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Review

Keratinous Natural Fibres as Sustainable Flame Retardants and Reinforcements in Polymer Composites

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Abstract: Natural fibres have been used as fibre reinforcements in composites as they offer eco-friendly and economic advantages, but their susceptibility to deterioration when exposed to heat and flames has limited their practical application in fibre-reinforced polymeric composites. Fire-reaction properties have been explored in reasonable detail for plant fibres, but a gap exists in the understanding of animal fibre-reinforced composites. Understanding the thermal and fire reactions of these keratin-rich animal fibres is crucial for material selection and advancing composite product development. The current paper critically discusses the existing research landscape and suggests future research directions. The use of keratinous fibres in composites can definitely improve their thermal stability and fire performance, but it also appears to adversely affect the composite's mechanical performance. The main part of this paper focuses on the flame-retardant treatment of keratinous fibres and polymer composites, and their behaviour under fire conditions. The final part of this paper includes a brief look at the environmental impact of the treatment methods; the overall processing of keratinous fibre-reinforced composites is also presented to gain further insight.

Keywords: keratinous fibre; composites; fire retardancy; mechanical properties

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1. Introduction

Natural fibre-reinforced composites (NFRCs) have garnered increasing attention as sustainable alternatives to traditional synthetic fibre-reinforced composites, owing to their renewable and biodegradable fibres, which have a low density, a high specific stiffness, and provide excellent thermal insulation [1,2]. Natural fibres, specifically plant and animal fibres, which may be carbon neutral, biodegradable, and capable of giving both mechanical and flame-retarding properties to the composites, form a salient topic for current researchers.

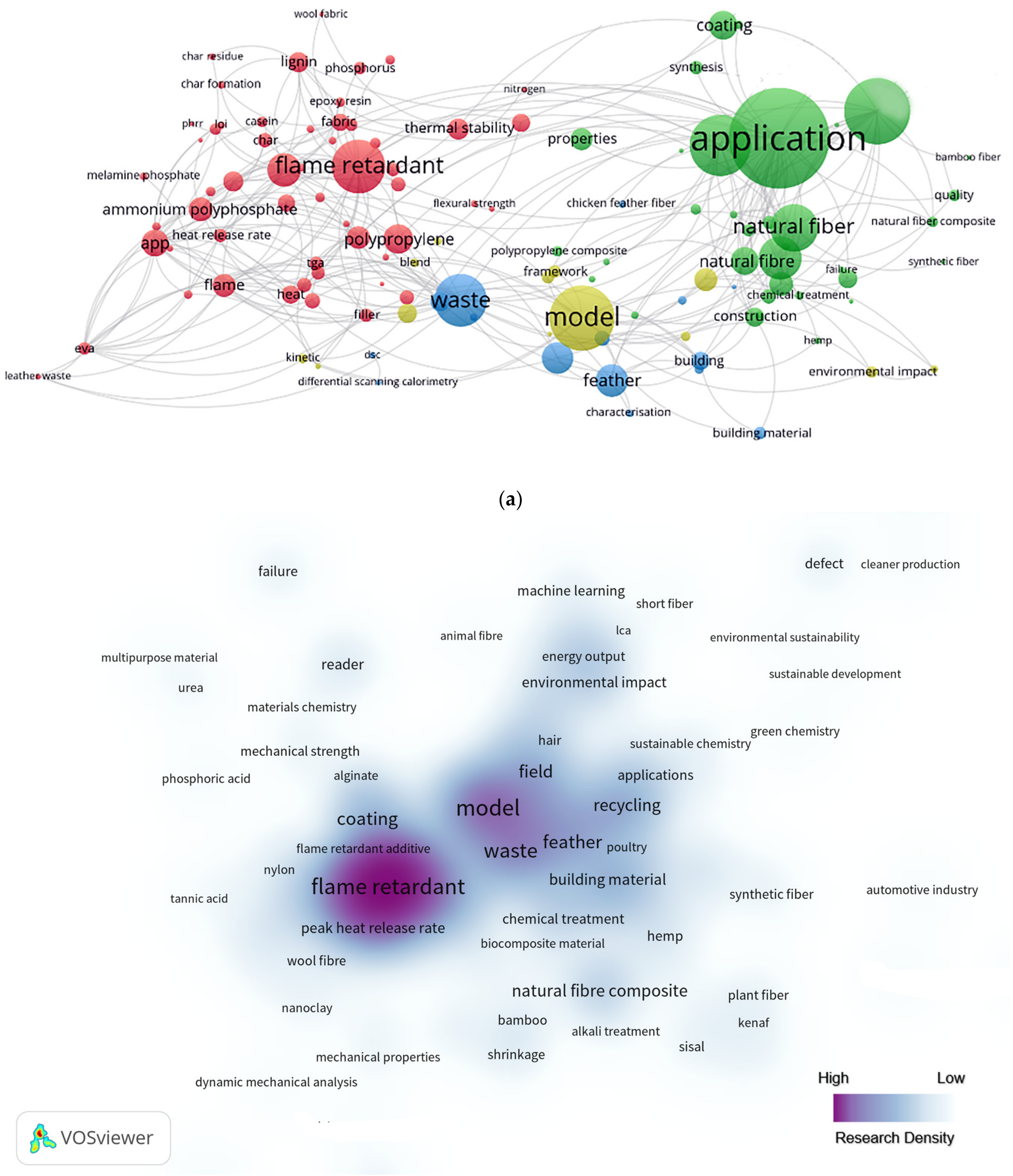
In recent years, the quest for sustainable and eco-friendly materials has driven researchers to explore innovative solutions that merge natural resources with advanced composite technology to facilitate structural applications, especially in automobile, aerospace, marine, and green energy applications [3,4]. However, the use of composites has often being hindered by their poor fire performance. This has severely hindered their application in areas that require both fire safety and mechanical properties [5–8].

Animal fibres with high keratin protein content, such as wool, chicken feathers, and horsehair, have been previously used as reinforcements in composites due to their eco-friendly nature, renewability, and economic advantages. Keratinous fibres are biodegradable and are potentially carbon neutral (depending on the processing methods). They also have the potential to enhance the mechanical properties and improve the flame-stalling abilities of composites [9–12]. Due to their moderate aspect ratios and partial adherence to polymeric matrices, keratinous fibres, which might exhibit hydrophilic and/or hydrophobic qualities as a result of polar and non-polar proteins, can help in providing reasonable reinforcements for polymeric composites [13–16]. A porous honeycomb fibre architecture [17,18] further helps in promoting light weight and excellent reinforcements to polymeric composites, and also helps to create flame-retardant materials for manufactured composite systems [19,20].

Recently, with growing interest in fire-retardant properties, several flammability assessment methods have been used to evaluate the fire properties of keratinous fibre-reinforced composites. Among them, the cone calorimeter remains widely used as it helps expose the material to controlled radiant heat, while measuring the heat release rate, the smoke production rate, and combustion gasses. This helps gain detailed insights into the material's behaviour under specific fire conditions [21]. Another method, the limited oxygen index (LOI) test determines the minimum concentration of oxygen needed to support combustion, implying that a higher LOI provides better fire resistance. Next among the most used methods is the UL-94 test, also termed the vertical burning test, which assesses the material's burning behaviour in a vertical position and then categorising materials into various flame spread categories based on their performance, for e.g., V-0, V-1, V-2, and NR (no rating). Horizontal burning tests are also performed, but they are not very popular. There are a few material characterisation techniques (e.g., TGA, thermogravimetric analysis) that help us make more sense of the aforementioned experimental results. TGA measures the material's weight loss as it undergoes thermal degradation, providing valuable correlations with the material's burning behaviour. Another such characterisation technique is differential scanning calorimetry (DSC), this thermoanalytical technique assesses the amount of heat required to increase the temperature of a sample and the reference sample as a function of temperature. With the multi-material nature of keratinous fibre-reinforced composites (KFRCs), their fire performance and fire reaction remain a complex subject. This review aims to cover different aspects of a composite's fire performance and, in the process, identify any gaps in the research and any potential topics of interest, including possible methods to achieve these objectives.

The organic nature of polymeric materials makes them highly flammable. Unlike thermoplastics, thermosets tend to char and burn if heat is applied for a prolonged period, usually they decompose before melting [22,23]. In the presence of natural fibres, the degradation and combustion process becomes complex and shows some degree of fire resistance. The dangers associated with the decomposition of polymers concern the high amount of heat generated and the toxicity of the smoke and soot particles, which can lead to acute or delayed health issues leading to death. In order to reduce the flammability of polymeric composites, flame retardants have been used. The burning characteristics of these modified composites help in investigating the complex flame-retardant mechanisms involved [24–28]. Looking at the bigger picture, the use of keratinous fibres as a form of reinforcement helps reduce the amount of plastic or polymer consumption, thus lessening the overall environmental impact. To attain the sustainability goals, we must follow the 3 Rs, namely reduce, reuse, and recycle. The use of available natural resources reduces the procurement of new materials and leads to a reduction in water and resource utilisation, eventually reducing the water footprint [29] and carbon footprint of products [30].

Figure 1 presents network and density visualisations of the research on flame-retardant composites, revealing key focus areas, emerging trends, and critical knowledge gaps. The network visualisation highlights prominent clusters around flame retardants, applications, and the use of waste materials, indicating substantial research on chemical additives, such as ammonium polyphosphate, and their practical application in construction and coatings. The emphasis on natural fibres and their environmental impact underscores a growing interest in sustainable materials. The density visualisation further supports these findings, showing high research activity around terms like "flame retardant", "model", and "waste", with emerging areas such as "environmental impact" and "recycling".



(**a**)

(**b**)

Figure 1. (**a**) The network visualisation highlights prominent clusters around flame retardants, applications, the use of waste materials, and associated research areas to better understand the amount of work conducted in the respective areas; (**b**) the density visualisation further supports these findings, showing high research activity with varying colour intensities around terms like "flame retardant", "model", and "waste", with emerging areas such as "environmental impact" and "recycling" having a low colour intensity; all the data were collected from the Web of Science and VOSviewer was used for the data visualisations.

This interdisciplinary research approach integrates chemical engineering, materials science, environmental studies, and practical engineering applications, reflecting a holistic effort to advance the field. However, significant knowledge gaps remain in understanding the long-term durability, environmental impact, and scalability of fire-retardant methods. Addressing these gaps through studies on the interplay between fire resistance and mechanical strength, along with lifecycle assessments, is crucial for balancing fire safety, material performance, and environmental sustainability [31].

