Review

Fire-Safe Biobased Composites: Enhancing the Applicability of Biocomposites with Improved Fire Performance

Dan Zhang

School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China; danzhang@njust.edu.cn

Abstract: Research has recently transitioned from the study of fossil-based materials to bio-sourced ones, following the quest to achieve sustainability. However, fire presents a unique hazard to bio-composite materials, which limits their applicability in various sectors. This necessitates an in-depth assessment of the fire behaviour of biobased composites used for specific applications. Improving the fire properties of bio-composites with flame retardants tends to reduce mechanical strength. Therefore, this review focused on biobased composite materials for packaging, structural, automotive, and aeronautical applications that are both mechanically strong and fire safe. It was noticed that the interfacial bonding between the matrix and the reinforcement should be optimized. In addition, optimum amounts of flame retardants are required for better fire performance. This article covers flame retardants for biobased composites, the optimum amount required, and the extent of improvement to the thermal stability and flammability of the materials. This research will help material scientists and the like in their selection of biomass feedstock, flame retardants, and general materials for different types of applications.

Keywords: renewable resources; flammability; biobased composites; packaging materials; automotive and aerospace materials

1. Introduction

The continual utilization of composite materials for applications in the aerospace, automotive, and construction industries, etc., has brought about a tremendous increase in the quantity produced annually [1,2]. These materials are preferred to petroleum-based ones due to their biodegradability, recyclability, and their part in the circular economy model [3,4]. Following this drastic increment, the global market value of composite materials is predicted to increase by 81% in 2023 [5]. Composite materials are made up of two or more components, a matrix and a reinforcement, that have dissimilar physical and chemical properties [6]. The matrix forms a greater part of the composite and serves as the load-bearing element of the material. The reinforcement, on the other hand, binds the matrix particles and provides strength to the composite.

The combination of the constituents produces a robust material with unique properties, which outperforms that of the matrix [7]. Composite materials generally have improved mechanical properties, durability, and weight, as well as low cost.

According to Perroud et al. [8], although the addition of reinforcements to matrices such as polymers improves the mechanical properties, they do not show any significant enhancement in the fire properties. On the other hand, the addition of flame retardants to such matrices increases fire safety but tends to be detrimental to mechanical properties [9]. Due to the extensive use of composite materials for packaging, transportation, structural applications, etc., it is highly critical to assess their fire behaviour to bestow fire safety in such products. It is also of the utmost importance to maintain a balance between mechanical and fire properties.
Researchers have reported that synthetic polymers such as nylon, polyethylene, etc., which are made from fossil fuels, burn rapidly and emit toxic gases such as carbon monoxide, methane, and ethylene that are harmful to the environment [10,11]. Therefore, in recent years, more attention is being drawn to bio-sourced polymers that are derived from renewable and environmentally friendly biomass materials [12]. The biomass materials usually used for the production of composites are derived from waste; for example, food waste such as sugarcane bagasse, wheat gluten, coconut husk, zein, etc. [13–15]. The production of such novel materials promotes waste management in the sense that the waste is converted into high-value products that are useful to society [16]. It has been shown that these types of polymers have a relatively low heat release rate (HRR) compared to their synthetic counterparts. For instance, in the work of Das et al. [17], the maximum HRR of neat polypropylene (a synthetic polymer) was 1054 kW/m², while that of pristine gluten-based polymer had a maximum HRR of 703 kW/m² [18].

To obtain the fire properties of such composites for flammability assessments, fire experiments are conducted. The apparatus for such tests can either be small-scale, bench-scale or room-scale, depending on the purpose of the tests [19,20]. For developmental research purposes, small- and bench-scale thermal analysis and fire experiments, such as thermogravimetric analysis (TGA), microscale combustion calorimetry (MCC), and cone calorimetry experiments, are used [21]. These experiments provide information on the most vital measure of material fire safety, which is the heat release rate. Supplementary information such as heat release capacity, total heat release, and char yield is obtained from the MCC, whereas the cone calorimeter uniquely records the time to ignition, mass loss rate, and smoke production [22]. In addition, the limiting oxygen index test, which shows the minimum oxygen required for combustion, and flammability rating tests, i.e., the Underwriter’s Laboratory tests, are also carried out for assessments.

