically [51]. Fibres treated with diammonium phosphate (DAP) used in biocomposites show a decrease in burning rate and the weight loss rate. Exposure to heat below the decomposition temperature of cellulose (<160°C) leads to the formation of phosphoric acid and ammonia. The phosphoric acid formed can phosphorylate the primary hydroxyl group of cellulose to form a phosphorus ester which catalyzes the dehydration of cellulose, promoting the formation of char and water at the expense of levoglucosan. The char residues increase with increasing DAP treatment. The acid may also cross-link with the cellulose, changing the normal pathway of pyrolysis to yield less flammable products. Untreated fibre composite disintegrated completely and formed ash after glowing. For PP composites, the addition of DAP showed poor compatibility between DAP on the fibre surface and PP due to absence of chemical interaction, hence, lowers mechanical properties of the composite [31].

At higher loading of flame retardant, the mechanical properties of the composites tend to decrease. Shubhra et al. [51] observed that biocomposites added with 0.5% AOs and 20% FRs contents gives the best dispersion of hybrid fibres in the matrix, leading to high performance on physical and mechanical properties. A study by Ayrilmis et al. [56] observed that water resistance of uncoupled wood/polymer composites (WPCs) significantly decreased with increasing FR content but improved with the addition of MAPP. At 6 wt.% MAPP, the negative effect of 12 wt.% FR suppressed the compatibility between wood fibre and polymer due to a high contamination of the wood surface by the crystalline deposits of the FR as shown in **Fig. 11**. The severity of the contamination of the wood surface increase with increasing volumetric percentage of the FRs, indicated by a decrease in particle density.

It was observed that phosphate treatments provided more improvements in fire performance than the boron treatments. WPC containing 4% FR and 2% MAPP produced optimum physical and mechanical properties. The addition of ammonium polyphosphate (APP) and silica as fire retardants in WPC shows a decrease in tensile strength and elongation at break. This could be attributed to the poor compatibility of the added FR with polymer, the existence of the cavities formed via thermal decomposition of fillers and release of steam during the process, and larger size of silica agglomerates at higher loading level that act as stress concentrators and mechanical failure points which can initiate the fracture of the specimens [50]. Despite the presence of a coupling agent, the addition of FRs shows a negative impact on the tensile and flexural properties of the natural fibre/PP composites. However, these composites exhibit better performance compared to pure polypropylene. Impact properties of the composites are not much affected by the addition of FRs. It was found that magnesium hydroxide can effectively reduce up to 50% of the flammability of these composites. Replacement of a part of it with boric acid or zinc borate results in a reduction of the retarding effect of magnesium hydroxide [49].

At the present time, it is impossible to compare various classes of fire retardants because, for example, studies on WPCs are done with different matrix materials, fire retardant contents and using a range of fire performance tests. Flame retardance is a complex nature whereby each fire retardant is effective via several mechanisms. For examples, Stark et al. [47] had performed a study on several FRs and observed that although the decomposition of both magnesium hydroxide and zinc borate compounds produce water vapour, only magnesium hydroxide contributes to fire retardant capabilities. Boron-based compounds, bromine-based compounds and ammonium polyphosphate are all char producers. However, only the later was observed to perform well. This study concluded that magnesium hydroxide and ammonium polyphosphate improved the fire performance of WPCs the most while a bromine-based fire retardant and zinc borate improved fire performance the least. It was also highlighted that although all fire retardants had a positive effect on fire performance of WPCs, the addition of wood flour alone into polyethylene (PE) can dramatically improve the fire performance (HRR) of PE. Figures 12 to 14 show improvement of fire performance of several natural fibre composites treated with different FRs using different tests. The graphs do not provide conclusive results as the parameters used in the studies widely differs from one another.

Various FRs were used in order to achieve improved fire resistance of composites with a wide range of results. It was observed from above reviews that magnesium hydroxide seems to provide a promising positive effect on fire durability of natural fibre/polymer composites. However, the strength of the composites was jeopardized with the addition of FRs.

5. Effects of Weathering on Degradation

Natural fibre composites exposed outdoor with direct sunlight are subjected to radiation which breaks the covalent bonds in organic polymers causing yellowing, colour fading, weight loss, surface roughening, mechanical property deterioration and embrittlement with more reduction in wetter condition [9, 10]. The important durability properties for outdoor application of these construction products include fungal resistance, ultraviolet (UV) resistance, moisture resistance, and dimensional stability [30, 44]. After weathering periods, the loss of tensile strength of composite occurs due to degradation of fibres and matrix [51].

Photodegradation causes changes in all scales of polymer dimension, including the monomer unit (oxidation), the chain (crosslinking or chain scission), the morphology (breakdown of tie molecules and crystal), and on the macroscopic scale [30]. The ultraviolet radiation absorbed by polymers modifies the chemical structure, providing molecular chain scission and/or chain crosslinking. Degradation processes by weathering which includes photo-radiation, thermal degradation, photo-oxidation and hydrolysis provide changes in the chemical, physical and mechanical properties of materials [29, 44]. Photodegradation of polymers due to photo-oxidation is promoted by UV irradiation. Oxygen is used up before it can diffuse to the interior thus degradation is concentrated near the surface, even in polymers in which high UV levels are present in the interior. The photo-oxidation process also occurs in amorphous regions because of their higher permeability to oxygen [29]. Oxidation gradients cause density gradients that results in stresses, and when combined with chain scission (reduction in molecular weight) which leads to shorter polymer chains, will initiate and propagate cracks. Cracks on surface leads to light diffusion (a whitening effect in appearance) and deterioration of mechanical properties [30, 57]. The presence of catalyst residues, hydroperoxide groups, and carbonyl groups can also be introduced during polymer manufacturing, processing, and storage. These species absorb UV light above 290 nm and may initiate photochemical reactions [30]. A schematic diagram of the degradation of natural fibre/polymer composite due to UV exposure is presented in **Fig.15**.

For lignocellulosic fibres, aging or degradation occurs due to ultraviolet radiation absorption by lignin, formation of quinoid structures, Norrish reactions, and reactions of photo yellowing that occur in lignin. UV degradation lead to the formation of chromophoric groups, such as carboxylic acids, quinones and hydroperoxy radicals which is responsible for the characteristic yellow colour associated with aging of paper [29]. Visible light carries energy less than 292.9 kJ/mol, which is not sufficient to break the major chemical bonds in the fibre components thus photodegradation of fibre results primarily from the ultraviolet aspect of sunlight. The degrees of photodegradation of fibre components largely depend on their ability to absorb UV light. Photodegradation or weathering of major components of natural fibres/polymer composite results from the combined effects of light, water, oxygen, and heat. All main polymeric components of fibres (cellulose, hemicellulose, lignin, and extractives) suffer from photodegradation. Location of most natural fibre chromophores is in lignin which accounts for 80-95% of light absorption. This makes it a significant contribution to discoloration [30].

Many weathering studies are performed on WPC as it is already being used in North America for non-structural and semi-structural outdoor applications such as decking, siding, railings, fences, window, roof tiles and door frames. It is more preferable compared to solid wood due to the presence of hydrophobic polymer phase in WPCs which improves resistance to water absorption and biological decay, hence increases durability and lowers maintenance requirements. WPCs have better thermal and acoustic isolation than aluminium and lower price than neat plastics with appearance rather similar to that of wood. However, their outdoor applicability is hindered by poor weathering properties. After weathering, WPCs show fading and swelling [30, 48, 58, 59].

Mechanical properties of natural fibre composites undergo changes after UV irradiation which can be attributed to composite surface oxidation, matrix crystallinity changes, and interfacial degradation [60]. Photodegradation of natural fibre/polymer composites involves several factors such as fibre content, coupling agents, manufacturing methods, and weathering conditions. Oxidation rate of the composites increases with fibre content and decreases with the presence of compatibilizer due to better dispersion of fibres in polymer matrix [30]. At low sisal content (<20%), the sisal fibre acts as a nucleating site, increasing crystallinity. However, when the sisal content is above 20%, crystallinity decreases as the fibre begins to hinder the molecular motion of polypropylene [59]. Composites experienced more lightening and mechanical properties loss when exposed to UV radiation with water spray cycle compared to UV radiation cycle alone [29, 30]. In terms of manufacturing methods, injection-molded composites degrades more slowly than extruded ones due to the formation of hydrophobic HDPE-rich surface layer on injection molded composites [30]. PP-based WPCs experienced quicker photodegradation in terms of lightness and wood loss as compared to HDPE-based WPCs [30, 57].

Upon UV exposure, WPCs underwent two competing redox reactions:

1. Formation of paraquinone chromophoric structures generated by the oxidation of lignin, resulting in yellowing.
2. The reduction of the paraquinone structures to hydroquinones, leading to photobleaching.

During the first 250 hours of exposure, yellowing of composite preceded the photo-bleaching mechanism that became dominant with increased exposure time [30].

Increase in the carbonyl groups for WPC implies that surface oxidation increased upon weathering. However, with longer exposure time, carbonyl (both carboxylic acids and esters) and vinyl concentrations began to decrease, most probably due to the decrease of wood and plastic concentrations in the outer surface and increased in the concentration of talc. Wood component was preferentially degraded during WPC weathering. This reveals that more attention needs to be focused on stabilizing the wood component rather than the polymer matrix [57].

Study of weathering effect on natural fibre composites should include the combined action of UV radiation, heat, and moisture. This study can be accomplished through natural or artificial aging [44]. The effects of degradation due to natural or artificial aging can be evaluated through the quantification of chemical degradation and/or by analysis of physical properties such as mechanical behaviour and visual appearance [61].

