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Review

Expandable Graphite as a Fire Retardant for Cellulosic Materials—A Review

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Abstract: A diversity of chemicals is used to produce fire retardants (FRs); some of the main group of chemicals are hazardous to the environment as well as to human life; however, expandable graphite (EG) can be a gateway to a more environmentally friendly FRs or intumescent fire retardants (IFRs). Researchers define intumescent as the swelling of a particular substance placed between a heat source and an underlying substrate when they are heated. EG is a material with extraordinary thermophysical and mechanical properties. The referred EG properties are unparalleled. EG is a low-density carbon material having a series of unique properties: developed specific surface, binder-free pressing capacity, stability to aggressive media, and low thermal conductivity. Therefore, EG is a promising material both for research work and for industrial applications. The primary goal of this literature review was to report current knowledge on the use of EG as a fire retardant for cellulose and cellulose-modified materials. EG is produced, among other methods, by thermal shock of graphite oxide under forming gas. When exposed to heat, EG will expand. The expansion mechanism was presented in this review. Equally important to this review is the knowledge related to cellulose thermal degradation and cellulose impact on the development of science and technology.

Keywords: cellulose; modification; coating; expandable graphite; fire retardant; thermal degradation

1. Introduction to the Mechanism of Fire Retardants

Fire retardants (FRs) are chemicals added to combustible materials to improve their resistance to ignition [1]. Depending on the processing methods, fire retardants (FR) are often categorized as an additive or reactive compounds. Additive FRs are often blended into the polymer matrix during its processing. These FRs do not chemically react with the polymer. Reactive FRs are dose polymerized with resin during the processing of cellulosic material to become integrated into its molecular network structure. These FRs are also known as chemically-modified FRs [2]. The footprints of fire retardants point to an effective ideal fire retardant that should comprise of the following characteristics: thermal stability, compatibility with the protected polymer, no change in the physical-chemical properties of the protected polymer, and low toxicity under heat exposure or during burning [3].

The amount of flame retardant that must be added to achieve the desired level of fire safety can range from less than 1% for highly effective flame retardants up to more than 50% for inorganic fillers; the typical range is 5% to 20%, by weight [1,4].

In works of Camino and Costa [3] and Nazaré [5], two types of FR mechanism can be identified: gas-phase mechanism and/or condensed phase mechanism. Whatever the case, the main goal of FR systems is to reduce the heat released from the polymer under combustion to levels that lead to flame stability of the polymer. This can be achieved by modifying the rate of chemical or physical processes taking place in one or more of the steps of the burning mechanism of the material [6].

In order to understand the mechanisms of fire retardants, it is required to have detailed knowledge of the mechanism of the thermal degradation process of the polymer and the thermal correlation of the additive and of the polymer-additive mixture. Organic polymeric materials (natural or synthetic) may start and/or propagate fire (thermal degradation) due to heat exposure involving combustible products in various concentrations over different temperature ranges [6,7].

In general, and according to studies [6], three main processes are involved in the thermal degradation of the majority of thermoplastic polymers. Focusing on the molecular weight (MW) of the polymer during the thermal degradation process, most authors agree that on the first stage, there is a very slight reduction in MW, on the middle stage, there is a slow decrease in MW, and on the final stage, a rapid drop in MW occurs.

These FRs are designed to minimize the risk of a fire starting in case of contact with a small heat source, such as a cigarette, candle, or an electrical fault. As organic and/or inorganic formulation, FR based on inorganic formulation may include aluminum trioxide ($Al(OH)_3$), magnesium hydroxide ($Mg(OH)_2$), Antimony trioxide (Sb_2O_3), ammonium polyphosphate ($(NH_4PO_3)_n$), red phosphorus, boric acid (H_3BO_3), and others. This group represents about 50% by volume of the global FR production. The remaining categories are organic FRs [1,8]. FRs are used in buildings and constructions, electronics, automotive and transportation, wires, cables, textiles, and others.

Environmental problems, toxicity, and hazards to human life are major factors that will force the reduction of use or even the total abandonment of these chemicals. Most fire retardant formulations are halogen-based. Inorganic acids, nitrogen, phosphorous, and intumescent-based FR formulations have been and will continue to be important in flame retardant researches. However, environmental concerns and health care issues are stimulating a strong interest in innovative alternatives to fire retardant systems.