The depletion of fossil fuels has considerably affected their sustainability and decreased the dependence on products derived from them [23,24]. In recent years, bio-based resources are being exploited as a viable alternative to fossil-based ones, especially in the production of composites for various applications [25]. The fire safety of biobased composites is crucial for their safe and prolonged use; hence, this article critically reviews the fire behaviour of bio-based composites for specific applications, such as packaging, automotive, and structural applications. The flame retardants used and the optimum amount needed for excellent fire performance are also analysed. The effect of these additives on the mechanical properties of the composites is also addressed, especially for structural applications. This research will shed more light on one of the major issues in composite production: the fire safety of biobased composites and the reduction in mechanical properties resulting from the addition of flame retardants.

2. Fire Behaviour of Biobased Composite Materials for Packaging Applications

The pollution from non-biodegradable plastics arising from fire outbreaks caused by plastics used as packaging has heightened interest in the use of biobased polymers for packaging [26,27]. In 2015, a horrifying fire gutted a packaging materials manufacturing plant and caused considerable damage. An investigation by fire safety personnel indicated that the fire was caused by the ignition of packaging material, including bubble wrap, foam rolls, and cardboard. Generally, most of the packaging materials were petroleum-based, which ignited and combusted at a very fast rate [28]. This instance clearly justifies the need for fire-resistant packaging materials that are not completely fossil-based. The fire behaviour of three biobased composites is presented in Table 1, which reveals the improvement in fire resistance when biobased retardants are added.

Over the last decade, polymer composites have been used as packaging materials for food, drugs, household items, etc., to increase their shelf life [29,30]. This has been achieved by protecting them against contamination from microbe attacks, moisture, and oxygen penetration [31]. Due to the high demand for packaging materials (31% of plastics produced globally are used for packaging), the use of non-biodegradable fossil-based
products has become an environmental concern [32]. Therefore, more attention is being paid to biobased packaging materials that are eco-friendly, recyclable, and sustainable. Biobased composite materials for packaging are selected based on durability, their capability to act as a gas barrier, and their high resistance to heat, impact resistance, and flexibility [33]. Reinforcing agents such as fibres and fillers are incorporated into polymers to enhance their performance in packaging. Some of the most recent research work on the types of biobased polymers used for packaging, the flame retardants used, and their performance, is critically analysed in this section.

Younis et al. [34] developed a packaging paper from bagasse reinforced with calcium carbonate (CaCO$_3$) and sodium bicarbonate (NaHCO$_3$). Starch was used as a binder to improve the mechanical properties, absorption ability, and interfacial bonding between the fibre and the fillers. The bagasse paper sheets were coated with 0.5% cyclolephosph(V)azine/1.5% CaCO$_3$ solution, 1.5% NaHCO$_3$ solution, and cellulose nanocrystals (CNCs) mixed with different concentrations of starch. The authors conducted a thermal analysis test using TGA. Flammability tests were carried out using a 45-degree flammability test to estimate the ignition time and the total time of burning of the samples. The test samples were positioned at a 45° angle and exposed to horizontal flames from a burner. The char length and oxygen index were also obtained. The thermal analysis showed that the increase in starch concentration from 3.5% to 5% improved the thermal stability and increased the decomposition temperatures from 110 °C to 248 °C. The highest char residue of 54% was seen in the addition of CNCs. From the flammability tests, it was seen that the CaCO$_3$ and NaHCO$_3$ stopped combustion after 5 s and the samples containing 5% starch and 10% CNCs obtained an LOI (limiting oxygen index) value between 27% and 29% compared to that of the control (19%). It was envisaged that the coating containing all the constituents formed a film that protected the surface of the bagasse paper from the flames, limited the absorption of air through the paper, and enhanced the mechanical properties. Figure 1 shows the burning rate of the prepared samples.