5.1 Natural Weathering

Natural aging process is influenced by natural elements, weathering or the action of the environment in which the material is subjected to conditions of use [61]. The long-term behaviour of materials due to environmental exposure is evaluated by real time observations for duration of several years. However, research programmes lasting 10 years or more are rare for organizational and economic reasons [29].

Weathering studies on jute/phenolic composites with 2 years of exposure showed resin cracking, bulging, fibrillation, and black spots with decreased tensile strength of over 50% [10]. A 9-month natural weathering study was conducted on palm fibre/PP composites. The composites show little drop in strength as compared to pure PP which shows a large drop in strength after 3 months of exposure. The drop increases and the PP loses more than 50% of its strength after 9 months of exposure. A minor increase in strength was observed at long exposure times in natural weathering possibly due to enhanced interfacial adhesion by degradation as a result of the formation of the carbonyl groups in PP, which is more compatible with the cellulose fibre surface [54]. Tensile strength of neat PP sample after 3 months exposure to UV radiation is decreased by 92.57% whereas that for 10% sisal fibre loading is 58%, for 20% sisal fibre loading is 37% and for 30% sisal fibre loading is 23% as studied by Joseph et al. [34]. Degradation of PP is due to photooxidation promoted by UV irradiation. Oxygen is used up in the reaction before it can diffuse to the interior so that degradation is concentrated near the surface. Surface cracks of composites can be caused by thermal stresses during outdoor exposures due to the day–night variations in temperature or due to the tensile residual stresses that develop at the surface of some polymers during weathering. Crack propagation can be controlled to some extent by the addition of fibres to PP, where with increase in fibre loading the extent of retention in tensile properties increases [34].

Natural weathering studies may at time prove impractical due to the amount of time required thus accelerated weathering tests are more preferred. However, the results from accelerated weathering tests have no exact correlation to what happen in real condition due to regularity of cycles, duration, intensity and exposure conditions [61]. It is difficult to transfer artificial weathering to life expectancy under natural weathering conditions since rate of fibre degradation in nature depends on various external factors such as intensity of radiation, temperature, humidity, and air pollution [13]. Different weathering regimes lead to different weathering patterns as discovered in [57]. The degree of WPC degradation in a 2-year natural test was not as severe as that in a 2000-h accelerated test but more severe than that observed in a 400-h test. It can be seen from the study done by Abu Sharkh et al. [54] that higher stability was displayed by compatibilized sample in artificial weathering compared to natural weathering. This can be attributed to the fact that UV source in the accelerated weatherometer does not reproduce the light spectrum produced by the solar radiation. Moreover, it is possible that the maleated polypropylene used as compatibilizer is susceptible to degradation by radiation frequencies that are more abundant in the solar radiation [54].

5.2 Accelerated Weathering

Accelerated aging process occurs in aging chambers that simulate a natural environment and the damaging effects of long term outdoor exposure by exposing test samples to ultraviolet radiation, moisture and heat in a controlled manner. The advantage includes faster testing than natural exposure and is reproducible [30, 54]. It is a more convenient alternative for assessing long-term behaviour. However, some variables must be considered such as exposure time, UV exposure as radiant energy over a specific wavelength range, and water exposure as a number of cycles or in time. For best comparison between studies, it is recommended that performance after weathering be reported after a specific radiant exposure, commonly termed the time integral of irradiance [29].

Fibre reinforced polymers exposed to accelerated weathering effects the polymeric matrix and the components within the matrix, i.e. pigments, processing additives and reinforcements [44]. From visual observation of samples subjected to accelerated weathering test shows colour fading and partial shrinkage resulting in bending of samples. Also, deposition of white chalky material was observed on the surface. During weathering process, lignin and water soluble products leach from the samples, which is apparent due to colour fading [13, 29, 61].

During the course of accelerated weathering of polymer composites, two mechanisms namely chain scission and cross-linking compete. Chain scission lowers molecular weight, whereas cross-linking raises molecular weight by increasing the bonding between polymer chains. Chain scission is directly indicated by accumulation of the carboxylic acids and vinyl groups, as well as increase in crystallinity. The shorter chains produced during chain scission are more mobile and are readily crystallized, which increases crystallization and embrittlement. In contrast, crosslinking does not affect polymer crystallinity. While chain scission occurs in the amorphous phase of the polymer and is controlled by the diffusion of oxygen in this region, UV-induced crosslinking occurs in imperfect crystalline regions [59]. The reduction in molecular size dominates in short-time exposures to weathering and favours crystallisation, whereas after extended period, the presence of many extraneous groups in the molecules of highly degraded polymer makes the crystallisation more difficult [58]. This phenomenon can be correlated with scanning electron microscopy (SEM) results of [43] whereby fibre breakage mainly occurred in short-term aged tensile samples while fibre debonding and pull-out occurred in long-term aged tensile samples.

Study on accelerated weathering of WPC by Stark et al. [59] shows that while neat HDPE may undergo crosslinking in the initial stages of accelerated weathering, wood fibre (WF) may physically hinder the ability of HDPE to crosslink, resulting in the potential for HDPE chain scission to dominate in the initial weathering stage up to 1000 h before decreasing. At this point, chain scission begins to affect the tie molecules, resulting in a net decrease in crystallinity.

Fibre tensile strength decreases with increased exposure time [13] while little change is observed for pure PP [29]. Tensile strength and modulus for the composites were found to decrease due to embrittlement of the matrix, degradation of fibre and fibre–matrix interfacial bonding which are evidenced by increased fibre pull out [29]. Increase in strength observed at long exposure times in the natural weathering is not present in the accelerated weathering. It seems that the fast rate of degradation in the accelerated weathering tests might offset any enhancement in interfacial adhesion caused by degradation [54]. Due to the short period of exposure, Beninia et al. [61] observed no changes in the ultimate tensile of high impact polystyrene (HIPS) matrix. However, there was a small increase in tensile modulus that might have been caused by the onset of a crosslinking process that occurs with some thermoplastics subjected to certain processes of degradation. Degradation process from accelerated weathering is influenced by fibre volume and chemical treatment. The impact of weathering exposure was found in [61] in composites when compared to pure HIPS, indicating that fibres decrease the degradation resistance of material. Through SEM analysis, the exposure did not cause degradation of fibre/matrix interface.

Most researchers acknowledge that accelerated weathering tests cannot be directly correlated with the natural weathering process. If time is not an issue, then it is more accurate to analyse the data from natural weathering tests, which gives the actual site condition. Accelerated weathering test provides basic understanding on the degradation mechanism of composites subjected to predetermined exposure cycles.

5.3 Effect of Moisture on Weathering of Composites

Weathering in the presence of water enhances the rate of degradation of WPC as wood cell walls swell when penetrated by water, facilitating light penetration further into the wood providing sites for further degradation. Swelling of wood particles creates microcracks in the matrix, and washes away loose wood particles, loose cellulose, and degraded lignin at the wood surface [29, 30]. Pure polypropylene has no significant change in weight while unbleached and bleached fibre composites showed an increase in weight after accelerated weathering. The overall increase in weight of the composites show that water absorption is dominant compared to leaching of lignin and water soluble products from the samples. Reduction in hardness for composites observed could also be due to plasticization by water. The degree of crystallinity of PP in composites was also found to decrease with weathering attributed to swelling of composites by absorbed water [29].

As a result of wetting and drying cycle, WPCs were differentially contracted between the surface and interior sections. Together with polymer chain scission, which results in highly crystallized polymer zones that crack, crazing was observed for both natural and accelerated weathering. Three stages of degradation were identified [57]:

1. Surface layer was eroded, creating several cavities on the surface of composites.
2. Frequency and size of the cavities increased upon extended exposure time.
3. Development of small cracks on the weathered surface of WPC.

A study on weathering effect of rice hull composite decking boards was conducted and the dimensional stability was studied. Dimensional changes of the composites were attributed to three components, which are:

1. The recoverable swelling and shrinking of the rice hull component under humidity changes;
2. Thermal expansion/contraction effects;
3. Irrecoverable swelling due to relaxation of the compressive stresses induced during the extrusion process.

It was found that moisture adsorption was the major factor of dimensional instability. Moisture adsorption/desorption was influenced by temperature whereby high temperature facilitated high and quick moisture adsorption; while low temperature trapped the already adsorbed moisture. The decking boards were found to achieve constant dimensions relatively quicker than moisture equilibrium when ambient conditions were changed [44]. In reality, moisture sorption of natural fibre composites in service is slow and seldom reaches an equilibrium condition in a moist environment. The surface of the composites may be saturated with water while the core layers may have significantly less moisture [14].

Hemp fibre/poly-hydroxybutyrate (PHB) films composites exposed to accelerated weathering suffers a decrease in molecular weight via chain scission from UV photo-oxidation and ester hydrolysis from exposure to moisture. Cracking of composites is caused by the incompatibility between the coefficients of thermal expansion of the polymer matrix and fibre and, in the presence of moisture, fibre swelling is dominated by free water bonding with readily available hydroxyl groups in the cellulosic fibres. Hoop stresses, generated by fibre swelling exceed the tensile capacity of the PHB surrounding the fibre. Hence, it was observed that mass changes in the composites depend more on the fibre/matrix interface and on the moisture content of the fibres than on the mass stability of the PHB matrix itself. With increased crystallinity and embrittlement from photo-oxidation, degradation of composites was accelerated [62].

It can be concluded that the presence of water worsen the weathering effects on natural fibre/polymer composites. Therefore, in outdoor applications where a composite will be exposed to direct sunlight and rain, it can be expected to undergo severe deterioration.