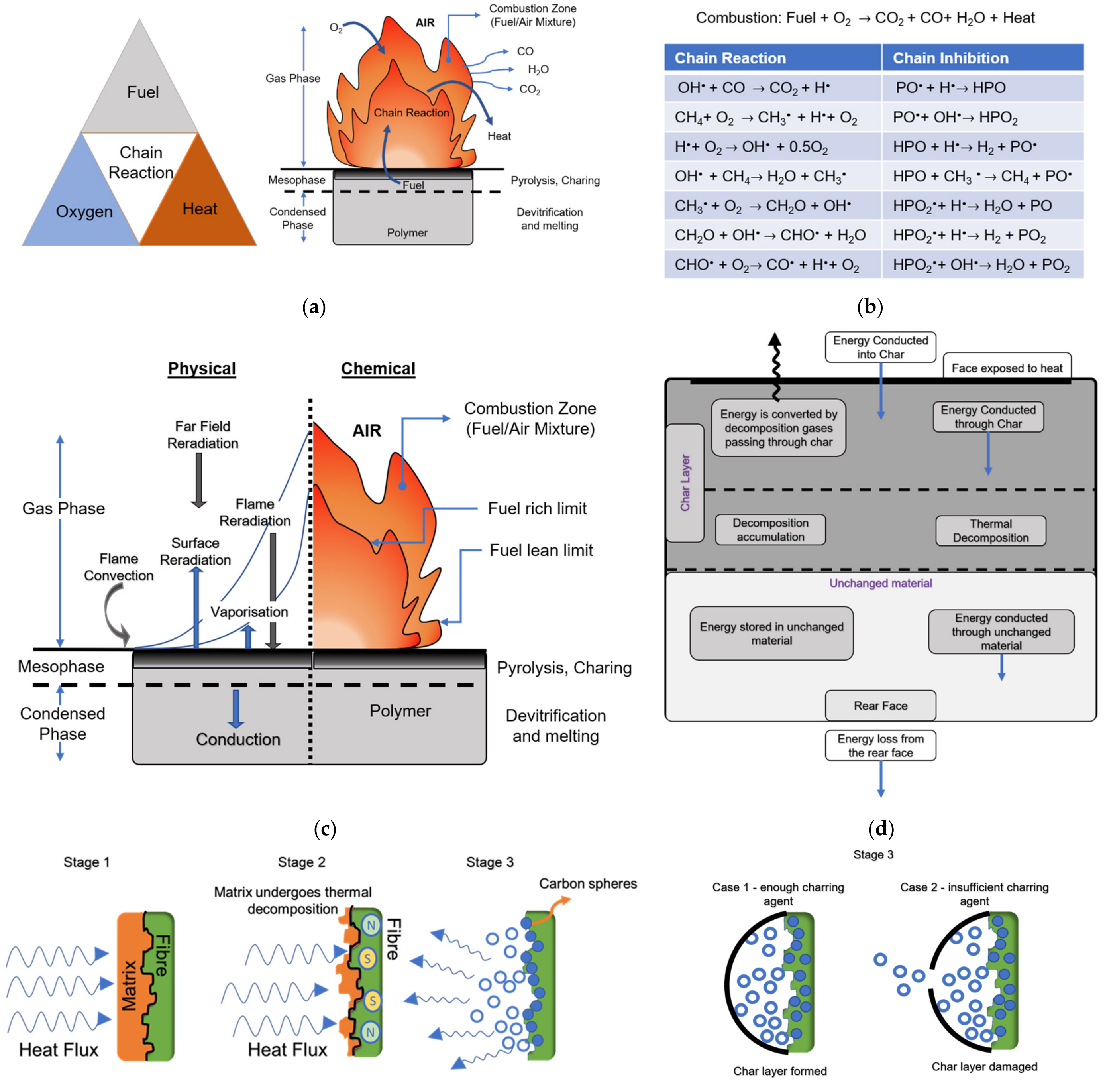
While many review papers exist, Figure 1 shows that current research predominantly covers the fire and mechanical aspects of cellulose-based fibres, whereas this review places emphasis on the flammability of keratinous fibre-reinforced composites (KFRCs). For these composites, the damage process is governed primarily by the chemical processes involved in the thermal decomposition of the matrix, which dictates the resulting flammability and mechanical characteristics. Understanding the long-term durability, environmental impact, and scalability of fire-retardant methods remains limited, necessitating further in-depth research. Thorough studies on the interplay between fire resistance and mechanical strength, along with the ecological footprint and lifecycle evaluations, are essential for a comprehensive analysis. Bridging these knowledge gaps and achieving a balance between fire safety, material performance, and environmental sustainability is crucial for advancing the adoption of natural fibre-reinforced polymer composites in critical industries, guiding the development of materials that are safer, more sustainable, and resilient [32–34].

The main section of this review focuses on flame-retardant methods to treat keratinous fibres, the polymeric matrix, and composites, and the pyrolysis mechanism of keratinous fibres and reinforced composites. Many of the flame-retardant mechanisms are explained with the aid of synthetic or plant-based fibre-reinforced composites and their behaviour under fire due to a lack of literature on the behaviour of keratinous fibre composites. To some extent, keratinous fibres mimic plant fibres, but the fibre architecture is very different and, hence, a better understanding warrants more research.

2. Thermal Mechanisms of Fibre-Reinforced Composites

This paper begins with a short review of the literature regarding the thermal mechanisms of fibre-reinforced composites. Irrespective of the type of heat, i.e., conductive, convective, radiative, or a combination of all of them, such materials continue to fuel the flame, resulting in a chain reaction that promotes flame growth. The importance of the surface treatment is realised as it localises the active flame suppressant at the most effective position, which helps to disrupt the chain reaction. For all materials, the decomposition rate and mechanism of the substrate influence the flame-retardant mode of action, helping us to understand the composite's fire inhibition mechanism.

The main objective of flame retardancy is to inhibit one or more of the fire tetrahedron components, as shown in Figure 2a, from initiating combustion. Under high heat conditions, pyrolysis of the constituents is inevitable, the flame retardants try to impede pyrolysis, deter the time to ignition (TTI), and suppress smoke production, while trying to control the flame spread rate (FSR) or flame growth rate (FGR), which allows more time for the safe evacuation of the premises. These capabilities are achieved either by chemical or physical means in gaseous or condensed phases, as shown in Figure 2c, by obstructing the fuel supply, dissipating the heat flow towards flammable components, limiting the oxygen supply, or inhibiting the ongoing reaction of the combustible decomposition products.



Combustion: Fuel + O_2 → CO_2 + CO+ H_2O + Heat

Chain Reaction	Chain Inhibition
$OH^{\cdot} + CO \rightarrow CO_2 + H^{\cdot}$	$PO^{\cdot} + H^{\cdot} \rightarrow HPO$
$CH_4 + O_2 \rightarrow CH_3^{\cdot} + H^{\cdot} + O_2$	$PO^{\cdot} + OH^{\cdot} \rightarrow HPO_2$
$H^{\cdot} + O_2 \rightarrow OH^{\cdot} + 0.5O_2$	$HPO + H^{\cdot} \rightarrow H_2 + PO^{\cdot}$
$OH^{\cdot} + CH_4 \rightarrow H_2O + CH_3^{\cdot}$	$HPO + CH_3^{\cdot} \rightarrow CH_4 + PO^{\cdot}$
$CH_3^{\cdot} + O_2 \rightarrow CH_2O + OH^{\cdot}$	$HPO_2^{\cdot} + H^{\cdot} \rightarrow H_2O + PO$
$CH_2O + OH^{\cdot} \rightarrow CHO^{\cdot} + H_2O$	$HPO_2^{\cdot} + H^{\cdot} \rightarrow H_2 + PO_2$
$CHO^{\cdot} + O_2 \rightarrow CO^{\cdot} + H^{\cdot} + O_2$	$HPO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + PO_2$

Figure 2. (**a**) Schematic representation of the associated fire tetrahedron and combustion mechanism; (**b**) chemical reaction for combustion and examples of phosphorus-based radicals that can scavenge unstable radicals in the gas phase; (**c**) physical and chemical processes in the flaming combustion of polymers; (**d**) identification of thermal transfers during combustion; (**e**) stages of thermal decomposition of fibre-reinforced composites; (**f**) variations in stage 3 of (**e**).

In the gaseous phase, small amounts of high-energy OH· and H· radicals are produced with the initiation of the chemical reaction in presence of oxygen, which generates fuel sufficient to ignite polymeric material [35]. Flame initiation or ignition leads to a series of chemical chain branching, propagation, and termination reactions that fuel the flame by changing the amount, type, and mole ratio of the radicals present in the gaseous phase [36]. Radicals with lower energy are necessary for scavenging the unstable OH· and H· radicals, this tends to inhibit the chain reaction of combustion and promotes self-extinguishing abilities in treated systems, as shown in Figure 2b. Flame-retardant abilities can also be physically achieved in the gaseous phase by lowering the amount of combustible gases through the endothermic release of non-flammable gases, such as N_2, H_2O, and CO_2.

In the condensed phase, mass and heat transfer constantly feed the flammable decomposition products that cause flame spread [35,37]. Reducing the amount of thermal feedback by creating a protective layer on the material's surface is one of the many ways to achieve flame retardancy. This protective layer is usually an insulating, thermally stable barrier applied to the surface, it may also be formed chemically at the interface during pyrolysis of the material [38].

In composites, after being exposed to heat flux radiated from the fire source, the top layer of the matrix begins to thermally decompose. This is similar to that of virgin polymer decomposition, which has been thoroughly investigated in previous studies [39,40]. During decomposition, there are several reactions happening simultaneously. Composites with natural fibres have a similar fire-reaction mechanism to keratinous fibres, the matrix degrades and softens, and phenomenon such as inter-ply delamination and matrix cracking follow, leading to a reduction in strength and stiffness, which could be a result of the fibre–matrix de-bonding [41]. The final stage of char formation relies on the char strength formed by the charring agent, where individual fibre characteristics play an important role.

Upon exposure to heat, the top surface of composites experiences thermal decomposition, followed by the conduction and diffusion of heat through the composite. The rate of heat transfer across the thickness direction is slower compared to that of the direction along the fibres, the reason being the thermal conductivity of fibres is higher in comparison to that of the matrix materials. The exposure of fibres or flame retardants in a composite could lead to the formation of a sustained char that helps protect the underlying layer (Figure 2d). As a result, a temperature gradient develops across the composite, which can be labelled the exposed region (i.e., the region closest to the heat source), the mesophase region (i.e., the region below the exposed region), and the condensed region (i.e., the region farthest from the heat source and near the rear end of the composite). With an increase in the time of exposure to fire, the matrix in the exposed region softens as the temperature nears the glass transition temperature (T_g). This reveals the fibre positions and weakens the fibre–matrix bonds, leading to a loss of strength. The conduction of heat progresses in the thickness direction and as the temperature nears the thermal decomposition range, matrix cracks and fibres encapsulated by the matrix are exposed, subsequently decreasing the composite's mechanical strength.

The thermal decomposition and heat conduction in the three regions release reactive volatiles in the mesophase region, and evaporated water from the condensed phase region flows through the char layer towards the surface. During this process, not all the developed gas pressure is liberated, resulting from the gas permeability of the composites. As such, internal pressure develops leading to the expansion of the composite, resulting in delamination cracks and gas-filled pores, rapid creeping, buckling, and various other composite failures under heat conditions [21,42–44]. This process continues until all the composite has been converted into volatiles, smoke, soot, and char. At this stage, the thermally induced decomposition process comes to a halt unless the temperature is high enough to induce pyrolysis reactions between the fibres and the char.

The preceding section provides an outline of the topics to be discussed to better understand the flammability of fibre-reinforced composites and their mechanical properties. This review provides insights on the performance of natural fibre composites, while drawing parallels with the performance of keratinous fibre composites.