![Figure 1. Burning rate of bagasse paper. Notes: SK0—neat bagasse paper, SK1—bagasse paper filled with 3.5% starch, SK2—bagasse paper with 3.5% starch and 0.5% p-chloroaniline dimer, SK3—bagasse paper with 3.5% starch and 0.5% Aniline dimer, SK4—bagasse paper filled with 5% starch, SK5—bagasse paper filled with 5% starch, 1.5% NaHCO$_3$ and 1.5% CaCO$_3$, SK6—bagasse paper filled with 5% starch, 0.5% Aniline dimer, 1.5% NaHCO$_3$ and 1.5% CaCO$_3$, SK7—bagasse paper filled with 5% starch, 0.5% p-chloroaniline dimer, 1.5% NaHCO$_3$ and 1.5% CaCO$_3$, SK8—bagasse paper filled with 5% starch, 0.5% Aniline dimer, 1.5% NaHCO$_3$, 1.5% CaCO$_3$ and 10% CNC, SK9—bagasse paper filled with 5% starch, 0.5% p-chloroaniline dimer, 1.5% NaHCO$_3$, 1.5% CaCO$_3$ and 10% CNC.](image-url)
### Table 1. Fire behaviour of various biobased composites used in packaging application.

<table>
<thead>
<tr>
<th>Base Material Type</th>
<th>Points to Notice</th>
<th>Fire Assessment Techniques</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse packaging paper</td>
<td>Coated with 0.5% cyclodiphosph(V)azane/CaCO$_3$ solution (1.5%), 1.5% NaHCO$_3$ solution, and CNCs mixed with 5.0% of starch.</td>
<td>TGA, UL-94 and LOI</td>
<td>With the inclusion of CNCs (SK8), the fire resistance improved by up to 27.5% in comparison to the untreated specimen and did not burn at room temperature.</td>
<td>[34]</td>
</tr>
<tr>
<td>DGELU/DFA</td>
<td>Mechanical and fire properties were compared with petroleum-based epoxy.</td>
<td>LOI, UL-94, Cone Calorimeter</td>
<td>Compared to DGEBA/DDM, the cured DGELU/DFA was found:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- To have a 67 °C higher $T_g$.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Respectively, 82% and 23% improved $E'$ and $\sigma$ at 30 °C.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- A relatively high LOI of 38.0% and a UL-94 V-0 classification.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- The PHRR (peak heat release rate) and THR were decreased by 58% and 12%.</td>
<td></td>
</tr>
<tr>
<td>TPAS films containing AF</td>
<td>A novel biodegradable thermoplastic.</td>
<td>Horizontal burning test and TGA</td>
<td>It was astounding to see that the TPAS/AF biocomposite films showed a noticeable rise in decomposition temperature from 298 to 313 °C, which indicated a substantial rise in thermal stability.</td>
<td>[36]</td>
</tr>
</tbody>
</table>

Note: CNC: Cellulose nanocrystals; $T_g$: Glass transition temperature; DGELU: Luteolin-derived epoxy resin; DFA: 5,5′-methylenedifurfurylamine; DGEBA: Diglycidyl ether of bisphenol A; DDM: 4,4′-diaminodiphenylmethane; $E'$ = Storage modulus; $\sigma$ = Tensile strength; TPAS: Thermoplastic arrowroot (*Maranta arundinacea*) starch; AF: Arrowroot fibre.

Sivaprasad et al. [37] developed a mycelium-based biocomposite as an alternative material for expanded polystyrene (EPS), fossil-based, packaging materials. For the biocomposites, sawdust and coir pith were used as the substrate for culturing mycelium. The mycelium, *Pleurotus ostreatus* oyster mushroom mycelia, covered the surface of the sawdust and coir pith and produced a natural polymer with properties comparable to EPS. The authors conducted thermal conductivity tests according to ISO 8301 and LOI tests. The results showed that the thermal conductivity of the mycelium-based biocomposite increased by 30% compared to EPS. The flammability tests showed that both samples ignited at the same time, 15 s; however, the LOI of the biocomposite was 23%, whereas that of EPS was 19%. This shows that the biocomposite had the best fire performance and self-extinguishing properties [38].

Polylactic acid (PLA) is a bio-sourced polymer derived from biomass feedstock such as corn or sugarcane. PLA is the most widely used biobased polymer since it requires less energy for production and releases fewer greenhouse gases [39,40]. For packaging applications, PLA is blended with biodegradable polymers such as polybutylene adipate terephthalate (PBAT). This combination of completely biodegradable and compostable polymers has been used for food packaging; for instance, for wrapping the head of broccoli, as shown in the work of Paulsen et al. [41].