5.4 Discoloration and Chemistry Changes of Composites Due to Weathering

A significant feature of WPC is its aesthetic value which becomes compromised by weathering through severe discoloration. Wood exposed to weathering initially becomes yellow and brown due to the photooxidation of lignin, and then gray due to leaching of the degraded product of lignin. This discoloration and yellowing result from the loss of methoxyl content of lignin, photo-dissociation of carbon-carbon bonds and formation of carbonyl-based chromophoric groups. Faster fading of composites was observed with the combination of fibre bleaching by UV radiation, and water spray which accelerates oxidation reactions, facilitate light penetration into the composites, and removed water-soluble wood extractives [30, 62]. Study showed that for both natural and accelerated weathering, longer exposure time increased the degree of colour change and lightness, carbonyl concentrations, and wood loss on weathered WPC surfaces [36].

Colour measurement of composites is analysed as per ASTM D2244 and is conducted in a spectrocolorimeter adapted to a colour-data software. It is determined by calculating the discolouration (ΔE) of the weathered samples in terms of lightness (L*) and chromaticity (a* and b*) of unweathered and weathered specimens. The equation is given as:

$$\Delta E = \sqrt{(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})} \quad (2)$$

where ΔL*, Δa*, and Δb* are the difference of initial and final values of the colour coordinates L*, a* and b*. L* ranges from 0 (black) to 100 (white) while a* (red-green) and b* (yellow-blue) [30, 62] are interpreted as: +a expresses redness, -a expresses greenness, +b expresses yellowness and –b expresses blueness [48, 57]. This can be represented in **Fig.16**. The relationships between chemical (wood lignin content and carbonyl concentrations) and colour changes (L) were established by Fabiyi et al. [57] where strong correlations between lightness and wood lignin degradation, lightness and carboxylic acid concentration, and lightness and esterification were observed. It was concluded that delignification and oxidation lead to an increased lightness.

Study by Butylina et al. [58] proved that higher wood fibre content led to more significant changes in colour. The decrease of yellowness (Δb) with exposure time can be linked to the reduction of paraquinones (chromophoric structures) to hydroquinones, which results in photobleaching and a more serious degradation of the surface layer. As fibre content exceeds 40%, encapsulation of wood fibres with polymer becomes impossible. Degradation was found to be limited to 0.5 mm depth and below this depth, the intensities of different bands were similar to those of the non-weathered composites.

Changes in surface chemistry can be studied using spectroscopic but they cannot distinguish between the surface oxidation of polymer and that of the fibre [58]. X-ray photoelectron spectroscopy (XPS) was used to verify the occurrence of surface oxidation by studying the concentration of carbon to oxygen atoms through equation 3 [59]:

$$C_{ox/unox} = C_{oxidized}/C_{unoxidized} = [C2+C3+C4]/C1 \quad (3)$$

Fourier transform infrared (FTIR) spectroscopy monitors the development of degradation products, such as carbonyl groups and vinyl groups, and to determine changes in polymer crystallinity [59]. The addition of WF to the HDPE matrix increased the concentration of carbon–oxygen bonds (C2,C3,C4) in the samples as expected since cellulose, hemicelluloses, and lignin of wood have a larger percentage of oxidized carbon in their chemical structure than does manufactured neat HDPE. Hydroxyl groups are the main carbon–oxygen functional groups in wood. Concentration of vinyl groups was larger for neat HDPE than for WPCs indicating that it is important for the degradation of only the polymer, not the wood [59].

A study performed by Matuana et al. [30] on coextruded and uncapped WPCs suggests that discoloration of WPCs upon UV weathering is a combination of both chemical and physical changes. Photo-oxidation of wood components is responsible for the chemical changes and determines the initial colour change. Coextrusion prevents surface erosion and removal of degraded wood components (maintains adhesion between fibres and matrix) thus the composites become dark and yellow but fades once the cap layer is damaged due to removal of loose wood components by water spray. The cap layer absorbed some UV light and reduced the availability of oxygen at the interface of coextruded composites, thus decreasing the photodegradation rate.

UV rays are responsible for colour changes in both synthetic and natural FRPs. These colour changes can be used to indicate the chemical changes on the surface of the composites which reflects the degree of deterioration. In a non-load bearing natural FRP, the importance of its physical appearance may exceed its mechanical strength thus the method selected to block the damaging effects of UV rays must not hide its aesthetic surface.

5.5 Effect of Surface Treatment and Additives on Weathering of Composites

For high degree of UV resistance, UV stabilizers are incorporated into polymer during manufacturing [9]. Coated polyurethane results in little surface deterioration and together with fibre modification (bleaching, alkalization, silanes) will help slow weathering effects [10]. However, chemically treated composites show a relatively greater extent of decrease in tensile strength with increase of exposure time compared to untreated composites. This proves that treated composites undergo severe degradation compared to untreated composites; with MAPP treated composites experienced the worst degradation [34]. It is also important to note that metallic-based additives and plasticizers may introduce chromophores into the composites, which will lead to the generation of phenyl and carbonyl groups during degradation [57, 62].

To provide colour stability against UV radiation, additives and fibre modifications can be incorporated during composite fabrication as per listed in Table 3. Oxidative degradation is the most common reason for failure of biocomposites after mechanical failure. Biocomposites are much more sensitive to oxidative degradation compared to pure plastics and its induction time, durability and lifetime is dependent on the antioxidants (AO) and their amounts [41]. Samples with 0.5 wt.% of antioxidants and 20 wt.% of fire retardants were observed in [41] to have the most reasonable strength and elasticity of recycled high density polyethylene (rHDPE) reinforced with a high loading hybrid of rice husks and sawdust. The AOs were consumed by protecting the polymer from oxidation and end up as stable peroxide, as an oxidized antioxidant, or as other stable structures. Although sample with AOs had higher water absorption rate compared to the sample with no antioxidant content added, it has better reinforcing effect as higher results of tensile, flexural and impact strengths were obtained.

Composites exposed to moisture and ultraviolet radiation brings more effect to lignocellulosic fibres than the fibre/matrix interfacial region. Bleached fibres have lesser amount of lignin from removal process of treatment which leads to higher mechanical interaction with the matrix. Mercerized fibres have higher amount of lignin than bleached fibres thus they are more susceptible to UV radiation and moisture [61]. Bleached fibre composites were found to have higher tensile strength, failure strain and impact strength than unbleached fibre composites due to removal of relatively weaker and more brittle non-cellulosic compounds which allows better fibre/matrix bonding. The crystallinity of PP in bleached fibre composites was better than unbleached fibre composites due to removal of lignin and hemicelluloses. This allows better packing of cellulose microfibrils which would provide a better substrate for crystal growth [29, 60]. After UV exposure, composites with bleached fibres showed greater decrease in tensile properties in comparison with untreated composites due to the change in the morphology upon UV irradiation. However, the lower level of surface damage of the irradiated composites than neat polycaprolactone (PCL) suggests some protection of PCL, indicating possible interaction of PCL with cellulose from sisal fibres as demonstrated by Fourier transform infra-red (FTIR) spectrum with increased carbonyl groups in the PCL. Strong fibre/matrix interaction and carboxyl/hydroxyl groups interaction contributed to retention of crystallinity, elasticity modulus, morphology and the structure of composites after UV irradiation [60].

Irgastab and Tinuvin-783 were used to stabilize pure PP, compatibilized and uncompatibilize composites for thermal and UV degradation during processing and weathering. It was found that the stabilizers enhanced stability imparted by the presence of the fibres in the composites, enhanced interfacial adhesion resulting from oxidation of the polymer matrix which is the source of retention of mechanical strength. The study concluded that compatibilized samples are generally less stable than uncompatibilized ones as a result of the lower stability of the maleated polypropylene. As for comparison with pure PP, the presence of natural antioxidants, for example lignin, in composites is known to provide stabilization to the natural fibres. The dark colour and the surface layer of fibres also act as a protective layer that prevents UV radiation from penetrating the sample and causing degradation in the bulk [54].

A stabilizer composed of a blend of hindered amine light stabilizers (HALS), UV filter and antioxidant was produced by Garcia et al. [48]. The blend gave better results compared to using HALS alone. No cracking or fracture took place in the aged WPCs. However, colour change of the stabilized composites was much lower than that of neat composites and most industrial samples. Oil palm fibre modified with vinyltrimethoxy silane (VTS) in an alcohol–wax mixture (60:40) soaked in water at different temperatures shows a reduced water uptake at all temperatures used. With this, the resulting polymer composites are drier under a moist environment thereby reducing the risk of environmental damage such as deformation and fungal decay [14]. Coir or oil palm fibre composites modified with methacryloxymethyltrimethoxy silane (MPS) were subjected to one year weathering. The mass loss due to fungal decay and the moisture content of modified composites is lesser compared to unmodified composites. The tensile and flexural strength of the modified composites were slightly reduced (up to 8%), which is distinctly less than over 30% for the untreated composites [14]. However, despite the incorporation of these chemical additives, natural fibre composites still undergo photo-degradation [57].

From the reviewed studies, there are a few chemical treatments available to improve UV resistance and weathering durability of natural fibre composites. However, there is a lack of references in this subject matter indicating that more research needs to be conducted to compare the effects of various chemical treatments in providing UV protection on a standardized weathering cycle. Additionally, it must be noted that treated natural fibre/polymer composites suffer more mechanical degradation than the untreated ones.