3. Factors Affecting the Combustion and Mechanical Behaviour of Composites

The thermal mechanism of fibre-reinforced composites is thoroughly explained in the previous section. The mechanism is influenced by several elements, such as the type of fibre used, their weight or volume fraction in the composite, their behaviour under fire conditions, the orientation of the fibre, and their interaction with the matrix. Keratinous fibres tend to burn and leave residue, but the amount of residue generated varies with the fibre type used. It has been noted that fibre treatment with flame-retardant chemicals or coatings helps improve their flame-retardant properties. Even the type of polymer used has an important role to play in determining the composite's fire-reaction properties, as the fibre's interaction with the matrix determines how the flame propagation happens through the composite. Environmental conditions can also affect flame retardancy, with high amounts of humidity and high temperatures promoting the flammability of composites. This necessitates fibre treatment for enhanced flame-retardant ability. The various methodologies for incorporating flame retardancy include integrating flame-retardant chemicals, coatings, and inorganic fillers. However, their effectiveness varies from one type of fibre to another and according to the composite formulation, leading to inconsistency and trade-offs to keep the product use valid. The combustion behaviour of KFRCs can be affected by the fibre type, fibre weight/volume fraction, thermal conductivity, fibre orientation, aspect ratio, fibre–matrix interface, and agent size, which makes understanding the fibre important [45–47]. Out of them, a few aspects have been discussed below to draw out the important factors and their influence on fire-reaction properties.

3.1. Fibre Type

Numerous types of animal fibres are used daily, and their major application is in the textile industry. However, large amounts of animal fibres go to waste, without proper applications due to the decreasing demand, resulting from the rapid development of synthetic fibres. As shown in Figure 3, animal fibres can be further classified into several types. Keratin is a common protein found in animal hair and avian fibres, referred to as keratinous fibres. Silk possesses the majority of fibroin, creating a separate classification of fibroin fibres. Keratin-derived materials have been identified to have intrinsic biocompatibility, biodegradability, mechanical durability, and natural abundance [48,49]. The utilisation of keratinous fibres is limited due to the complicated pre-treatment processes, such as washing, sterilisation, and sorting processes. Although special types and parts of keratinous fibres have been used as fillers in apparel, bedding, and pillows, while some are transformed into animal feed and fertilisers, most low-quality keratinous fibres are incinerated or end up in landfills. For instance, the demand for coarse wool fibre is decreasing, with no new applications, and the more than 2 million tons of chicken feathers produced every year around the world has become a societal nuisance [9]. However, the usage of keratinous fibre has been highlighted as a source of thermoplastic materials [16,50,51] and also as a flame-retardant fibre reinforcement, due to its excellent ability to support flame-inhibition properties [9,10,52,53].

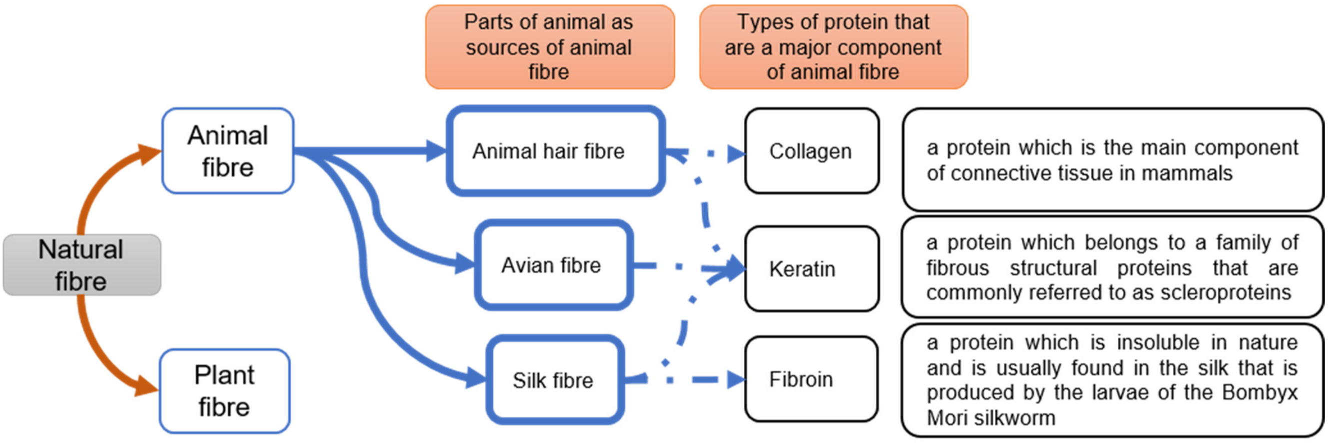


Figure 3. Animal fibre hierarchical schematic.

The very popular hierarchical structure of wool fibres is shown in Figure 4, whose core is made up of keratin fibres. Keratin is usually the main constituent of animal fibres, it is a polypeptide consisting of amino acids with intermolecular bonding of cysteine and some intermolecular bonding of polar and non-polar groups. Cysteine residues have thiol groups that interact to form disulphide bonds, leading to the crosslinking of the matrix molecule [54]. It has been identified that keratin proteins generally consist of α-helix and β-sheet structures in different proportions, and they tend to influence the architecture of keratinous fibres.

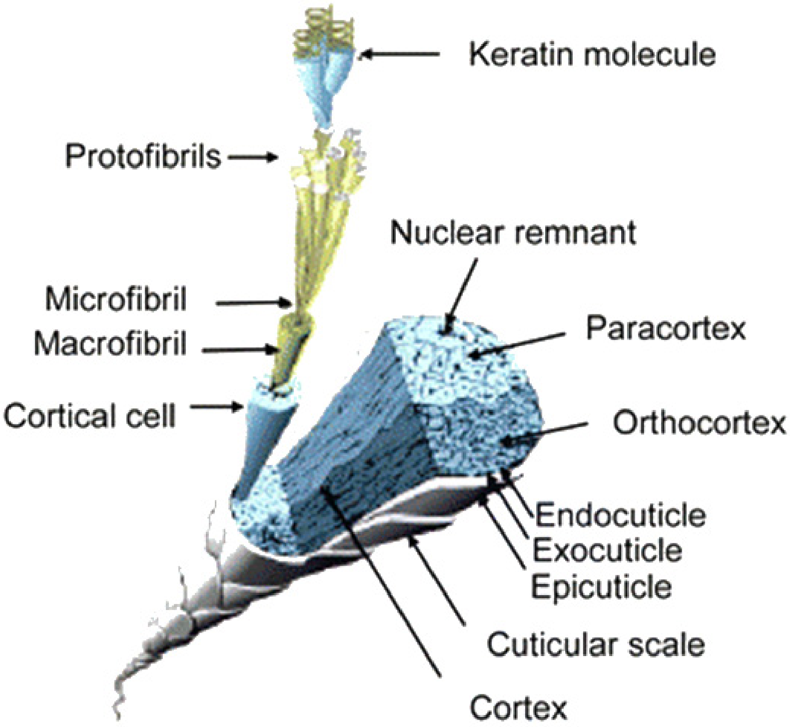


Figure 4. Hierarchical structure of wool fibres. Reproduced with permission from [55]. Copyright 2012 Springer.

The fibre's backbone is formed from α-helix keratin, and keratin with a β-sheet structure fills the space between the α-helix tubes (Figure 5). The elastic nature of keratin fibre is due to the interplay between the α-helix and β-sheet configuration in the protein. Hydrogen bonding between separate segments of amino acid chains provide high strength to the material [56]. The abovementioned articles have identified the high porosity at nano and micro-levels resulting from the crystalline segments and hollow cylindrical microstructure, which accounts for the fibre's low density (Table 1).

Table 1. Mechanical properties of various animal fibres [57,58].

Fibre	Density (g/cm^3)	Diameter (μm)	Tensile Strength (MPa)	Elongation at Break (%)
Wool	1.28~1.32	19~41	147~245	25~45
Angora	1.14	10~18	167~255	30~35
Alpaca	1.3	18~35	151~221	34~37
Mohair	-----	22~40	------	42.7
Silk	1.34~1.38	10~13	600	25~40
Chicken feather	0.89	5~40	175~275	7.7

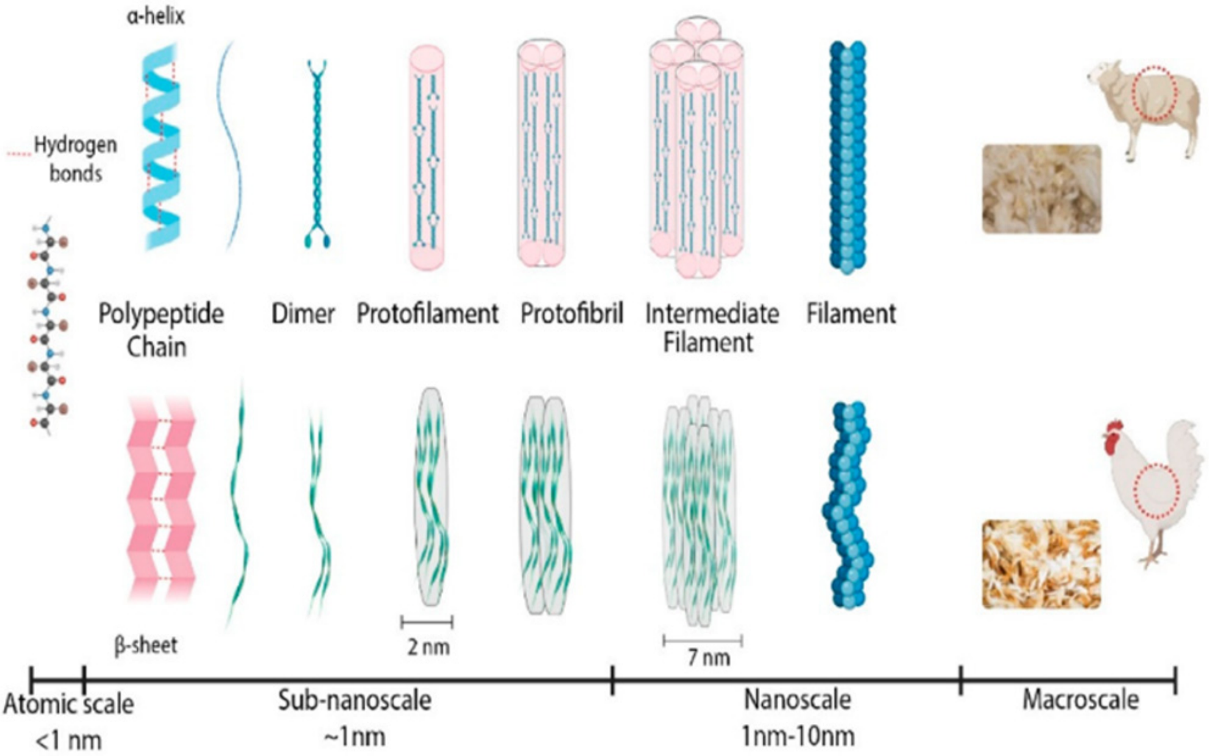


Figure 5. Schematic of the hierarchical structure of keratin, from the nanoscale to the centimetre scale, for wool and feathers; reproduced with permission from [59]. Copyright 2023 MDPI.