Chaiwutthinan et al. [42] employed the melt blending method to process a mixture of PLA and 10–50% PBAT. It was seen that the optimum amount of PBAT needed to achieve excellent mechanical properties was 30% PBAT. The authors then used 70% PLA/30% PBAT as the matrix and reinforced it with wood fibre and wollastonite. The thermal stability of the samples was determined using TGA and flammability tests by UL-94 and LOI experiments. The thermal analysis results showed similar onset and decomposition temperatures for all the samples; however, the char residue increased significantly with the addition of PBAT to PLA and blending with wood fibre and wollastonite. 30% PBAT increased the char residue of PLA (0.3 wt%) by 90% (2.9 wt%), whereas adding equal amounts of wood fibre and wollastonite to the blend caused an increment of up to 19.2 wt%. The highest
quantity of char was obtained in the 70% PLA, 30% PBAT, and 30 phr wollastonite blend, which produced a char residue of 27.4 wt.%. The LOI and UL-94 results, presented in Figure 2, showed that the samples with blends of wood fibre and wollastonite had low fire performance, low LOI (19.5–19.8%), and a high flame rate (3.3–5.4 mm/s), compared to the plastics. This showed that although the reinforcements enhanced the mechanical properties, they were detrimental to the fire properties and not suitable as far as fire safety is concerned.

Figure 2. Results from the flammability tests: UL-94 (flame rate) and LOI [42].

In another work, Yu et al. [43] integrated a cyclophosphamide-based flame retardant containing phosphorus and nitrogen in PLA to augment both the mechanical and flammability characteristics. In their research, Hexa (ethylene oxide)-cyclotriphosphazene (HCCP-EP) was synthesized into the PLA using melt blending at concentrations of 1%, 3%, and 5% HCCP-EP. The flammability characterizations were performed using cone calorimeter tests, thermogravimetric analysis, LOI, and vertical burn tests (UL-94). The LOI of PLA was 19.5%, which increased to 25%, 27.3%, and 27.8% with the addition of 1%, 3%, and 5% HCCP-EP, respectively. The neat PLA sample ignited and dripped immediately during the vertical burning test. However, the addition of 1% HCCP-EP increased the ignition time to ca. 11 s with less dripping. The 3% loading further improved the flammability and the 5% HCCP-EP did not experience ignition. A carbon layer was formed on the surface of the PLA, which insulated it from the flames. From the cone calorimeter experiments, the 5% HCCP-EP reduced the time to ignition of the neat PLA by 17% and the peak heat release rate by 13%. According to the TGA experiments, the 5% and maximum decomposition temperatures increased with increments in the loading amounts of HCCP-EP. Figure 3 shows the synthesis and flame retardant mechanism of HCCP-EP in PLA.
Alam et al. [44] grafted phenyltrithoxysilane (PTES) onto neat sepiolite to obtain PTES-grafted sepiolite (PSP). The authors added poly-3-hydroxyoctanoate (PHO), which is a nanocomposite to the PSP, and subjected it to the melt blending process to fabricate a biodegradable polymer for packaging. Low melting point and thermal stability are the major drawbacks of utilizing these plastics; therefore, they were exposed to gamma radiation at two doses, 10 and 25 kGy, to observe the effect on the thermal properties. Exposing polymers to radiation causes them to crosslink, which increases their thermal and mechanical stability [45]. Gamma radiation is also applied for the sterilization of packages, especially in the area of food. TGA experiments were conducted to assess thermal behaviour. The experiments showed that all decompositions, for the control sample and those exposed to 10 and 25 kGy of radiation, occurred in a single step. The 5% decomposition temperature increased by ca. 30 °C for the radiation-exposed samples, although the maximum decomposition temperatures were similar. The char residue increased by 470% with the exposure to 10 kGy and by 667% at 25 kGy. This showed that the gamma radiation improved the thermal stability of the novel biobased polymers.

Several other novel biobased composites for packaging have been developed with excellent mechanical and fire properties. However, most are still in the research and development stage. The commercialization of such products will be a game changer as far as fire safety is concerned.