6. Conclusion

The degradability of polymer composites based on natural fibres was reviewed in this article. This includes the degradation due to moisture, thermal effects, fire and ultraviolet rays. The fundamental points can be summarised as follows:

1. Natural fibres are susceptible to biodegradation thus composites based on them face higher risk of degradation when subjected to outdoor applications as compared to composites with synthetic fibres. Different cell wall polymers of lignocellulosics fibres have different influence on their properties and degradability. For instance, cellulose is responsible for strength of fibres, hemicelluloses for thermal, biological and moisture degradation, while lignin for UV degradation and char formation.
2. Fibre content is the major factor affecting water absorption of composites as it enhances matrix porosity by creating more moisture path into the matrices. Poor adhesion between fibre particles and polymer matrix generates void spaces around the fibre particles. Higher fibre volume composites immersed in water generally have greater decrement in tensile and flexural properties compared to dry samples. Moisture absorption can be reduced through fibre modifications such as alkalization and addition of coupling agents.
3. Polymer matrix decomposes at 300-500°C. Flame retardant is one of the methods used to improve its thermal durability. The best potential for flame retardant of natural FRP is by combining char-forming cellulosic material with an intumescent system. FRs from inorganic compounds such as metallic hydroxide additives are preferred due to environmental and health safety reasons, with magnesium hydroxide showing very good results.
4. Weathering causes degradation of polymer composite through photo-radiation, thermal degradation, photo-oxidation and hydrolysis. These processes result in changes in their chemical, physical and mechanical properties. Water enhances rate of degradation through swelling of fibre and this leads to further light penetration. Weathered chemically treated composites show a relatively greater extent of decrease in tensile strength which proves that treated composites undergo more degradation compared to untreated composites.

7. Future Developments

From the highlighted degradation characteristics of natural fibre composites, improvement plans can be further researched to increase their durability for outdoor applications. The outcomes of these researches are expected to assist the future developments and wider acceptance of natural fibre composite as a reliable civil engineering material. Some of the issues that need to be considered for future studies on the degradability of natural fibre composites includes:

1. Natural fibres are prone to moisture attack so it is expected that the moisture durability of a natural fibre composite will decrease with increased fibre content. Thus the amount of fibre in a composite shall be limited to its optimum fibre/matrix ratio in order to achieve maximum strength capacity and limit its moisture susceptibility. Fibre treatments are essential to enhance strength and moisture durability of composite by promoting improved fibre/matrix interface. Water resistant coating can be applied on composite surface to avoid contact between moisture and fibre.
2. Low lignin content in a natural fibre leads to better thermal performance of its composite. However, lignin is a source of char that can provide protection to the inner layers of composites during a fire. With the removal of lignin through fibre treatment, FRs that form chars can be added to provide improved thermal resistance of composite. However, FRs worsened outdoor durability thus an optimum blend ratio shall be employed to achieve a balance between strength and fire safety of composites.
3. Generally, chemically treated composites possess higher strength, higher moisture durability and better thermal performance but poorer UV resistance. Various additives can be added to a natural FRP to stabilize it against the damaging effects of UV rays. However, more research is required to compare the effect of these additives on a more standardized weathering cycle. Coloured coating may not be an option if the natural element is to be preserved.

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List of Tables:

List of Figures:

Table 1: Three Main Stages of Weight Loss of Natural Fibres

Stage 1	Stage 2	Stage 3	Reference
50-100 °C: Evaporation of moisture in the fibres	200-300 ° C: Decomposition of hemicelluloses	400-500 ° C: Weight loss due to lignin and cellulose degradation	[14]
300 °C: Corresponds to the thermal decomposition of hemicellulose and the glycosidic links of cellulose.	360 °C: Corresponds to the thermal decomposition of α-cellulose.	200- 500°C, max at 350 °C: Lignin peak is wider and appears superposed on the other two peaks.	[12,26,55]
250-300 °C: Characteristic of low molecular weight components, such as hemicelluloses.	300-400 °C: Corresponds to the thermal degradation of cellulose.	Near 420 °C: Due to lignin decomposition	[41]
220–315 °C: Pyrolysis of hemicelluloses.	315–400 °C: Pyrolysis of cellulose.	160–900 °C: Pyrolysis of lignin.	[33]
97 °C: Attributed to water loss.	325 °C: Attributed to protein degradation.	Major thermal decomposition of the composites began at about 260 °C and beyond 390 °C the rate of decomposition was slow.	[34] For Natural Silk Fibre Reinforced Gelatin Composites.

Table 2: Fire Retardants and Their Mechanism of Flame Retardancies

Fire Retardant	Description
Phosphorous compounds Example: • Ammonium polyphosphate • Sodium phosphate	• An intumescent material, char formers [50] and leads to auto-extinguishing behaviour. • Generation of solid form of phosphoric acid, inhibits access to oxygen and shields it from releasing flammable gases able to feed flames [49,52]. • Only increase char in polyolefins when there is another char forming additive present, typically a nitrogen containing compound (phosphorous-nitrogen synergism) [49]. • Ammonium polyphosphate: water soluble, not suitable for products exposed to exterior environments [49].
Bromine-based compounds Example: • Decabromodiphenyl oxide	• Act in the condensed phase to redirect or terminate chemical reactions involved in combustion. Heavy-bromine gases protect the material from exposure to oxygen and heat. Bromine-based flame retardants are practically always used with an antimony synergist, often antimony trioxide [49].
Antimony- based compounds Example: • Antimony trioxide	• The compounds alone do very little, but in combination with halogens form antimony trihalides. Antimony trihalides both scavenge free radicals and increase char formation [49].
Metal hydroxides Examples: • Aluminium-based • Magnesium-based	• An inorganic compound thus health and environmentally safe [51]. • More effective as hydrated compounds [49] and provide effective flame retarding effects by releasing contained water at high temperatures, absorbing heat from the combustion zone, producing char, generating metal oxide coating that act as insulator [38] and reducing smoke [49]. • $Mg(OH)_2$ has superior endothermic flame retarding reaction and are more suitable for polyolefins, polypropylene and polyamides because it decomposes at a higher temperature (300–320 °C) thus allowing it to be processed in plastics, for which $Al(OH)_3$ (decomposition temperature: 200 °C) is not thermally stable enough [51].

Boron-based compounds Example: • Zinc borate	• Are generally char producers. • Zinc borate compounds reduce smoke production and are mostly used as hydrates. • The heat required for dehydration also contributes to fire retardant capability [49].
Melamine-based compounds Example: • Melamine cyanurate	• Aids in char formation. • Compounded with phosphates to achieve a phosphorous-nitrogen synergism. • Creates endothermic reactions and scavenges free radicals. Decomposition produces nitrogen and ammonia, which dilutes fuel gases [49]. • Melamine cyanurate: undergoes endothermic decomposition above 320°C to melamine and cyanuric acid, acting as a heat sink in the process. Vaporized melamine acts as an inert gas source diluting the oxygen and the fuel gases present at the point of combustion [49].
Silica	• Recognized as inert diluents and shows some flame retardant effect. • Synergistic effect with APP, accumulate on the surface in fire and consequently forms a charred layer by combining with APP. Smoother and more compact char is formed which prevents heat transfer and transportation of degraded products between melting polymer and surface [52].
Halogenated compounds	• Function primarily by a vapour phase flame inhibiting mechanism through radical reaction [51].

Table 3: Composite Treatment for Colour Stability

Treatment	Description
Photostabilizers	Classified into two types according to their action mode: 1. Ultraviolet Light Absorber (UVA): Absorbs some UV radiation. Act by shielding the material from ultraviolet light [50]. 2. HALS (hindered amine light stabilizers). Act by scavenging the radical intermediates formed in the photooxidation process [50]. High effectiveness in the initial stage due to their fast diffusion to the surface but alternatively, low effectiveness with increased exposure time due to their loss by surface evaporation [32].
Pigments/Colorant	Pigments are added as photo-blockers at material surface for cost effective production because weathering primarily occurs in this region. Composites containing darker colour pigments had better colour stability [60]. Blocks the penetration of UV radiation as well as masking the bleaching of fibres [32].
Colour Dye	Colouring fibres with an oil-based stain significantly improved the colour stability of composites upon weathering while water-based dye does not improve the colour stability [32].
Coating	Opaque pigmented coatings block UV/visible light. Non-photostabilized UV, curable acrylic clear films fails to protect wood against discoloration. Photodegradation of the interfacial layer led to flaking and peeling of the coating [32]. Disadvantages: difficulty in coating plastic composite due to the low surface energy of plastic, solvent evaporation and often causes environmental concerns, drying stage of coating requires additional time [32].
Lamination	Lamination is achieved by melt fusion or an adhesive layer. Delamination often occurs with the bending of the laminated composites. Disadvantage: the difficulty to use lamination technology to manufacture a fully encapsulated structure in plastic composites

	rather than a planar layered structure [32].
Coextrusion	Coextrusion provides a protective surface by producing a multilayered product with different properties at outer and inner layers. By coextruding a hydrophobic clear cap layer onto WPCs, discoloration due to water effect can be retarded [32].