Wool fibres are inherently flame retardant due to their high nitrogen and sulphur content, thereby forming a stable char layer during combustion, while acting as a thermal barrier and reducing smoke production, making them suitable for enhanced fire safety applications [60]. Chicken feathers, on the other hand, decompose at higher temperatures, releasing gases that dilute flammable volatiles and contribute to robust char formation, enhancing fire resistance and reducing overall flammability [16,60]. Horsehair fibres also exhibit inherent flame-retardant properties due to their chemical composition, contributing positively to fire resistance [55,61]. This comparative analysis highlights that while all keratinous fibres provide some level of flame retardancy, their effectiveness varies based on their chemical composition and structural properties. Future research should focus on optimising composite formulations to balance the mechanical properties and flame retardancy, and exploring advanced treatment methods to enhance the fire resistance of keratinous fibre-reinforced composites.

3.2. Fibre Content

The fibre weight in a composite affects its overall flammability. Keratinous fibres have a self-extinguishing property because of the amino acid groups in the fibres that are composed of nitrogen and sulphur compounds, which imparts intumescent flame retardancy during combustion. The thermal decomposition process of KFRCs is largely governed by the decomposition of the polymer matrix in the presence of keratinous fibre, which has a tendency to char under fire conditions [62,63]. The wt.% of keratinous fibres defines the combustion of the composite, as the released volatiles and smoke could lead to fire growth unless there is enough flame-retardant fibre to promote self-extinguishment.

Pyrolysis chemistry related to keratin fibres under thermal decomposition helps us understand how increasing or decreasing the fibre content can affect the overall flammability of the composite. Hence, it is logical to say that an increase in the keratinous fibre content in composites (Table 2) helps inhibit flame propagation but only up to a limit, and finding the right balance is important.

Table 2. Various chicken feather fibre content in composites and their peak heat release rates (PHRRs).

Fibre	Matrix	FR	Fibre Content (wt.%)	Average PHRR (kW/m^2)	References
CFF	SPUR		10	283	[64]
CFF	SPUR	10ATH	10	307	[64]
CFF	SPUR	10GE	10	165	[64]
CFF	SPUR	10APP	10	341	[64]
CFF	PP	EDAP	13	216.1 ± 18.1	[10]
CFF	PP	MP + 6APP	14.3	276.707 ± 20.85	[17]
CFF	PP	EDAP	16	280.5 ± 16.6	[10]
CFF	PP		40	1234.1 ± 109.8	[10]

The effect of fibre content is governed by the thermal characteristics of keratinous fibre, which refers to the fibre's behaviour when exposed to high temperatures. This relates predominantly to the thermal conductivity, thermal expansion, and thermal stability of the material. Thermal conductivity refers to the material's ability to transport heat; thermal expansion indicates a dimensional change in the material due to a change in temperature. Natural fibres are known to decompose at high temperatures, producing volatiles and char, suggesting lower thermal stability, which is concerning. To address this issue, researchers have been developing strategies to enhance thermal stability by incorporating flame-retardant chemicals and coatings [65].

Prior research suggests that keratinous fibres have helped to improve the mechanical properties of composites in one way or another [9,12,16,19,53,66]. Similarly, to introduce their benefits as flame-retardant adjuvants, a brief introduction to their pyrolysis mechanisms is presented in a later section, in order to gain a better understanding.

3.3. Pyrolysis of Keratinous Fibres

Whether the fibre used is wool, any type of avian feather, or animal hair, the type of fibre can greatly affect the fire-reaction properties of the composite. Wool has better insulation against thermal conduction (Table 3) than feathers. However, from an economic perspective, feathers, especially chicken feathers, have the upper hand as compared to other keratinous fibres.

Table 3. Thermal properties of keratinous fibres.

Fibre Type	Thermal Conductivity (W/Mk)	TG–DTG						Final Residue Wt.%	References
		First Stage Degradation Temperature (°C)	Mass Loss (%)	Second Stage Degradation Temperature (°C)	Mass Loss (%)	Third Stage Degradation Temperature (°C)	Mass Loss (%)		
Sheep wool	0.0327–0.0779	30–135	14.2	218–390	51.1	390–500	23.5	11.2	[67,68]
Goat wool	0.0314–0.0771	31–140	14.8	220–383	46.6	383–500	16.3	22.3	[67,68]
Horse mane	0.0389–0.0867	31–133	13.8	224–370	41.2	370–500	21.9	23.1	[67,68]
Duck feather	0.05	50–100	8	210–340	58	340–520	15	19	[69,70]
Chicken feather	0.036	25–230	12.9–13.4	230–380	~33	380–550	35.75–37.70	16.5	[13]

Keratin, which is a structural protein, naturally occurring in hair, feathers, wool, and nails, has impressive mechanical properties pertaining to its high degree of disulphide crosslinks, hydrogen bonds, and partial hydrophobic nature [50,71,72]. Feathers are made up of 91% protein (keratin) and about 8% water [14], out of its amino acids, the cysteine content is 7%, and these cysteine residues oxidise to form inter- and intramolecular disulphide bonds, which helps to stabilise and crosslink the filaments to attain higher mechanical and thermal stability of the protein [73,74]. Cysteine contains thiol-bearing amino acids (Figure 6), typically referring to the R-SH form of these chemical moieties, which are subject to deprotonation (loss of H+) to form charged thiolates (R-S-). In proteins, certain hydrogen bond donors and a local electropositive environment have a tendency to lower the pKa by stabilising the thiolate; in this context, pH denotes the systemic acidity, whereas pKa relates to acidity at the molecular level. While thiolates are better nucleophiles than thiols, in a given ionisation state (e.g., thiolates), nucleophilicity (the affinity of a base for a carbon atom in a displacement reaction transition state) increases with the pKa. It should also be noted that the protonation/deprotonation process influences the relative populations of the two species.

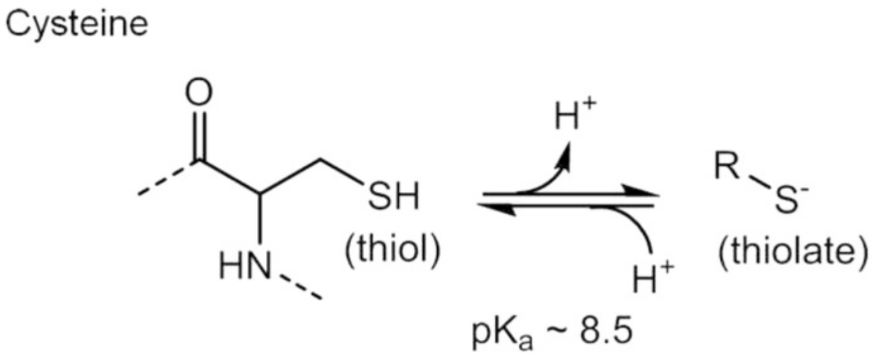
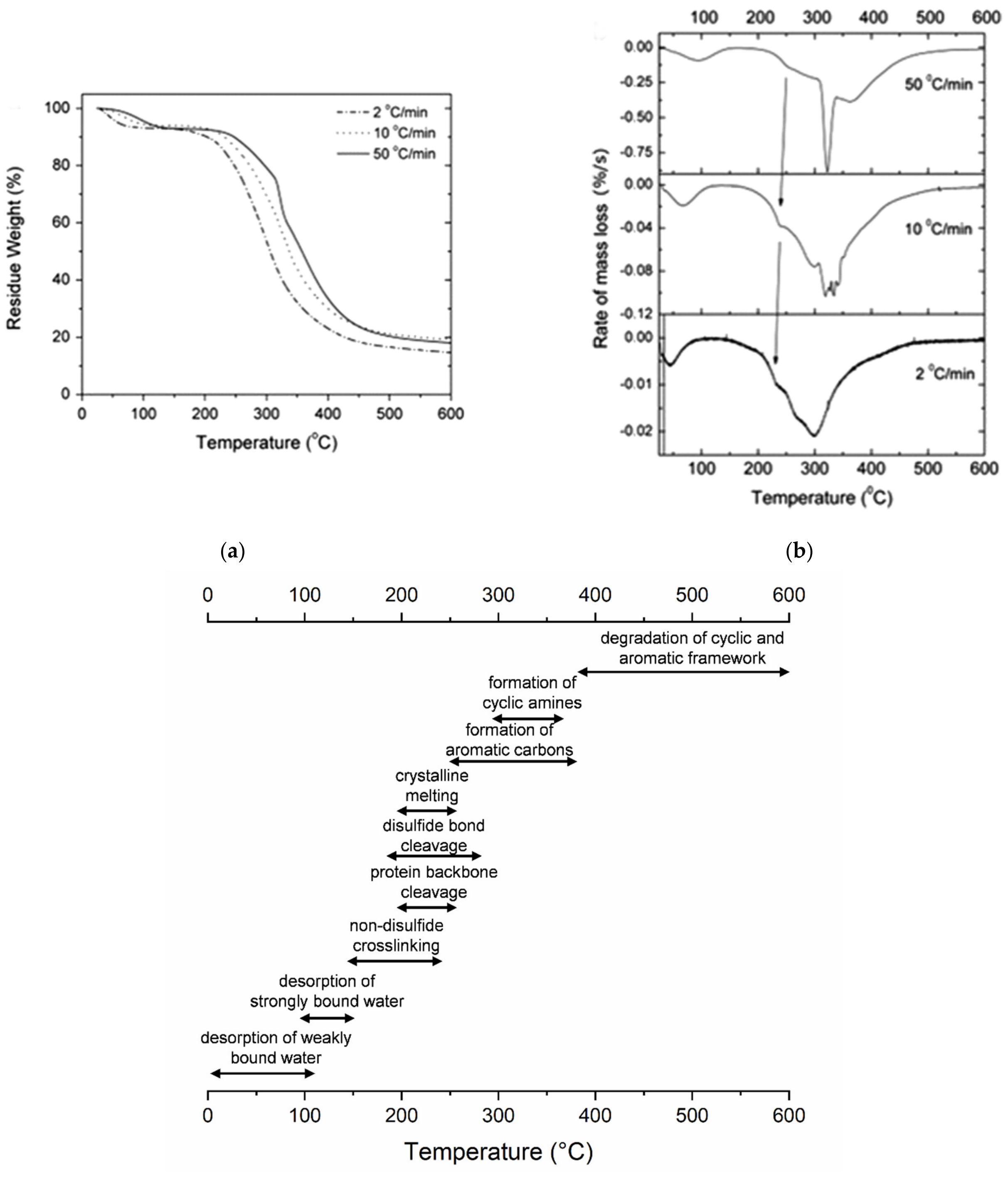


Figure 6. Structures of cysteinyl residues within proteins. The aminoacyl groups are shown to the left, with dotted lines representing peptide bonds towards the next residue on either side. Both protonated (**left**) and deprotonated (**right**) forms of these amino acids are depicted with average pKa values (which can vary in particular protein microenvironments). Reproduced with permission from [75]. Copyright 2015 Elsevier.