3. Fire Behaviour of Biobased Composite Materials for Structural Applications

The construction industry consumes about 40% of the total energy produced on the global scale. It has been reported that for every ton of cement used for construction, one ton of carbon dioxide is released [46]. This goes to prove that the construction industry not only consumes energy, it also releases a lot of emissions (33% of the world’s emissions), which contributes to global warming [47,48]. Therefore, global efforts to achieve sustainability and circularity will require an enormous contribution from the building sector [49]. Over the years, as a result of their environmental impact, there has been a shift from conventional building materials to engineered ones such as composites [50]. In addition, with the continual demolition and renovation of structures, recycling conventional materials such as concrete is challenging; hence, they end up in landfills [51]. Modern structures have evolved into more sustainable, lightweight, and economical designs. Structural engineers have adopted the use of bio-sourced composite materials due to their recyclability, renewability, and low cost [52]. Bio fibres such as kenaf, jute, sisal, flax, etc., have been added to building materials to improve their strength [53,54]. In structures, biobased composites are used as façade cladding, fences, terrace decking, etc. Due to recent fire outbreaks such as the Grenfell Tower and Dubai Torch Tower fires, which were caused by the ignition of façades, it
has become more crucial to observe fire safety in building materials [55]. The fire behaviour of some of the novel materials developed is discussed in this section. Table 2 illustrates the low-fire-risk types of biocomposites used in structural applications.

Gonzalez-Lopez et al. [56] prepared calcium aluminate cement (CAC) composites containing different concentrations (0–40 wt.%) of metakaolin (MK), made from kaolin clay and reinforced with non-woven flax fabrics that are 6 cm long. The authors determined the fire and thermal behaviour using an epiradiator according to UNE standard 23725:1990, exposing the samples to the ISO 834 fire curve and TGA tests. In the epiradiator tests, it was seen that the samples did not ignite even above 400 °C but developed microcracks, as seen in Figure 4a–c. No spalling was seen in the samples and this was due to the fibre reinforcements that held the parts of the samples in place. A ca. 14% weight loss was realized, which was attributed to dehydration upon exposure to fire and the transformation of CAC to oxides. In addition, after exposure to the standard fire curve, no ignition and combustion occurred; however, the cracks in this test were more distributed and widened due to higher temperatures ca. 900 °C. For the TGA tests, the mass loss was more prominent in the fibre-reinforced concrete than in the control. It was also seen that the decomposition temperature for each phase was lower in the control samples than in the samples with the fibres.

Elsewhere, Nguyen et al. [57] explored the potential of substituting conventional building materials such as metals and concrete with glass fibre-reinforced polymer (GFRP) in high-rise buildings. In this work, multilayer sandwich panels made from GFRP and polyethylene foam core were treated with unsaturated polyester resins, flame retardant, aluminium hydroxide hydrate (ATH), and gel coats. Both small-scale and full-scale tests, TGA and single burning item (according to EN 13823:2010 standard) tests respectively, were conducted to observe and analyse the reaction to fire. The highest mass loss from the TGA tests was recorded for the unsaturated resin, followed by the gel coats and then the ATH. The temperatures at the initiation, peak and end of decomposition reactions were 300 °C, 415 °C, and 450 °C for the unsaturated resin, 290 °C, 310 °C, and 460 °C for the gel coat, and 238 °C, 329 °C, and 400 °C for ATH addition. Overall, the samples with ATH had the lowest peak of reaction. With the SBI (single burning item) tests, the average heat release rate curves, fire growth rate, and total heat release for the samples were below the critical limits for 600 s.

Earth is a sustainable building material, which is readily available, has a very low impact on the environment, and can be used to maintain indoor moisture conditions [58,59]. Laborel-Préneron et al. [60] produced biobased composites for construction using unfired earth bricks as the matrix and plant aggregate as the reinforcement, as shown in Figure 5. To fabricate a lightweight brick, the authors reinforced the earth with 3 wt.% and 6 wt.% barley straw and hemp shiv. The fire performance of the samples was assessed using data from MCC tests performed at 1 °C/min, and ignition time and extinguishing ability tests.
MCC tests of the plant aggregates showed a PHRR of ca. 93–103 W/g with maximum decomposition temperatures ranging from 330–360 °C. It was seen that the barley straw had better fire properties compared to the hemp shiv. The ignitability and the flame out test performed on the earth/plant aggregate showed no flames; however, the plant aggregate smouldered and released smoke. The quantity of smoke released increased as the concentration of aggregate increased. It was also seen that the thermal conductivity of the samples decreased with increasing exposed temperature as the porosity increased (due to plant aggregate addition). This implies that as more plant aggregate was added, the longer it took for the samples to respond to temperature changes.