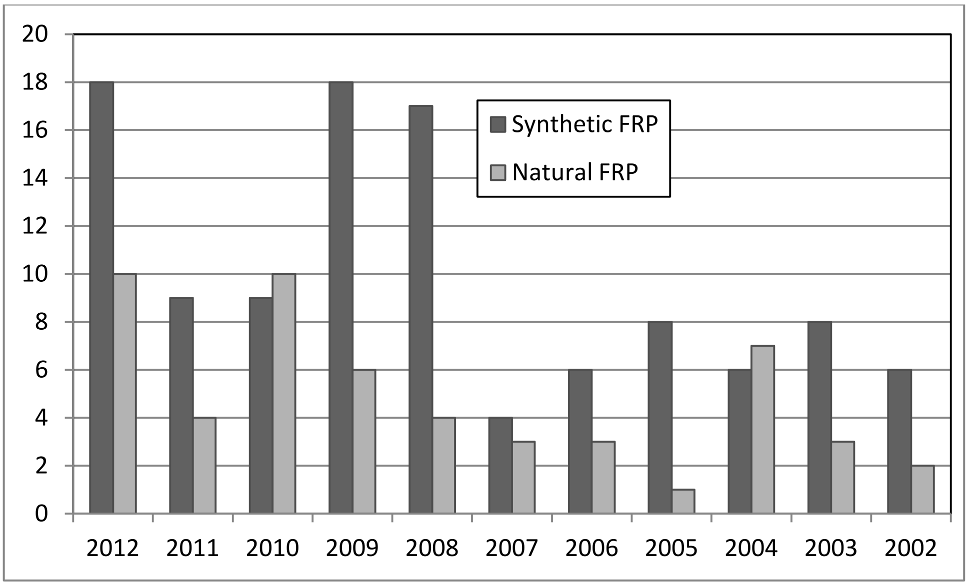


Figure 1: Number of journals published on the degradability of synthetic and natural fibre reinforced polymeric composites due to moisture, thermal, fire and UV exposures. Source: www.science direct.com; Keywords: fibre composites, degradation.

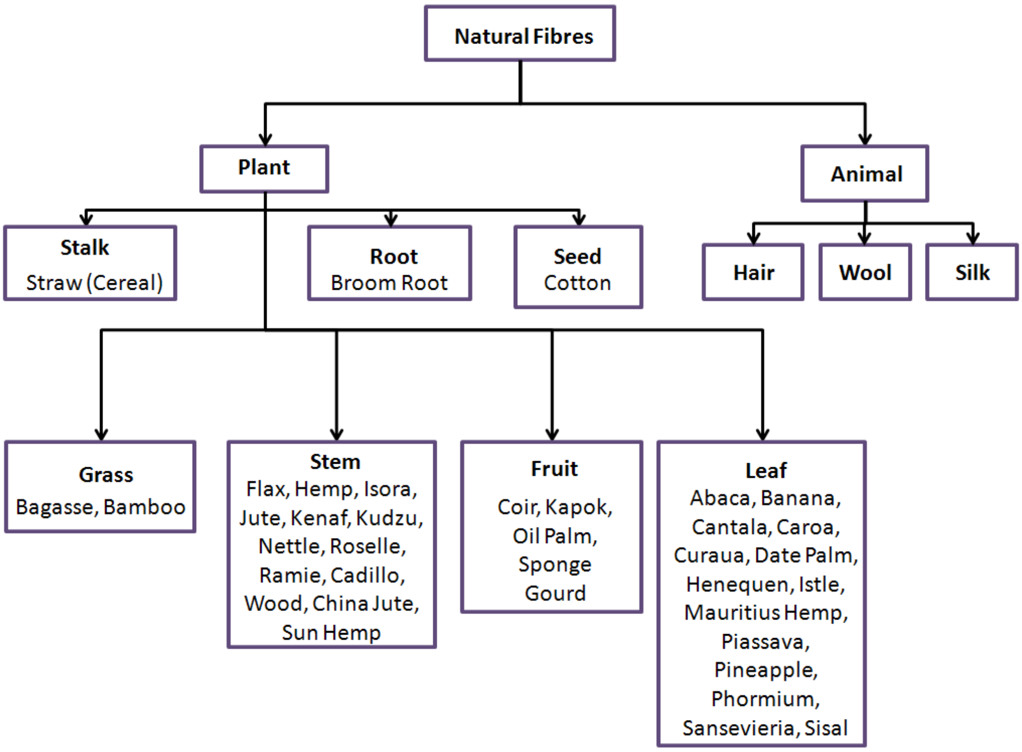


Figure 2: Subdivision of Natural Fibres Based on Origin, Adapted from [19]

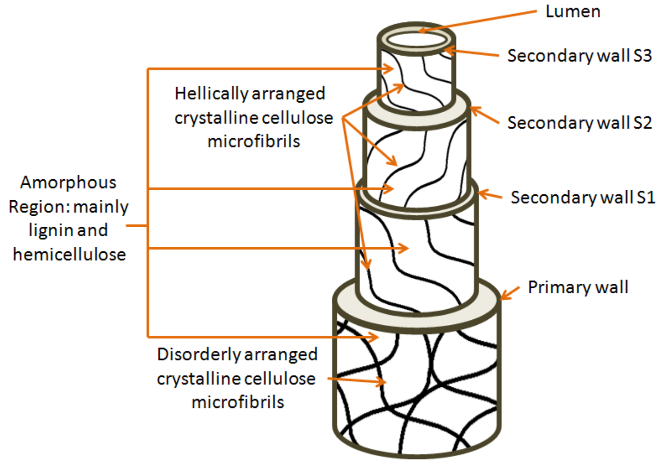


Figure 3: Structure of Biofibre, Adapted from [19]