The intramolecular and intermolecular crosslinking and the affinity of the keratin protein to degrade at temperatures below the melting transition complicates the interpretation of the thermal analysis. Thermal decomposition of keratinous fibres takes place in three different stages. The first stage is the loss of water mass from the sample that occurs below 200 °C, followed by degradation of the keratin matrix in the range of 200–400 °C, as seen in Figure 7. During this, the release of volatile compounds, such as carbon monoxide, carbon dioxide, ammonia, hydrogen sulphide, sulphur dioxide, methane, and hydrogen cyanide occurs, along with the release of sulphur resulting from the disulphide bond cleavage in the cysteine residue [50,60,76]. This stage is followed by the final stage of decomposition, in the temperature range of 400–650 °C; after the third stage, almost 95.5% of the sample mass has been decomposed [60,76]. The DSC analysis available in the literature shows the relationship between cysteine degradation and the temperature range during which the crystal transition (melting) occurs. This is in line with the relationship of cysteine residues that influence the thermostability of keratin fibres. Breaking disulphide bonds makes the keratinous fibres susceptible to heat and weakens the conformation of the protein, eventually leading to melting.



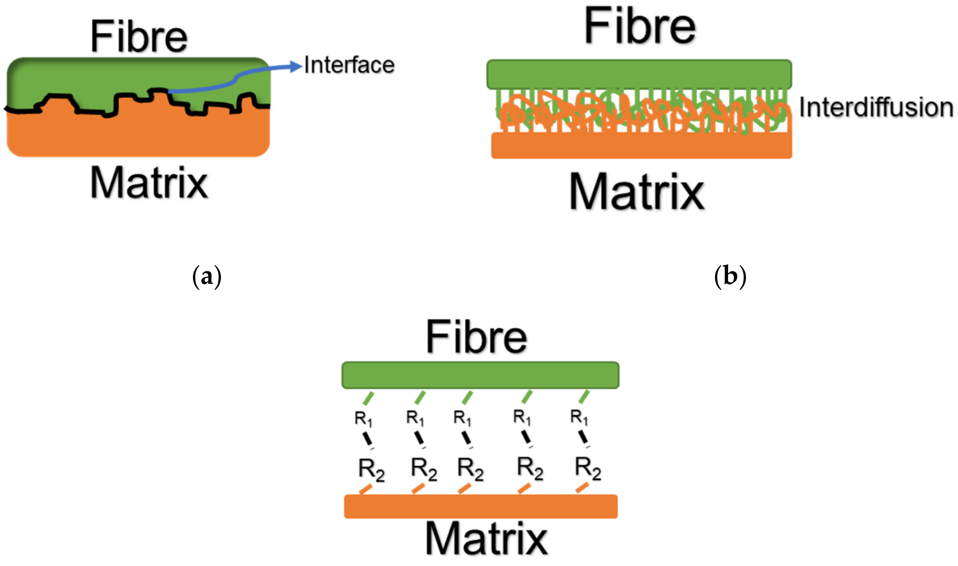
(**a**) (**b**)

(**c**)

Figure 7. (**a**) Thermal gravimetric analysis; (**b**) derivative thermal gravimetric analysis curves of untreated CFF at various heating rates; (**c**) identified physical and chemical changes in feather fibres during pyrolysis. Reproduced with permission from [77]. Copyright 2012 Elsevier.

3.4. Interfacial Adhesion

The fire mechanism, after a fibre is treated and introduced into a composite as a reinforcement, is affected mostly by how it reacts or interacts with the matrix. Fibres interact with the matrix in three possible ways, which can work alone or collaborate to influence the interfacial strength of the type of composite, namely [78]: mechanical interlocking, interdiffusion bonding, and chemical bonding (Figure 8). Different research articles have found that these bonds vary in strength. Chemical bonding between the fibre and the matrix provides the best interaction among the three types. In terms of flame retardancy, it is imperative to hypothesise that upon the application of heat, it would take more energy to break the chemical bond rather than mechanical interlocking. This could help improve the thermal stability and char strength, while promoting the barrier effect relating to the underlying polymer. The char strength, as discussed in [64], is dependent on the heating rate and temperature; both parameters affect the overall energy provided to break the molecular bonds, promoting thermal degradation. As described by Muller et al. [78], the thermal stress experienced by materials due to the heating temperature, especially the heating rate, are crucial parameters affecting the char strength.



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

(**c**)

Figure 8. Fibre–matrix bonding schematics: (**a**) mechanical interlocking, (**b**) interdiffusion bonding, and (**c**) chemical bonding.

3.4.1. Mechanical Interlocking

With a rough and jagged surface, the fibre and matrix experience mechanical interlocking. As a result, there is an increase in the interfacial shear strength, while reducing the slip between the fibres and the matrix. Alkaline pre-treatment has been found to be effective in achieving rough surfaces with cleaner fibres, assisting in better mechanical interlocking [79,80]. Alkali treatment removes fat and wax from the fibre surface, improving its surface roughness and hydrophobicity. During the acetylation of keratinous fibres preceded by an alkaline treatment, esterification occurs because of the acetyl groups (CH3CO-) and the hydroxyl groups (-OH) present on the fibre surface, which leads to an increase in fibre hydrophobicity. Supri Abdul Ghani et al. [79] reported that an alkali treatment of chicken feather fibres could lead to an increase in tensile strength and Young's modulus of the composite material, while affecting its ductility or elongation at break, when compared to the untreated feather composite samples. This could also occur due to exposing more chemical groups or structures to allow chemical bonding or interdiffusion bonding. Compared to untreated feather fibres, a rougher surface of treated fibres was observed in the research, which was believed to have contributed to enhanced interfacial adhesion between the fibres and the matrix. L. Conzatti et al. [81] observed a similar trend with a silane treatment of wool fibres, which helped improve the thermo-oxidative stability with respect to the neat polyolefin matrix. On the contrary, analysis of the mechanical behaviour of the composites revealed that the wool fibres had a reduced reinforcing effect on the polypropylene matrix because of wool fragmentation caused by solarisation. The fragmentation was alleviated by the treatment, and the fibre lengths were not enough to overcome the critical value of the fibre–matrix pair.

3.4.2. Interdiffusion Bonding

For interfaces involving polymers, interdiffusion bonding occurs when polymer chains from each component entangle and intertwine. Zhou et al. [82] describes this phenomenon as being considerable when the reinforcing fibre is compatible with the matrix. An overview of the interface and bonding mechanism helps us draw some similarities between plant fibre behaviour with polymers and animal fibres. Keratinous fibre architecture is thought to form interdiffusion bonds with a compatible polymer. The strength of this bonding is related to the length of the intertwined chains, the degree of entanglement, and the number of chains per unit area [82–85].

3.4.3. Chemical Bonding

Chemical bonding provides significant advantages over mechanical interlocking in enhancing the flame-retardant properties of composites. Chemical bonds, such as covalent and hydrogen bonds, create stronger and more stable interactions between fibres and the polymer matrix, ensuring uniform distribution and firm retention of flame-retardant additives, which enhances overall fire resistance [86]. These bonds facilitate the formation of a cohesive and protective char layer during combustion, which acts as a barrier to reduce heat release and slow down material degradation, crucial for improving flame retardancy. Chemical bonding occurs when functional groups on the fibre surface react with reactive chemical groups within the matrix. The effect of this type of bonding depends on the strength of each chemical bond and the number of bonds per unit area. Pickering et al. [76], in their review, explain two kinds of common chemical bonds, including covalent bonding and hydrogen bonding, and their strength is 200–800 kJ/mol, and 10–40 kJ/mol, respectively. The most common method to achieve chemical bonding between fibres and matrices is to utilise coupling agents.

Moreover, chemical bonds offer higher thermal stability than the physical forces involved in mechanical interlocking, allowing composites to withstand higher temperatures without degrading. This is particularly beneficial for maintaining structural integrity under thermal stress, as demonstrated in various studies [87]. Strong chemical bonds also minimise the rate of thermal decomposition, further enhancing fire resistance.

In terms of char strength, chemical bonds promote the formation of a robust char layer that serves as a thermal insulator and enhances the composite's structural integrity, preventing further flame propagation [88]. This char is denser and more cohesive compared to that formed through mechanical interlocking, providing better protection against heat and maintaining mechanical properties under fire conditions. By fostering strong chemical interactions between the fibres and the matrix, the composite achieves superior flame-retardant properties, enhanced thermal stability, and robust char strength, making it more effective in applications requiring high fire safety standards.

Maleic anhydride polypropylene (MA-PP) is a common coupling agent for fibre-reinforced polymers to improve its mechanical performance. MA-PP can react at one end with the hydroxyl groups on the surface of fibres to form strong covalent bonds. The other end of MA-PP is a polypropylene chain, which can entangle with the matrix during mixing. In addition to using coupling agents, polymers that are compatible with the matrix can be grafted onto some active sites of the fibre surface, such as the thiol groups on cysteine amino acid and hydroxyl sections. Martínez-Hernández et al. obtained PMMA-grafted keratin fibres using a redox initiation system consisting of potassium permanganate, sulfuric acid, and maleic acid [66]. Mu and Liu also achieved PS-grafted horsehair via surface-initiated atom transfer radical polymerisation [89]. These grafted groups can cause interdiffusion with the polymer matrix to enhance the strength of the composite's material. Casadesús et al. laid out the chemical modification of chicken feather fibres to improve their compatibility with thermoplastic biocomposites [89].

4. Techniques to Incorporate Flame Retardancy

In composites, strength plays an important role. Mechanical strength shows a considerable improvement up to a certain fibre loading percentage, while flame-retardant chemical additives are known to reduce mechanical strength, which have been a limitation to the applicability of NFRCs in general and so is the case for keratinous fibre-reinforced composites. Researchers are dedicated to finding new flame-retardant composite strategies to satisfy the growing need for composites that adhere to increasingly strict fire safety requirements [90,91].

Table 4 lists some of the common types of flame retardants. The performance of an intumescent flame retardant depends on the combination of its constituents, namely the carbonising agent or char former, the blowing agent, and the acid source [47,92,93]. Its efficiency depends on the char forming rate and char strength, both of which occur during the condensed phase, therefore research is usually focused on attaining the best combination for char formation. The strategies developed are polymer matrix modification, fibre treatment, or a combination of both. An overview of various methods is discussed below, based on the abovementioned strategies.

Table 4. A few examples of different types of flame retardants.

Flame Retardant	Examples
Active fillers	Hydrotalcite, silica, hydrated oxides, aluminium hydroxides, magnesium hydroxide
Halogenated compounds	Chlorinated, brominated compounds
Phosphorylated compounds	Organophosphates, phosphonates, and phosphinates
Nano-particulated flame retardants	Nanoclay, nanotube, and graphite

4.1. Polymer Matrix Modification

Since the polymer matrix is a major component in composites, incorporating flame retardancy into it is relatively easier than other methods. However, the percentage of FR additives has a best-performing range that is not linear in regard to the loading percentage. As mentioned earlier, FR loading affects the mechanical strength of the composite adversely due to lack of synergism between the additive and the polymer. Properties like the initial decomposition temperature ($T_{5\%}$, temperature corresponding to a weight loss of 5%) and maximum decomposition temperature (T_{max}) undergo shifts due to the incorporation of FR additives. They do improve the residue percentage at a higher temperature, with improved thermal stability.

The incorporation of FR additives into the matrix changes the internal structure, resulting in a change in viscosity and a change in the gel time of the polymer melt, which results in processability difficulties. Without proper synergism between the solid phase additives and the matrix, the homogeneity of the composites is affected, as filtering by the reinforcement layers occurs. It has been found that if the particles are small enough or liquid, composites can be assumed to have a heterogenous performance [94].