Figure 5. A typical application of composites in high-rise buildings and the cross-section of multilayer sandwich panels with flame retardant coating [57].

The fire behaviour of materials used for structural applications is critical due to the extent of damage caused by structural fires. The development of building materials that are both mechanically strong and fire safe will help to preserve the structural integrity of buildings in the event of fires. This also helps to reduce the cost of renovations after fire outbreaks.
Table 2. Improvement of fire behaviour of different biocomposites.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Type of Composite</th>
<th>Observations from Fire Tests</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-6/BF and CF Hybrid</td>
<td>The maximum average rate of heat emission was shown to decrease with increasing fibre load. It was 207 kW/m² in composites with 10 wt.% basalt fibres and 10 wt.% CF’s, which was less than the unaltered polymer by about 37%.</td>
<td>[61]</td>
<td></td>
</tr>
<tr>
<td>Mycelium and mycelium-wheat grain Biomass</td>
<td>Mycelium’s corresponding combustion propensity was considerably lower than that of PMMA and PLA, according to the PCFC analyses, revealing that it is substantially less likely to ignite and burn violently, and is, therefore, safer to use. The cone calorimetry test results revealed that the existence of mycelium had a favourable impact on the characteristics of the wheat grain fire reaction. Mycelium has been discovered to have some flame-retardant qualities (such as high char residue and water vapour emission) and could be employed as an affordable, environmentally friendly, and fire-safe substitute for synthetic polymers in binding matrices.</td>
<td>[62]</td>
<td></td>
</tr>
<tr>
<td>PLA/KF/r-carbon with a cashew nut shell liquid Hybrid</td>
<td>Cardanol enhanced the thermal stability of kenaf; hybridization with r-carbon also increased the thermal stability of the finished composite. It was found that the fire retardancy of cardanol was unaffected by the KF’s presence.</td>
<td>[63]</td>
<td></td>
</tr>
<tr>
<td>PLA/hemp/sepiolite NC/MWCNT Hybrid</td>
<td>The hybrid ternary composites showed 58% reduced HRC and 45% reduced pHRR, which showed lower flammability than neat PLA. Another interesting finding was the 25% drop in pHRR that occurred after hemp fibre was added to the PLA nanocomposite. Towards the end of the thermal ramp, TGA revealed an appreciable increase in the residual char.</td>
<td>[64]</td>
<td></td>
</tr>
<tr>
<td>PLA/starch/microencapsulated MEAPP Biocomposite</td>
<td>According to the MCC findings, the PLA/starch biocomposites’ pHRR and THR were significantly lower than those of neat PLA. The PHRR and THR were decreased because the inclusion of IFR stimulated the degradation of PLA and caused the thermal degradation process to produce less combustible gas products.</td>
<td>[65]</td>
<td></td>
</tr>
</tbody>
</table>


4. Fire Behaviour of Composite Materials for Aviation and Automotive Applications

The incorporation of lightweight materials in the automotive industry enhances engine efficiency and fuel economy in the sense that less energy is required for operation (acceleration) [66,67]. Due to this, the automotive and aviation industries are moving towards the production of lightweight vehicles and aeroplanes, respectively, which has increased the use of biobased composite materials in this sector [68]. Industries have shifted from the use of glass fibre, aluminium alloys, and other fossil-based materials to utilizing carbon and other natural fibres [69,70].

To date, 50% of the parts in Boeing 787 by weight are made from biobased composites [71]. A life cycle assessment carried out by Timmis et al. [72] showed that the carbon fibre-reinforced polymers used in aircraft reduce both fuel consumption and greenhouse gas emissions. The authors reported that the use of biobased composites instead of fossil-based ones reduced carbon dioxide emissions by 20–25%.

In the automotive industry, bio-sourced reinforcements such as wood, hemp, jute, etc., are used [73]. It is reported that approximately 80,000 tonnes of wood and plant fibres are used as reinforcement in composites in the European car industry yearly [74].
A major drawback of using these novel materials in these sectors is their high flammability, which is detrimental to fire safety. Hence, in this section, the fire performance of composites used in these sectors is analysed to ascertain the enhancement achieved.