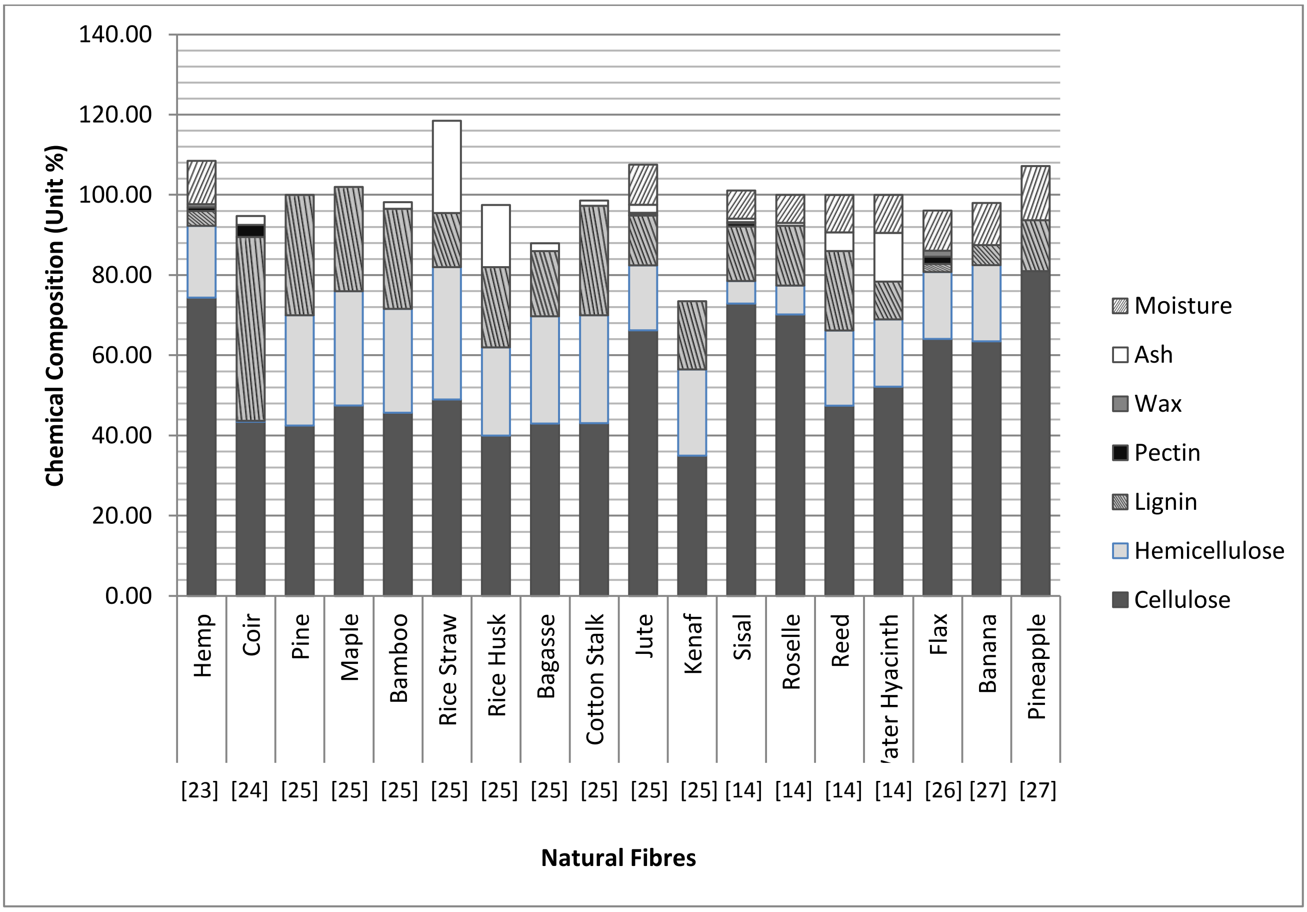


Figure 4: Chemical Composition of Various Natural Fibres

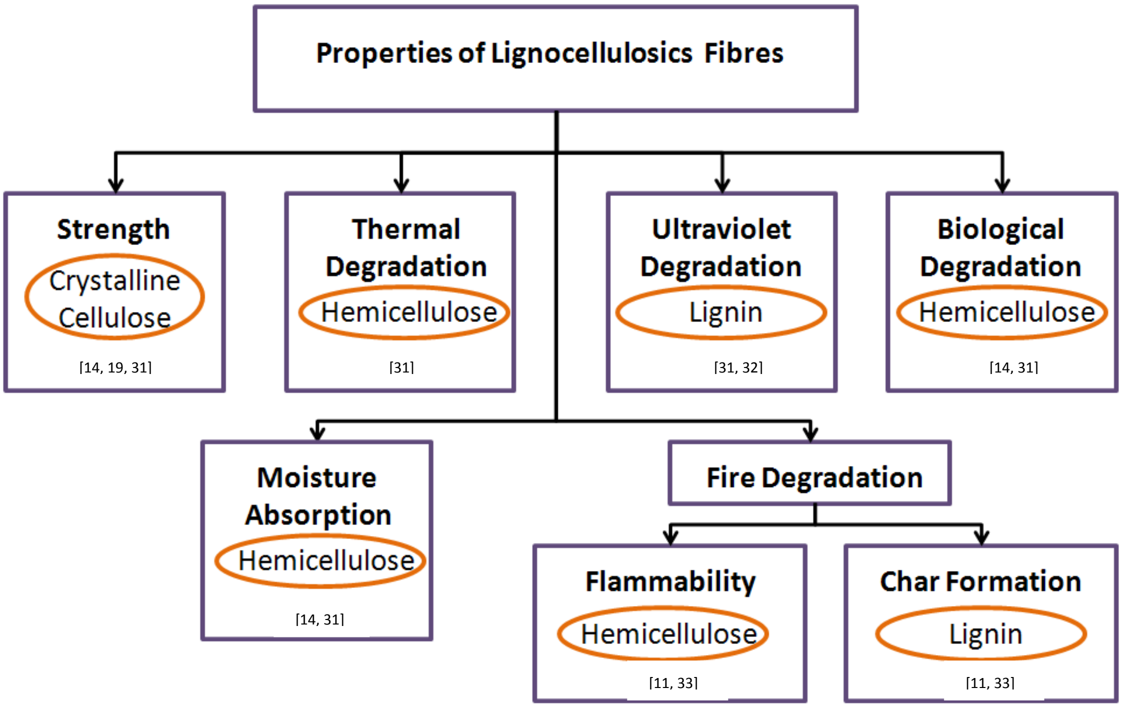
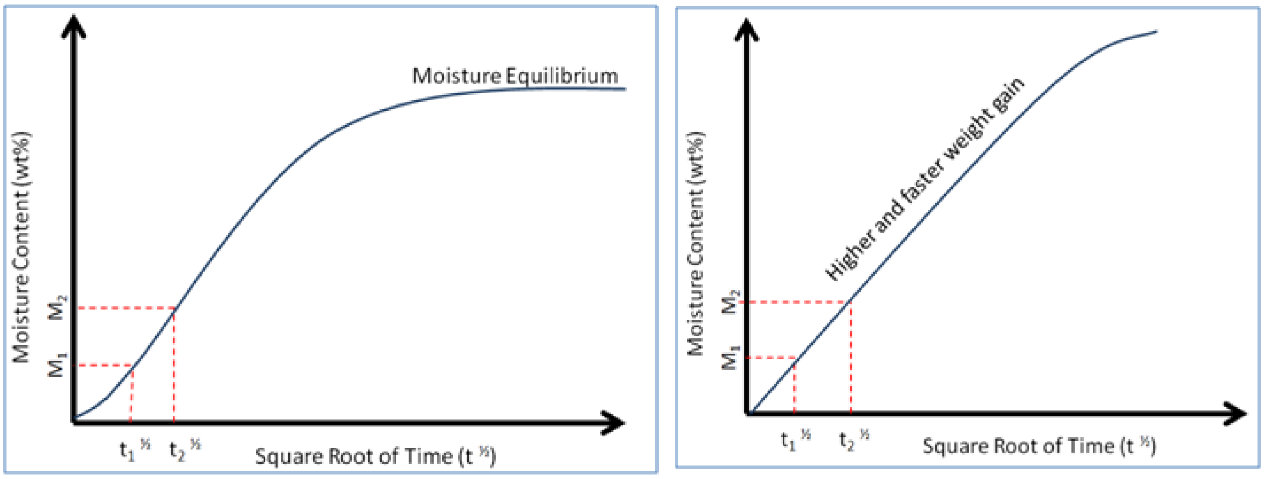


Figure 5: Cell Wall Polymers Responsible for the Properties of Lignocellulosics



(a) (b)

Figure 6: (a) Fickian Diffusion at Room Temperature, (b) Non-Fickian Diffusion at Elevated Temperature, Adapted from [23]

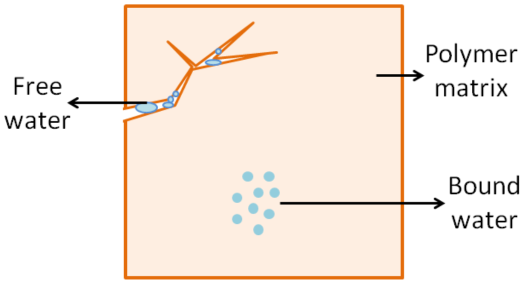


Figure 7: Free Water and Bound Water in Polymer Matrix

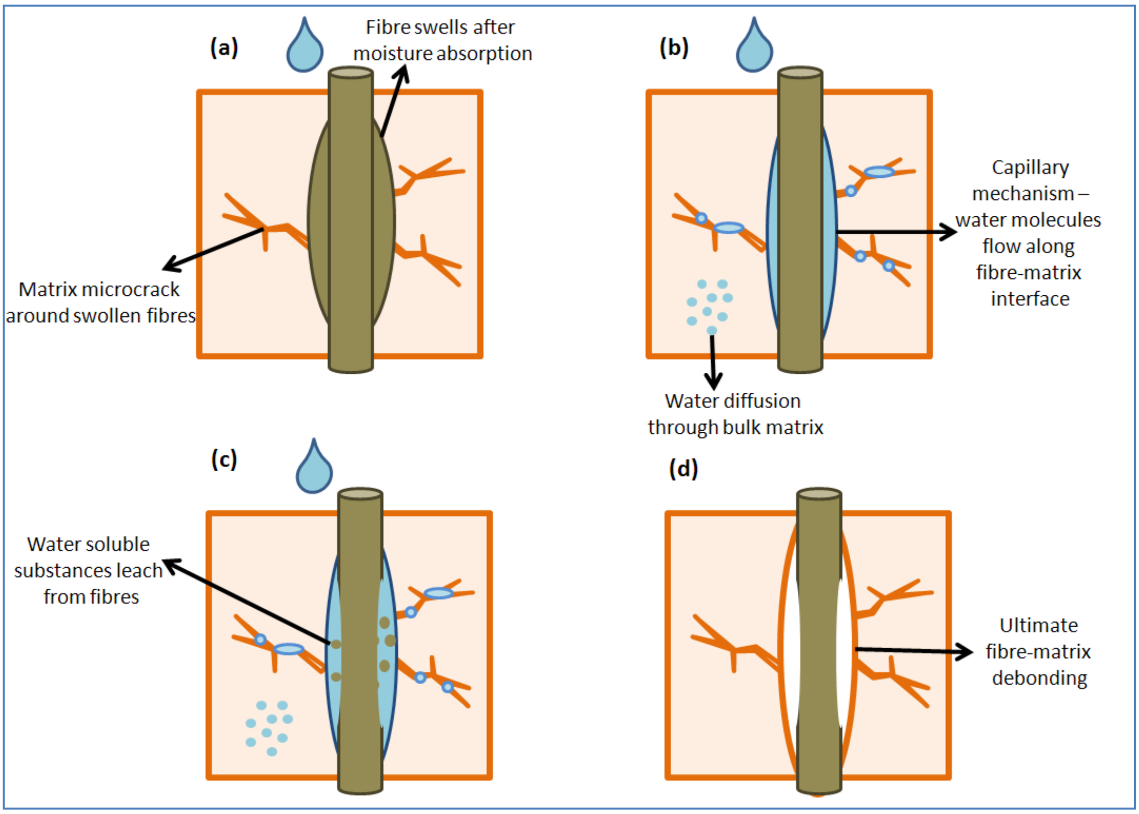


Figure 8: Effect of Water on Fibre-Matrix Interface

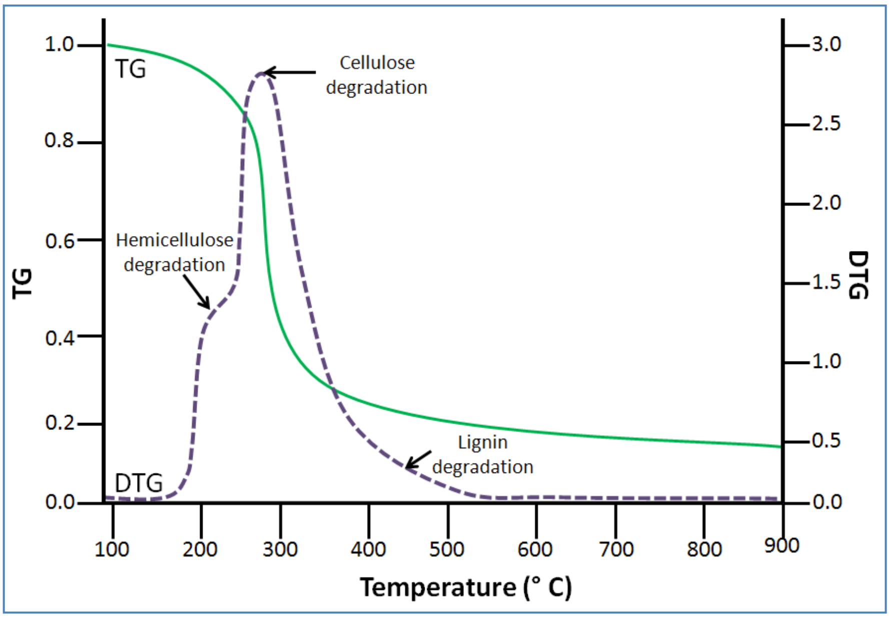


Figure 9: Typical Thermogravimetric Decomposition Process of Natural Fibres [33, 41, 54]