Some FRs react with the matrix causing chemical and structural alterations that improve their flammability, which can resolve the previously stated problems. On the other hand, on the negative side, it might change the processing conditions like the curing time and extrusion temperature [63,95]. The flame-retardant mechanism of FRPCs (flame-retardant polymeric composites) through the incorporation of FR additives or reactive FR additives has been well researched [45,96,97]. Current researchers proceed with the assumption that the FR additives and the polymer are well blended and well distributed across the composite. Hence, the flame-retardant effect at each section of the composite remains similar to that of the FR polymer.

4.1.1. Thermoset Polymer Modification

Thermoset resin as a matrix in composites displays FR properties during processing and its usage is accompanied with other undesirable effects, as it lacks chemical bonding between the polymer and the additive. DOPO (9,10-dihydro-9-oxa-10-phosphaphenantherene-10-oxide) derivatives have been identified as having good dispersion and were able to provide improved flame retardancy, with a low concentration of phosphorus of about 2–3 wt.% [98]. Predominantly epoxy or thermoset resins have been used along with synthetic fibres and their fire-reaction properties have been well researched [6,99,100]. Although natural fibres have attracted attention from researchers over the years, only the interaction of plant fibres with thermoset resins and their respective flammability have been studied. Keratinous fibre-reinforced thermoset composites have been extensively studied, but the literature on their flammability characteristics is sparse.

In general, phosphorus–nitrogen synergism can improve the flame retardancy of fibre-reinforced epoxy composites [3,101–103]. The presence of fibres in a composite with flame-retardant additives that act during the condensed phase can experience hinderance and impede the intumescent behaviour. The use of thermoset resins in composites can improve the thermal stability and flame retardancy, as they increase the aromatic content of the matrix. Aromatic structure decomposition provides an insulating surface layer of carbonaceous char, this in turn slows down heat conduction through the composite, resulting in lower flammable gas emissions.

4.1.2. Thermoplastic Polymer Modifications

Thermoplastic polymers ranging from commodity polymers to high-performance engineering polymers have been used as the matrix for several keratinous fibre-reinforced polymeric composites. For modifying thermoplastic matrix DOPO derivatives, phosphorus–nitrogen compounds, metallic oxides like aluminium hydroxide, and nano materials have been employed. Tawiah et al. [104] developed a novel phosphorus FR Phenyl phosphonic 3(2-aminoben-zothiazole) (P-TAB) and added it to PLA using combinatory solvent mixing to enhance its flame retardancy and mechanical properties. They further incorporated varying percentages of recycled wool fibres, which aided in attaining a V0 rating in the UL-94 test. The P-TAB/PLA composites did show a drop in the peak heat release rate by almost half in comparison to PLA. Adding 20% recycled wool to P-TAB/PLA composites reduced the PHRR from 408 kW/m^2 to 300 kW/m^2 compared to PLA, while improving the tensile strength of the composites by 17%. It has been noted that the use of APP leads to a significant drop in mechanical strength, which has been compensated for by FR additives like Ni–PO (nickel-based metal–organic frameworks), OMMT (organ–montmorillonite), and PN-DOPO (a DOPO derivative), owing to their higher surface volume, as compared to APP, in the presence of keratinous fibres with a hollow architecture, which would be an advantage for the composite's performance.

Chicken feather fibre (CFF) was also employed for reducing the flammability of polymeric materials. As a matter of fact, the utilisation of chicken feathers for the thermal and mechanical enhancement of polymers has been investigated for several decades [16,77] due to the high aspect ratio, heat resistance properties, and cost reduction potential. Barone and Schmidt [16] suggested that CFF with little modifications can attain good stiffness and specific strength, hence making it an effective form of reinforcement in composite applications. Senoz et al. [77] studied the changed physical and chemical properties of CFF during pyrolysis, for high temperature applications. However, only recently, researchers have begun studying CFF properties for flame-retardant applications. Kuru et al. [105] investigated the effect of chicken feather barbs and a boron compound combination on the FR properties of a polyester composite prepared via direct compounding. The composite with 8 vol% CFF and 8 vol% boron oxide accomplished a ~26% reduction in the LOI compared to the neat polymer. The flexural strength of the composite was continuously improved up to 8 wt.% of the fibre loading but, after the boron compound addition, the reinforcing effect from the fibre addition was diminished. The research on the use of CFF as a reinforcement [16,64] commonly showed that CFF is more effective than wool fibre for strengthening polymers because of its significantly higher aspect ratio (Table 1). On the other hand, Wrześniewska-Tosik et al. [64] incorporated ball-milled CFF (18~185 µm) into the PU, allowing the fibre to avoid undergoing the complicated sorting process. Owing to the reduced CFF volume after milling, 10~17 wt.% of the CFFs were homogeneously mixed with polyol, resulting in a PU composite foam, with the particle sizes in the range of several tens of µm. With only a 17 wt.% fibre addition to the composite, a 34% improvement in the LOI was achieved compared to the neat PU.

4.2. Fibre Treatment

The flammability of fibre-reinforced composites, as explained in Section 3, is greatly influenced by the interface region between the polymer region and the reinforcement fibre. The capillary effect involving keratinous fibres, otherwise known as the wicking effect, intensifies the burning behaviour. Fibre wetting with polymer melts occurs at the combustion temperature, which results in rapid oriented flow of the polymer melt along the fibre surface. This aids the fuel supply and intensifies the combustion of fibre-reinforced thermoplastic composites, more than that of a reinforced thermoset composite. Fibre treatment is suggested to keep changes in the processing conditions to a minimum. This approach is suitable for keratinous fibres or natural fibres as they are easily functionalised with FR additives [106], unlike synthetic fibres. Synthetic fibres have fewer polar groups and have an excessively inert surface, which hinders interfacial modifications unlike keratinous fibres, making them an excellent playground for the creation of novel and greener flame-retardant adjuvants.

Previous research has established that fibre surface modifications can enhance the natural fibre/matrix interfacial bonding [107], thus providing better mechanical properties. The fibre's surface morphology, chemical structure, and matrix polarity are primarily responsible for mechanical and chemical bonding at the interface [108]. In terms of specific mechanical properties, natural fibres show comparable or better results than those of many synthetic fibres (e.g., glass fibres) [26,107,109], due to their lower density. Increased utilisation of naturally available materials is needed to reduce the environmental impact and the energy required to manufacture composites, which is high for synthetic fibres.

Natural fibres are amenable to modifications due to the presence of stabilised hydrogen bonds from keratin, cellulose, and lignin, depending on their original sources. Processing fibres to activate hydrogen bonds at interaction sites can improve the interfacial adhesion with the polymer matrix. Chemical alterations, like chemical bleaching, can improve surface roughness, enhancing the possibility of mechanical interlocking at the interface. The generation of heat from chemical reactions enables sequential loading of materials onto the fibres, creating modified fibres that have undergone structural or chemical modifications [17]. Therefore, fibre processing techniques are of significance for obtaining improved composite properties, as explained in a few studies [110–112].

It has been stated that flame-retardant-treated fibres do not affect the gas phase mechanism of the composite's thermal decomposition. However, FR-treated fibres increase the FR additive concentration at the interface rather than in the matrix. Upon thermal decomposition, the increased surface roughness and reduced surface energy helps promote char formation along the fibres. This, in turn, reduces the wicking action promoting improved flame retardancy for composites. It has been noted that phosphorus-based FR additives help produce char along the fibres creating a perfect fibre shield, protecting the underlying material against heat, oxygen, and degraded volatiles.

Patented work conducted by Bhattacharyya et al., relating to the treatment of keratinous fibre with a reactive amine and an inorganic acid, acknowledges how fibre treatments can be effective [113]. Kim et al. [53] presented the possible application of keratinous fibre as a flame-retardant additive; several approaches have been taken using different types of animal fibres to impart flame retardancy. Although most types of keratinous fibres can be used for this purpose due to the similarity in their molecular structure, typically wool fibre and chicken feather fibre have been investigated more frequently. Kim et al. used coarse wool fibre and APP for PP modification. Specifically, 30% of PHRR reduction compared to that of PP was achieved by adding only 30 wt.% wool fibre. Furthermore, the extra addition of 20 wt.% of APP led to an 81% reduction in PHRR and a V0 (UL-94) grade. As exemplified by another study conducted to investigate the difference in the FR properties between plant and animal fibres, Rabe et al. [114] used two types of natural fibres, i.e., coconut fibre and waste animal hairs from the beam house tanning process (keratinous fibre), for a thermoplastic starch-based polymer (TPS) modification. Significantly changed flame retardancy and mechanical properties were demonstrated before and after the fibre addition. As shown in Figure 9, the coconut fibre addition was more efficient than that of the keratinous fibre (KF) addition in regard to improving the mechanical properties of the composite, although every type of fibre addition resulted in reduced tensile strength and elongation at break. On the other hand, in terms of the cone calorimeter test, keratinous fibre tended to provide better flame retardancy than coconut fibres, although the composites could not gain a UL-94 grade. After the addition of 15 wt.% APP, the composite with 15 wt.% KF achieved a V0 grade, whereas the composite with coconut fibre gained a V2 grade. Despite increasing the modulus for every APP/natural fibre composite, the tensile strength and elongation at break are reduced drastically to ~48% and ~96%, respectively, as compared to those involving a TPS. This demonstrates that animal fibre utilisation is advantageous for flame retardancy compared to that of plant fibre, but several limitations, such as the reduction in mechanical properties and insufficient flame retardancy, need to be overcome.

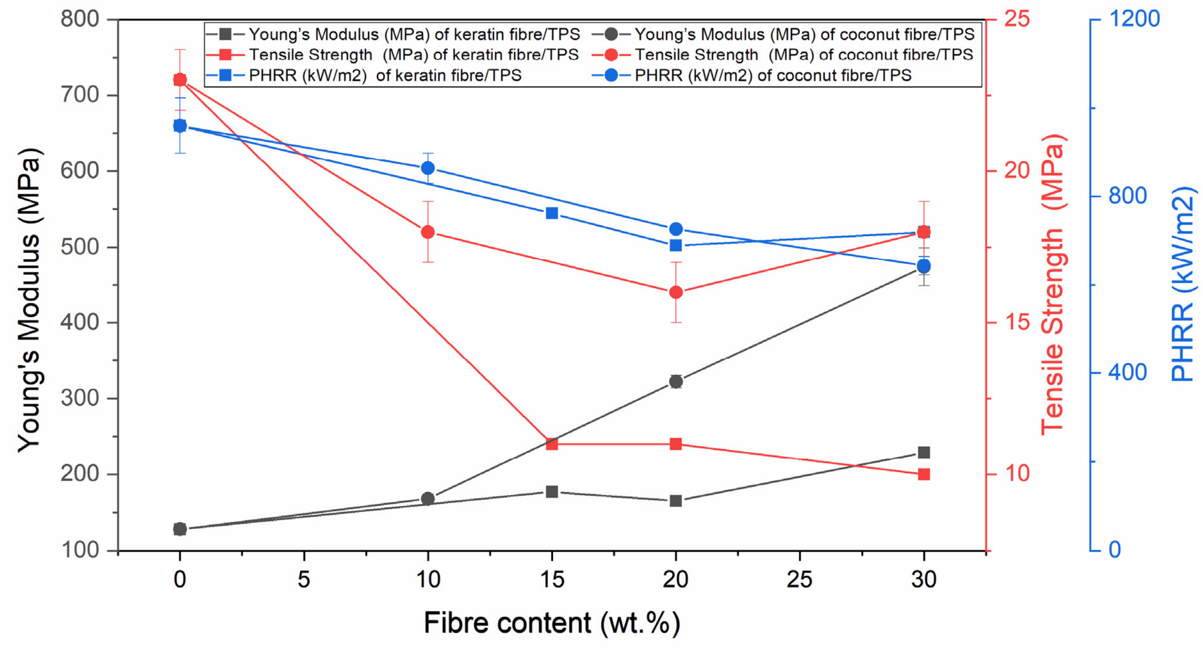


Figure 9. Mechanical and fire-reaction properties of natural fibre-modified TPS composites. Data adapted with permission from [114]. Copyright 2019 MDPI.