Polyamide (PA) 6 is a biobased material that is used for manifolds, airbag containers, exterior parts of vehicles, etc. [75]. Mazur et al. [69] developed a hybrid basalt, carbon fibre and PA 6 blend by injection moulding. The basalt and carbon fibre were added at concentrations of 5/5 wt.%, 7/7 wt.%, and 10/10 wt.%. The reaction to fire properties of the samples at 35 kW/m² was obtained using the cone calorimeter following the ISO 5660-1 standard. The results from the cone calorimeter experiments showed that the addition of 5/5 wt.% and 7/7 wt.% of basalt/carbon fibre reduced the time to ignition by 36% and 6%, respectively; however, the addition of 10/10 wt.% increased it by 45% compared to that of neat PA 6. This was because, in the sample with the highest amount of reinforcement, basalt powder was dispersed on the surface, which formed an insulating layer that protected the surface of the sample from the heat. The HRR recorded for the samples is shown in Figure 6. It shows that the peak heat release rate drastically reduced (50% or more) with the addition of the reinforcement. The inclusion of 10/10 wt.% basalt/carbon fibre reduced the peak heat release rate by ca. 59%. Interestingly, the mechanical properties were also significantly improved. Therefore, the hybrid basalt/carbon fibre PA6 biocomposite was proposed as a mechanically strong and fire-safe material to use in automotive, aircraft and even structural applications.

Wool fibres are excellent insulating materials; however, they have high flammability. Usually in polymer composites, low concentrations of wool fibre are combined with flame retardants, which increases the cost of the products. To resolve this issue, Guna et al. [76] fabricated a novel composite using 80–90 wt.% short wool fibre and 20–10% polypropylene (PP) by adopting the compression moulding technique. The authors assessed the thermal conductivity, thermal stability and flammability (UL-94) of the composites to determine the optimal ratio. The results showed that the composites displayed good thermal insulating properties as the thermal conductivities ranged from 0.058 to 0.083 W/mK, increasing with an increase in PP. The values obtained were higher than those obtained for gypsum boards.

![Heat release rate versus time curves of PA6 containing 5/5 wt.%, 7/7 wt.%, and 10/10 wt.% of basalt and carbon fibre](image_url)

Figure 6. Heat release rate versus time curves of PA6 containing 5/5 wt.%, 7/7 wt.%, and 10/10 wt.% of basalt and carbon fibre [69].
In the flame resistance test, the wool exhibited a charring ability that protected the samples from the fire. The samples had a V-0 rating, no dripping was observed, and the flame was extinguished in less than 30 s. The TGA results showed reasonable thermal stability up to 250 °C with a weight loss of 1.2%; at 400 °C a major weight loss was seen and this was due to the breakdown of the disulfide bonds and peptide chains in the wool. The weight of residue for all the samples was about 1.5% of the initial weight.

For aeronautical application, Boccarusso et al. [77] produced a fire-resistant composite made from hemp fabric/epoxy and ammonium polyphosphate (APP) blend. The hemp fibre was pretreated with NaOH before the fabrication of the composites to enhance the fibre/matrix adhesion. The ratio of fibre to epoxy resin was kept constant; thus, 35:65 APP was added at 5, 15 and 30 wt.%. The blends were fabricated using a resin infusion process. The samples were subjected to the cone calorimeter and vertical burning tests. According to the cone calorimeter tests, the sample with no fire retardant had the worst fire performance with a peak heat release rate of 720.5 kW/m² and a total heat release of 68 MJ/m². The addition of APP significantly decreased the values for these parameters, such that 5%, 15%, and 30% APP reduced the PHRR by 48%, 59%, and 74%, respectively. Similarly, the total heat release was reduced by 38%, 52%, and 60%, corresponding to the inclusion of 5%, 15%, and 30% APP. Additionally, the sample with 30% APP had the highest amount of char residue after the test. The time to ignition of all the samples, including the neat composite, was statistically similar; however, the time to peak heat release rate decreased with increasing quantities of APP. From the vertical burning tests, the length of the damaged area of the samples (Lb) and the time for the flame to extinguish decreased with an increment in APP. Lb decreased by 98% with the 30% APP sample compared to the composite without APP. The specimens with 15% and 30% APP passed the vertical burning tests. Figure 7 shows the hemp fibre, composite and heat release rate curves recorded from the cone calorimeter tests.