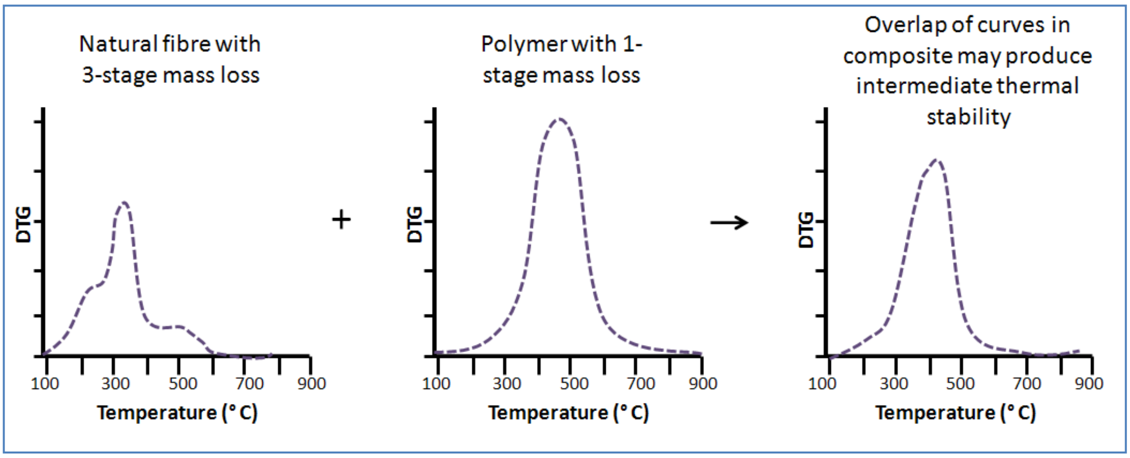


Figure 10: Curve Overlap in TG Analysis of Natural Fibre/Polymer Composite [33, 55, 57]

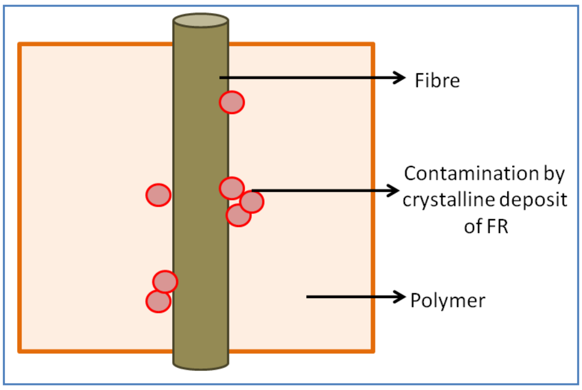


Figure 11: FR Contamination on Fibre Surface

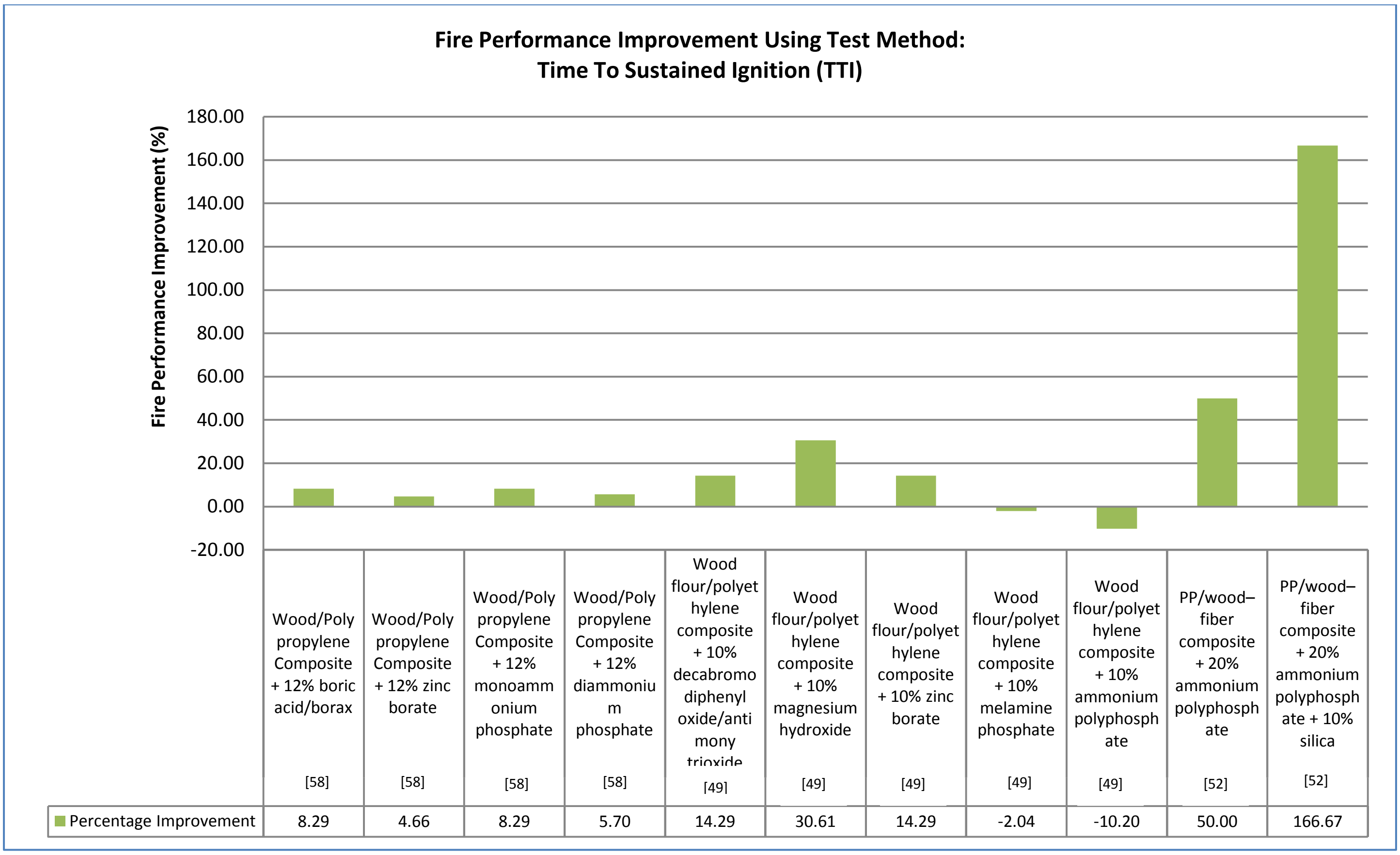


Figure 12: Fire Performance Improvement Using Test Method: Time To Sustain Ignition