A similar result was reported when ATH [90] was used as a FR additive for a keratinous Fibre/PLA modification. While 3 wt.% KF and 30 wt.% ATH allowed the reinforced PLA composite to gain a V0 grade, the tensile strength of the composite decreased to 19% compared to neat PLA. In order to address the drop in strength, Kim et al. used a compatibiliser [53,90], maleic anhydride-grafted PP (MA-g-PP), for improved interfacial bonding between the fibre and the matrix, PP. In fact, MA-g-PP incorporation is widely used for improving the mechanical properties of plant fibre/polymer composites and it has also been effective in regard to keratinous fibres. Owing to the addition of 3 wt.% MA-g-PP, all PP composites modified with either flax or wool fibre exhibited a simultaneously increasing modulus and strength in the tensile and impact tests. Furthermore, every natural fibre/PP composite with 15 wt.% APP achieved a higher strength than that of neat PP in both the tensile and impact tests. This demonstrated that the strength drop due to the APP addition can be mitigated by improving the compatibility between the fibre and the matrix, although the strength improvement is dependent on the types of fibres and polymer matrix involved. As shown in Figure 10a,b, both flax and wool fibres are evenly distributed in the composite and exhibit good bonding with the matrix, by presenting a minimal number of fibre pull-outs. On the contrary, because of the APP addition, there is an increase in the number of fibres pulled out (yellow circles), as shown in Figure 10c,d, as compared to that shown in Figure 10a,b, but it is also noticeable that most of the fibres are still firmly combined with the polymer matrix, demonstrating strong bonding. Aside from the mechanical properties, the combination of APP and natural fibre in the presence of MA-g-PP was also effective for improving the flame retardancy of the composites. Wool fibre was more effective than flax fibre as an FR additive, which shows good agreement with the research using keratinous fibre-based FRs [12,114]. While the composite with 25 wt.% flax fibre and 15 wt.% APP could not achieve a UL-94 grade, despite the 65% reduction in the PHRR compared to that of the PP, the composite with 25 wt.% wool fibre and the same APP loading gained a V0 grade, along with a 68% reduction in the PHRR.

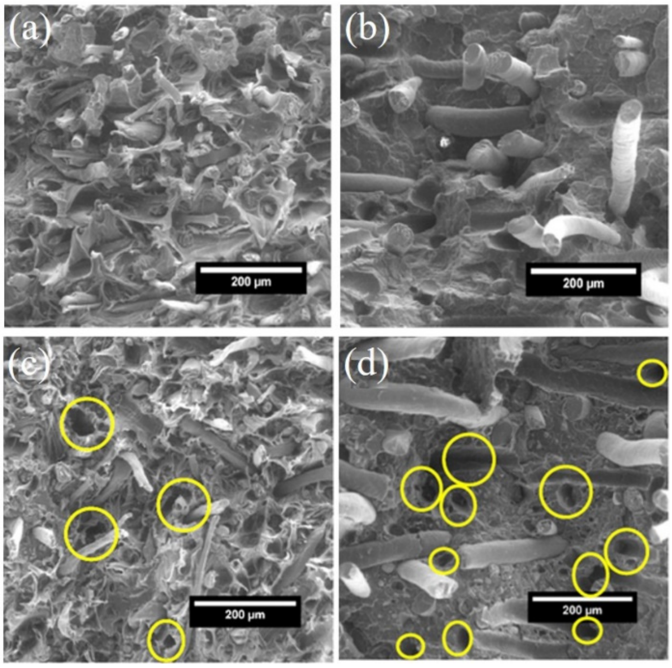


Figure 10. SEM images of the tensile fractured surface of various types of composites: (**a**) flax/PP, (**b**) wool/PP, (**c**) flax/APP/PP, and (**d**) wool/APP/PP. Yellow circles in (**c**,**d**) show fibre pull out on composites' fractured surface. Adapted with permission from [90]. Copyright 2017 Elsevier.

While CFF was successfully applied for flammability reduction with polymers via the matrix treatment method, research exploring the benefits of the fibre treatment method has also been conducted. Jung and Bhattacharyya [9,10] treated keratinous fibres with ethylenediamine phosphate (EDAP), i.e., wool fibre and chicken feathers, as shown in Figure 11. They sequentially infiltrated the phosphoric acid and ethylenediamine into the fibres to accomplish EDAP loading inside and outside the fibres (Figure 11b,c). They demonstrated that keratinous fibres could be used as a container holding all types of intumescent flame-retardant constituents, namely the acid source, blowing agent, and char former. Therefore, this technique has an advantage in that it can control the loading of all the IFR constituents by adjusting the amount of phosphate and keratinous fibre. Apart from the loaded phosphate, keratinous fibres also play an important role as a blowing agent and char former due to the abundant nitrogen and carbon sources in the fibre. By adding the flame-retardant CFF (FR CFF), they achieved a V0 UL-94 grade for the PP composite with 20 wt.% EDAP and 20 wt.% keratinous fibres [9]. More specific research using FR CFF on the potential cost reduction of a PP composite was performed by the same research group [17]. Notably, the FR CFF-modified PP composite successfully held its tensile strength compared to that of the neat PP, along with its V0 grade.

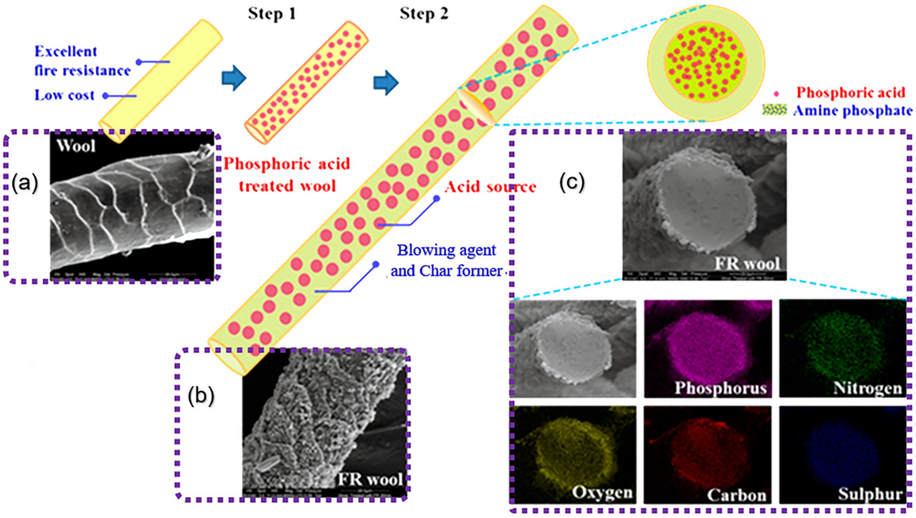


Figure 11. Schematic diagram of the fabrication of FR wool and SEM images of: (**a**) untreated wool, (**b**) FR wool, (**c**) FR wool surface. Adapted with permission from [9]. Copyright 2018 American Chemical Society.

The complicated sorting process for avian fibres can limit their practical application, despite their possible thermal and mechanical reinforcement abilities. Unlike animal hairs, feathers composed of several parts, such as the barb, barbule, shaft, and rachis, possibly lead to irregular stress transfer when they are incorporated into a polymer composite [105] if they are not sorted properly. Therefore, various approaches, such as chemical (hydroxide) treatment [115] and ball milling [116], have been applied due to their ability to create a uniform shape. To address this question, the whole part of feather fibres without fibre sorting processes or special pre-treatments was used. The size of the final product was controlled along with several factors, such as the concentration of chemical compounds, treatment temperature, and time (Figure 11). Despite the chemical treatment, the interfacial bonding between the FR wool and the matrix was strong enough to protect against a reduction in tensile strength, which is a known disadvantage caused by the addition of phosphorus-based flame retardants. This result showed good agreement with the previous research [117,118] involving plant fibres, which helps us conclude that fibre treatment is more effective than matrix modification to mitigate the tensile strength drop. Although this fibre treatment method successfully reduced the flammability and drop in tensile strength, the decrease in ductility due to a large amount of fibre loading needs to be solved. Furthermore, a method to promote a higher FR performance in natural fibre should be investigated, with lower synthetic chemical compound usage.

The nano silicate, montmorillonite (MMT) [65], was used for the surface treatment of FR CFFs. However, it was concluded that although the nanomaterials were effective in reducing the flammability of the polymeric materials, they could not provide sufficient self-extinguishing properties due to the lack of char networks suppressing the air and fuel transfer to the under layers, during combustion. However, the limitation of the nanomaterials as an FR additive was overcome by its hybridisation with keratinous fibres (Figure 12a). After the hybridisation, the performance of the FR CFFs was significantly improved due to the silicate-reinforced char formation (Figure 12c). The intumescent char generated by the FR CFFs effectively prohibited the MMT aggregation during the composite's combustion, as the MMT particles on the fibre expanded resulting in carbonaceous char formation without aggregation. As a result, the addition of only <0.5 wt.% MMT led to a ~27% reduction in EDAP usage for the equivalent flame retardancy. By adding 35 wt.% of modified FR

CFF (with 0.4 wt.% MMT), the PP composites achieved an 82% reduction in the PHRR and a V0 grade in the UL-94 test (Figure 12d). Furthermore, phosphate efficiency was measured to compare the FR performance in respect of the same amount of phosphate utilisation (Figure 12d). Based on the achieved values, the modified FR CFF exhibited a 14% higher efficiency for PP modification, as compared to commercial intumescent APP. In addition, the FR CFF successfully achieved an 85% increase in the tensile modulus with a minimal strength drop as compared to that of neat polypropylene samples. For a more environmentally friendly approach, Cheng et al. [119] used phytic acid (PA) instead of synthetic phosphate for wool fabric modification. The LOI of the treated fabric increased proportionally in regard to the increasing PA loading of the fibre and the tensile strength of a single fibre was not significantly affected by the PA loading. This highlighted the possible application of natural phosphorus compounds for FR modification. On the other hand, Mosnáčková et al. studied how to overcome the ductility drop due to the addition of keratinous fibre [120]. In that study, the reduction in elongation caused by the addition of hydrolysed wool ranged from 1 to 2 orders of magnitude, depending on the fibre quantity in the PLA composite. To overcome this, acetyl tributyl citrate (ATBC) and poly(3-hydroxybutyrate) (PHB) were used. Although the keratin loading increased the stiffness of the composite, the addition of ATBC (acetyl tributyl citrate) led to a ductility improvement by exhibiting a sufficiently high elongation at break of >140% until the keratin content reached up to 20 wt.%. This approach can be useful to widen the application range for keratinous fibre utilisation for FR polymer composites.