![Figure 7. Illustration of (a) Hemp fibre, (b) Hemp fibre/epoxy composite, (c) Heat release rate curves of hemp fibre/epoxy composite treated with different concentrations of APP.](image)

In a similar work, Babu et al. [78] developed coir-reinforced biocomposites. Coir fibre possesses a higher lignin content (46%), which makes it more thermally stable compared to other natural fibres [79]. In this work, different loading amounts of raw and alkali-treated coir fibre (with 5% sodium hydroxide) were used as reinforcements in a high-density polyethylene (HDPE) matrix. The effects of variable loading amounts (10%, 20%, and 30%) of untreated and pretreated coir fibre on the thermal stability of HDPE were examined. TGA experiments were adopted for thermal analysis and LOI for flammability assessments. The treatment of coir fibre in NaOH destabilized the lignin content; hence, in the TGA test of the coir fibres, the treated one degraded at a faster rate. It was also seen that the char residue of the treated fibre was higher due to the high amounts of cellulose present. The composites degraded at an early stage compared to the neat HDPE; however, the char residue increased with increasing fibre concentrations. Overall, the alkali-treated samples were more thermally stable than the untreated or raw coir fibre composites. HDPE
has an LOI value of 17% and showed dripping during burning, and the inclusion of the coir fibres drastically reduced the dripping effect. In addition, the raw fibres displayed a higher improvement in flammability compared to the alkali ones and the enhancement was directly proportional to fibre loading. Figure 8 shows the results from the TGA tests and the LOI experiments for both the raw and alkaline-treated coir fibre HDPE composites.

![Figure 8. Mass loss versus temperature curves of neat HDPE. Notes: (a) HDPE reinforced with raw or untreated coir fibre, (b) HDPE reinforced with alkaline treated coir fibre, (c) Comparison of LOI values of neat HDPE and coir fibre reinforced HDPE. HDPE-RCP—raw coir fibre, HDPE-ACP—alkaline treated coir fibre.](image)

It is quite evident from the studies analysed that completely or semi-biobased composites have the potential to serve as a viable alternative to synthetic or conventional polymers used in the automotive and aeronautic industries without compromising fire safety and strength. Since transportation is one of the basic needs, providing sustainable transportation with biocomposites will not only reduce the emission of greenhouse gases, it will also reduce cost [80].

5. Conclusions and Future Research Focus

Research has recently transitioned from the study of synthetic or petroleum-based materials to biobased ones. Although this transition ensures sustainability and fits with the circular economy model, it still cannot solve the major risk of all materials: their flammability. In the event of a fire, it is required that materials maintain their structural integrity. Hence, the fire performance and mechanical properties of materials go hand in hand. This review focused on bio-sourced composite materials for packing, structural, automotive, and aerospace applications. The type of biomass feedstock used as reinforcement for specific applications is crucial; hence, some of the most extensively used natural fibres for reinforcing various matrices are discussed. The flame retardants used and the optimum amount required to achieve the best performance were clearly reviewed. The effect of these
substances on the thermal stability, flammability rating, heat release rate, and the oxygen required for combustion was analysed. In addition, the effect of mechanical properties was briefly mentioned. To achieve the best fire performance and strength, the optimization of the interfacial bonding between the matrix and the reinforcement should be ensured.

Furthermore, most of these novel materials produced remain at the research and development stage. To commercialize them, policies should be put in place to break the existing market barriers, thus, fully completing the transition to renewable and sustainable materials. Lastly, production companies for packaging, structural, automotive, and aerospace industries could invest more funds into innovative materials that could actually promote fire safety. It is believed that there are several effective natural fibres and flame retardants that have not yet been discovered. This could help to improve the services needed in these sectors.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: No new data were created.

Conflicts of Interest: The author declares no conflict of interest.

References
2. Aaliya, B.; Sunooj, K.V.; Lackner, M. Biopolymer composites: A review. *Int. J. Biobased Plast.* 2021, 3, 40–84. [CrossRef]


43. Yu, W.; Yang, W.; Xu, P.; Dai, C.; Liu, Q.; Ma, P. Simultaneously enhance the fire safety and mechanical properties of PLA by incorporating a cyclophosphazene-based flame retardant. e-Polymers 2022, 22, 411–429. [CrossRef]


**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.