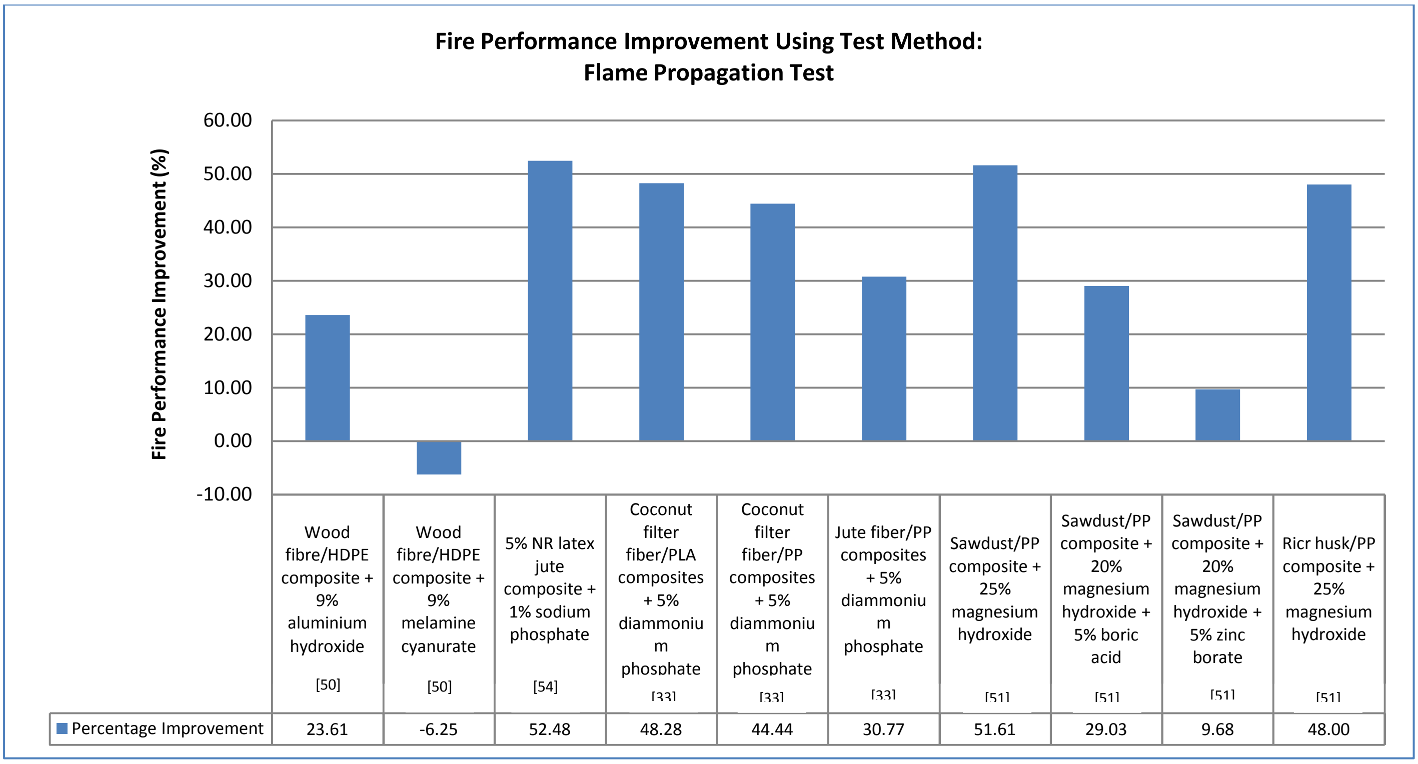
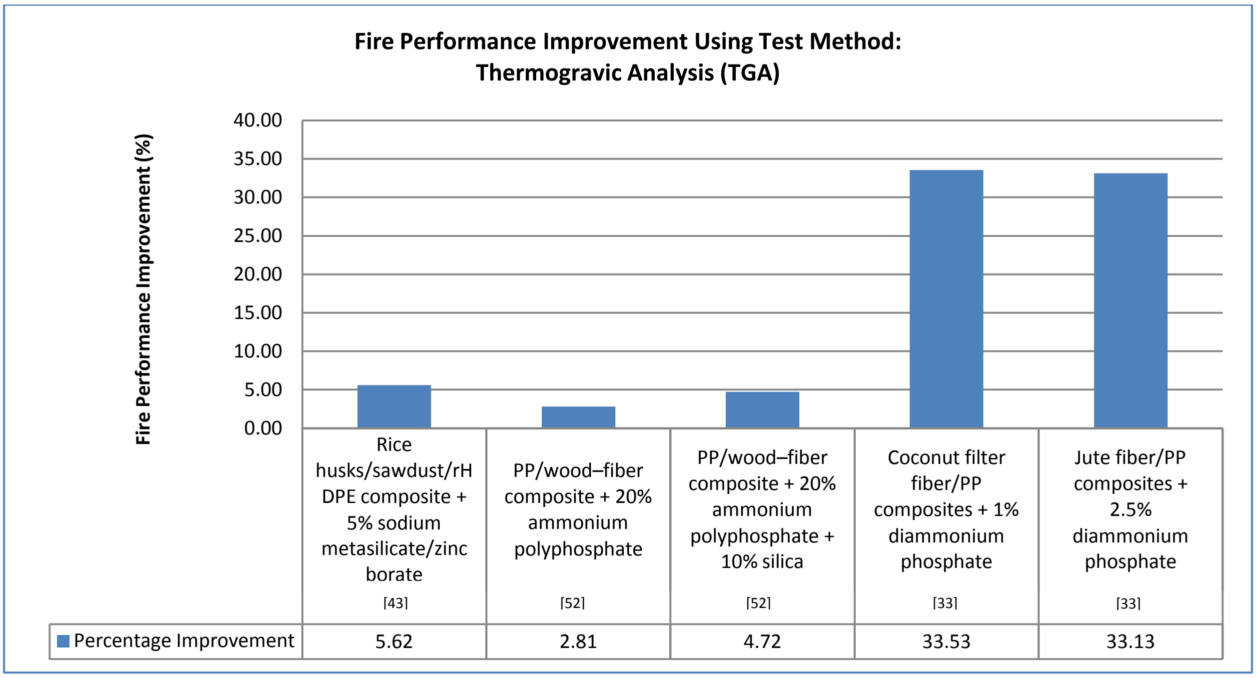


Figure 13: Fire Performance Improvement Using Test Method: Flame Propagation Test



	Rice husks/sawdust/rHDPE composite + 5% sodium metasilicate/zinc borate [43]	PP/wood–fiber composite + 20% ammonium polyphosphate [52]	PP/wood–fiber composite + 20% ammonium polyphosphate + 10% silica [52]	Coconut filter fiber/PP composites + 1% diammonium phosphate [33]	Jute fiber/PP composites + 2.5% diammonium phosphate [33]
■ Percentage Improvement	5.62	2.81	4.72	33.53	33.13

Figure 14: Fire Performance Improvement Using Test Method: Thermogravic Analysis (TGA)

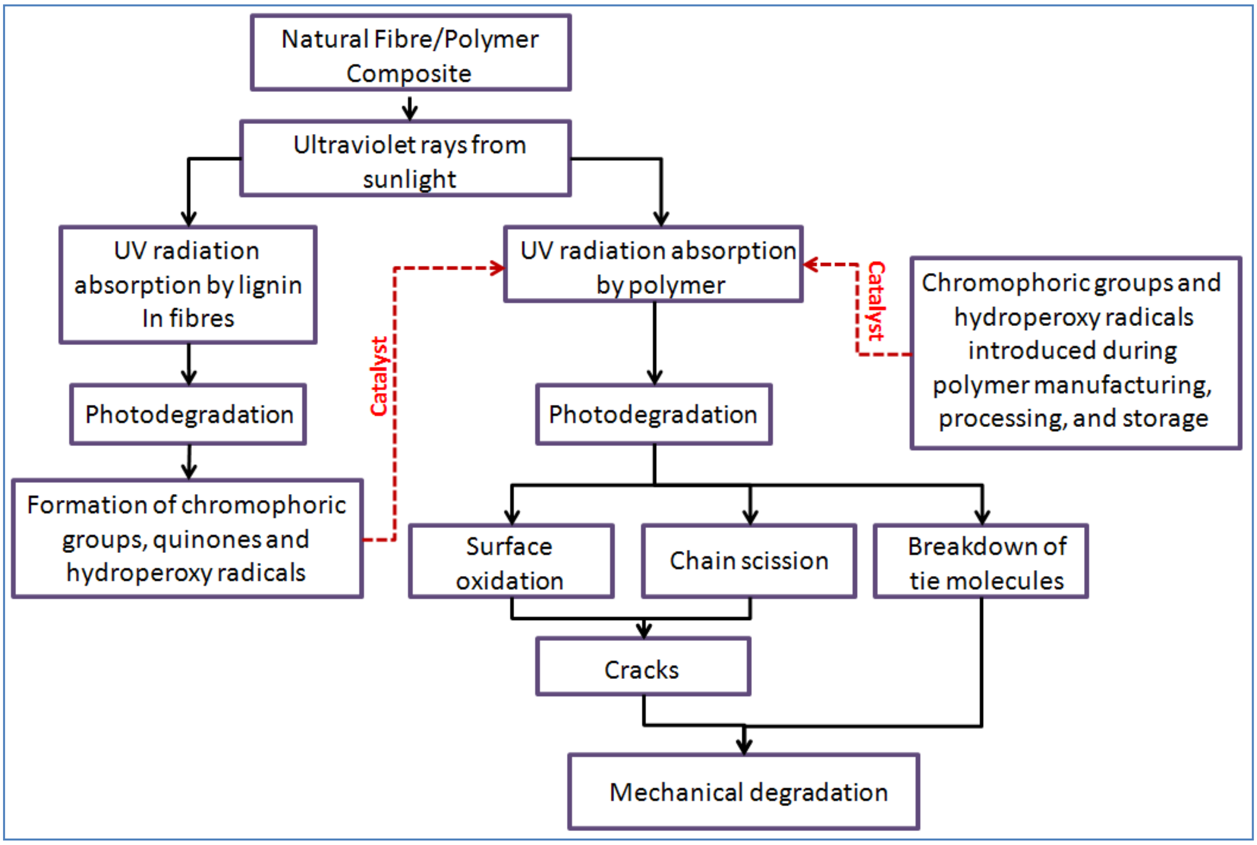


Figure 15: UV Degradation of Natural Fibre/Polymer Composite and Its Components

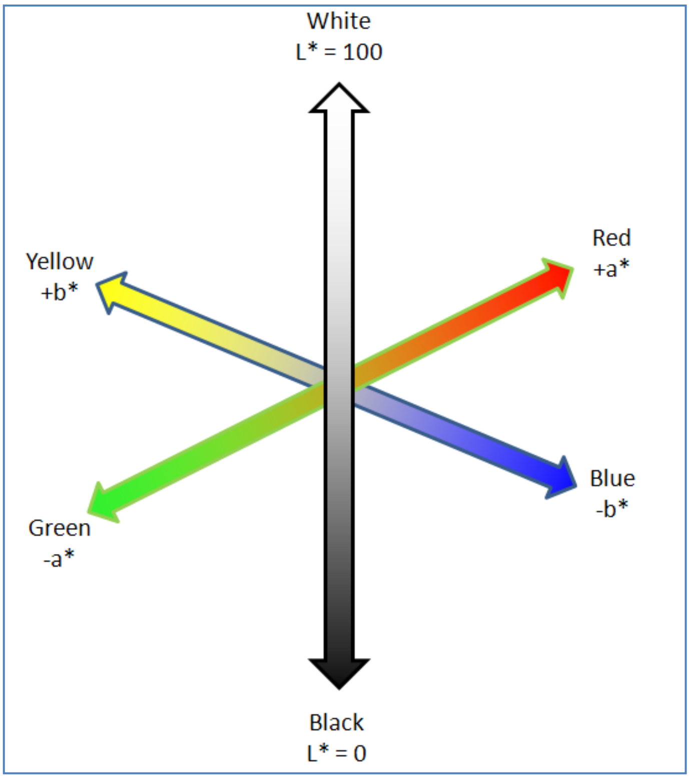


Figure 16: L*a*b* Colour Space adapted from [66]