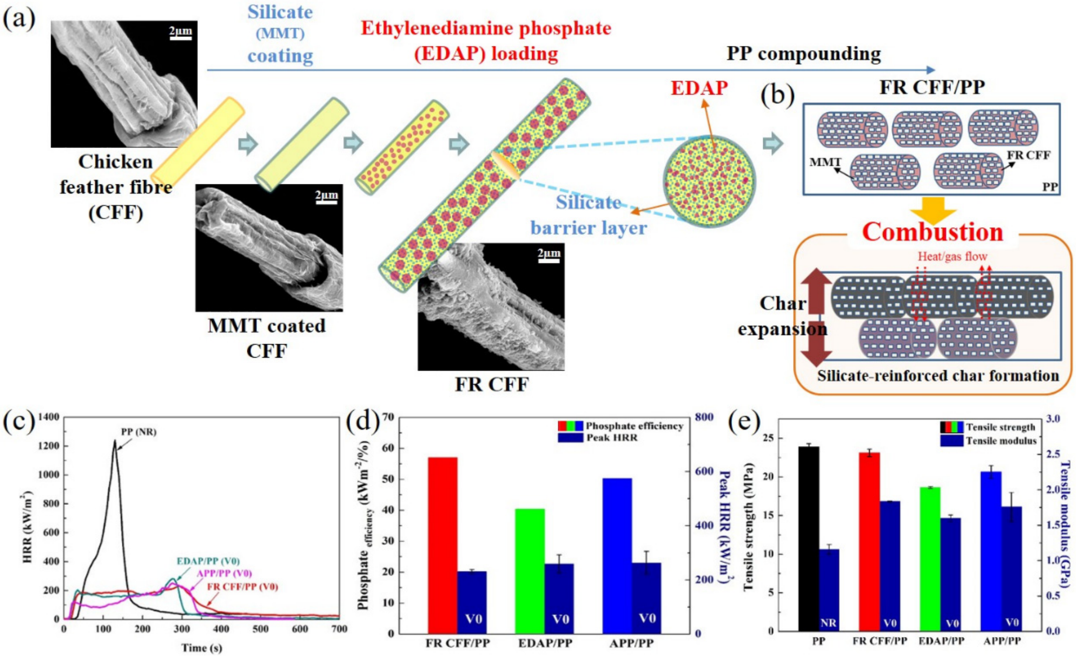


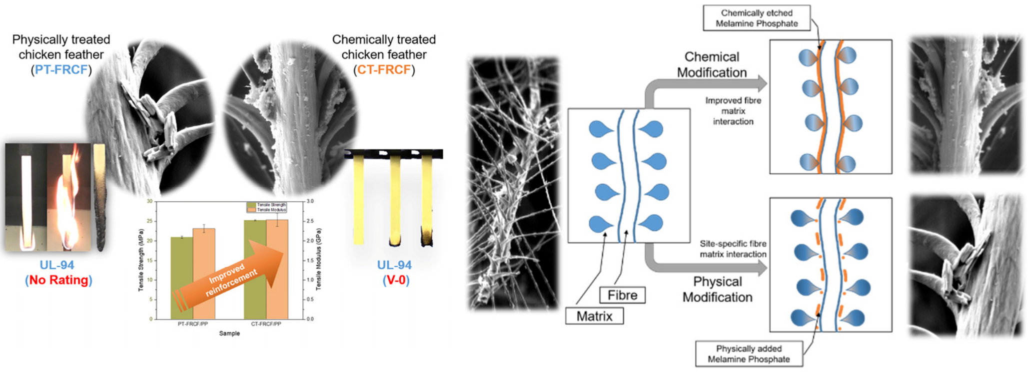
Figure 12. (**a**) Schematic diagram of fabrication of FR keratinous fibres and SEM images of (**b**) the schematic of the method, (**c**) evaluation of the heat release rate, (**d**) phosphate efficiency for each treatment against their respective peak heat release rates, (**e**) mechanical parameters of PP composites with various flame retardant fillers. Adapted with permission from [65]. Copyright 2021 Elsevier.

In the previous sections, experimental studies highlighting the flammability and mechanical properties of keratinous fibre composites that have achieved flame retardancy by incorporating different methods were discussed. In Section 3.2, it was outlined how varied the flammability requirements are for different applications and, hence, that the methods cannot be ranked or generalised as being the best out of all those available. Some keratinous fibre-reinforced composites are listed in Table 5 with their fire-related and mechanical performance for comparison and a selection of composite systems are listed that can be applied to suitable applications. Selection criteria and performance matching on aspects like the heat release rate, delayed time to ignition, and mechanical tensile strength, etc., could help drive research on implementing keratinous fibre composites into different applications.

Table 5. Fire-related performance and mechanical performance of keratinous fibre-reinforced composites.

Ref.	Fibre Type	Matrix	Flame Retardant	Thermal and Flammability Test	Mechanical Properties
[64]	Chicken feathers	Single rigid foams (SRPUF)	Fyrol PNX; expandable graphite (GE); AlOH; zinc Oxide; APP	PHRR: −21% (for 10% keratin fibre); −54% (keratin + GE); −59% (keratin + GE + Fyrol)	
[121]	Chicken feathers	TPU	Melamine derivatives (MC, MP, MPP)	PHRR: −21% (for 20% MC + chicken feather + TPU); −43% (for 20% MP + chicken feather + TPU); −48% (for 20% MPP + chicken feather + TPU)	
[10]	Chicken feathers	Polypropylene	EDAP	PHRR: −80% (for 30% chicken feather + 20% APP); −82% (for 20 wt.% APP)	Tensile strength: −6% (PP + FR-chicken feather);
[122]	Chicken feathers	Cotton fabric	P-N flame retardant, Borax, Boric acid	LOI: 30.1 for P-N flame retardant, 39.9 for combination of P-N, boric acid, borax	
[17]	Chicken feathers	PP	Melamine derivatives (MP); APP	FGR: 1.75 for chemical treatment and 2.21 for physical treated CF–PP composites; 8.76 for PP	Tensile strength: −8% (PP + FR-chicken feather);
[29]	Chicken feathers	PP	Melamine derivatives (MP); APP	PHRR: −22% ((for water treated FR- chicken feather + APP); FGR: −27% (for water as solvent in treated FR- chicken feather + APP)	Tensile strength: −14% (PP + FR-chicken feather);
[9]	Wool fibre, chicken feathers	Polypropylene	EDAP	PHRR: −30% for chicken feathers -PP composites compared to wool–PP composites	Tensile strength: FR-Wool/PP performed better than FR-Chicken feather/PP composites
[53]	Wool fibre	PP	APP	PHRR: −30% (for 30% wool fibre + 20% APP); −82% (for 20 wt.% APP)	Tensile strength: +16% (PP + wool); −15% (PP + wool + APP)
[12]	Wool fibre	PP		TGA: 1.1 wt.% residue (neat PP); 7.9 wt.% residue (30 wt.% wool + PP)	Interfacial shear strength: +4% with addition of 2 wt.% MA-PP
[123]	PP fibre	Wool fibre		UL-94: V0 grade achieved (for 85 wt.% wool +15 wt.% PP fibres)	Tensile strength: +7.2% (wool + PP)

The particle size of treated flame retardants has been seen to play an important role in improving the dispersion of flame-retardant-treated fibres through the matrix. It was observed by Mishra et al. that similar particle size compositions do have a significant effect on the flammability and mechanical performance of the composite (Figure 13). The cohesiveness between PP and treated chicken feathers was identified to be due to the availability of phosphorylated polar groups and crosslinking via P/P–N/P–O bonds. The development of tenacious polyaromatic intumescent char improved the flame retardancy of chemically treated over physically treated chicken feathers, where the particle size of melamine phosphate impregnation was found to be ~19 times higher than that with the chemical process, hence placing emphasis on the particle size of the fibre treatment methods.



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

Figure 13. (**a**) UL-94 and mechanical performance of treated composites, (**b**) schematic model of fibre modification process. Adapted with permission from [17]. Copyright 2023 Elsevier.

5. Future Directions

The long-term durability of KFRCs: There is limited understanding of the long-term durability of keratinous fibre-reinforced composites (KFRCs). Future research should focus on the longevity and performance of these composites under various environmental conditions over extended periods.

Environmental impact assessments: Comprehensive studies assessing the environmental impact of using keratinous fibres in composites are lacking. This includes an entire lifecycle analysis, from sourcing raw materials to end-of-life disposal or recycling. Research is needed to quantify the ecological footprint, such as the carbon and water footprint, of these materials.

The scalability of fire-retardant methods: The scalability of the current fire-retardant methods for KFRCs is not well documented. Investigating scalable and cost-effective fire-retardant treatments that can be applied in industrial settings is essential for broader adoption.

Analytical and predictive modelling: There is a need for developing robust analytical and predictive models to visualise the thermal response and fire-induced damage to KFRCs. These models would help in understanding the complex thermal decomposition mechanisms and optimising the design for better fire resistance and mechanical performance.

The interplay between fire resistance and mechanical strength: More in-depth research is required to understand the interplay between fire resistance and mechanical strength in KFRCs. This involves studying how various fire-retardant treatments affect the structural integrity and mechanical properties of composites.

Novel fibre treatments: Exploring new fibre treatment methods that enhance both mechanical and fire-retardant properties is necessary. Research could focus on developing eco-friendly treatments that do not compromise the biodegradability and sustainability of the fibres.

These research gaps highlight critical areas that need to be addressed to advance the development and application of keratinous fibre-reinforced composites in various industries. Addressing these gaps will contribute to creating safer, more sustainable, and high-performance composite materials.

6. Conclusions

This review enables one to engage keratinous fibres as a flame-retardant form of reinforcement for polymeric composites. The fire-reaction mechanisms and requirements for deciding on the process to impart flame retardancy have been explained. The flame-retardant (FR) methods, such as polymeric modifications with FR, FR loading on the fibre surface, and their combination, have been briefly laid out in order to have a better understanding of such processes. Their advantages and disadvantages have been discussed, although some adverse effects related to interfacial strength and processability are outlined. This review helps in understanding what a well-balanced keratinous fibre-reinforced polymeric composite with flame-retardant capabilities would look like.

To minimise the adverse effects of FR additives, low concentrations should be utilised for better performing fibre-reinforced composites. Nanomaterials and hybrid FR systems have been identified to avoid a loss of strength and improve flame retardancy. Synergism in regard to the abovementioned methods is also a promising area to look into for improved flame retardancy.

Most important of all is the lab-scale manufacturing of most FR additives, the scale and cost-effectiveness of such processes limit their applicability. From the methods under review, it can be realised that the synergies between the polymer matrix of intrinsic flame retardants and FR-treated fibre surfaces can help compensate for the loss of strength experienced in most FR systems. The relationships between the test results, such as the cone calorimeter, UL-94, LOI, and TGA, help to save a lot of time and resources as it is cost intensive and time consuming to conduct a full-scale fire experiment for each scenario. Therefore, developing analytical and predictive models to visualise the thermal response and fire-induced damage are some areas to work on in future research.

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