Intumescent flame retardants are the most promising candidate to substitute the halogen-containing flame retardants, which are free of halogen and with relatively high FR efficiency. In general, the intumescent fire retardant (IFR) systems are composed of three components, i.e., an acid source, a carbonization agent (or char forming agent), and a blowing agent. However, the traditional IFR additives are susceptible to migration onto the polymer surface during the processing due to their low molecular weight and thus decrease the FR efficiency. To solve the shortcomings, high molecular weight, namely, oligomeric or polymeric, IFRs have been developed, which provide a good strategy to solve the above problems [9].

In general, an IFR mechanism works on the basis of promoting a char layer between the heat source and the protected substrate during expansion due to heat exposure [10,11]. A char layer that might be able to protect the underlying structure should simultaneously combine the following characteristics: low thermal conductivity in the thickness direction, high in-planar thermal, high stability, low heat absorption, high heat capacity, and a compact structure (low porosity and permeability system) to limit mass loss in thickness direction fundamentally [12]. Other advantages of using IFR are decreased flame spread, low smoke emission, and the performance of the substrate would not be altered. Applying IFR coatings is one of the most efficient ways of providing fire retardancy to flammable materials [11].

2. Combustion Properties of Cellulose

Cellulose is present in large volumes on the planet. As one of the most abundant materials on earth, cellulose is the most common organic polymer [13], representing more than 1 trillion tons of annual biomass production. Cellulose is considered the main chemical component in many lignocellulosic resources. Of all biomass, cellulose (Figure 1) represents more than 50% by weight. It is comprised of two anhydroglucose rings ($(C_6H_{10}O_5)_n$) with a linear homopolymer of glucopyranose residues connected by β-1, 4-glycosidic bond. Understanding the pyrolysis of cellulose can be beneficial towards a successful explanation of its pyrolytic mechanism [14]. The degree of polymerization, n, varies between 10,000 and 15,000, where n is dependent on the cellulose source material. A cellulose molecule unit is presented in Figure 1.

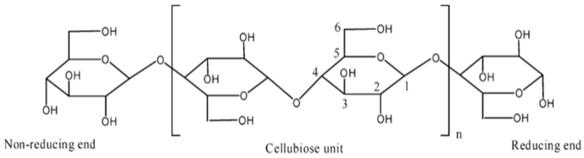

Figure 1. Cellulose molecule unit [14].

2.1. *Combustibility of Cellulose*

Cellulose derived from wood pulp has an average of 3000 repeated units. A large number of hydroxyl groups on the sugar molecule, which leaves the polymer as water molecules during the decomposition, results in char formation [15]. Due to its strength, charring ability, and biodegradability, cellulose-based reinforced polymers have received considerable attention. The burning characteristics of cellulosic fibers vary depending on their chemical composition. For example, lignin, as natural polymer, could improve the flame resistance of the fibers; in fact, it is reported that a low concentration of lignin (~10 wt%) in cellulose fiber improves the char formation during thermal decomposition processes [16].

2.2. *Thermal Decomposition of Cellulose*

During the decomposition (combustion) of flammable materials, some carbonaceous substances tend to swell. Some methods of anti-fire protection achieve flame retarding action by accelerating the formation of a char layer, derived from the intumescent carbon located on the surface of the treated cellulosic material [17]. The comprehension of the pyrolytic behavior of cellulose is essential to biomass thermochemical conversion. Early work for cellulose pyrolysis emphasizes the classic kinetic schemes of three main chemical pathways. It has been found that at low temperatures, the initial process is delayed, which leads to a reduction in the degree of polymerization and the formation of active cellulose [18]. On the other hand, high-temperature pyrolysis of cellulose is developed through two competitive degradation reactions: the first reaction is fundamentally the formation of char and gas. In the second reaction, the degradation process promotes the formation, mainly of tars. Recent researches have excluded the concept of anhydrocellulose formation during the degradation process [18].

Schematically, the literature shows a diversity of diagrams that usually emphasize three main points on cellulose thermal degradation (the polymer, char formation and volatile tars, char and gas). These three points are related to three kinetic points (k_1, k_2, and k_3) [14]. A combination of all these schematics in a two-phase diagram (condensed and gas phase) is presented in Figure 2.

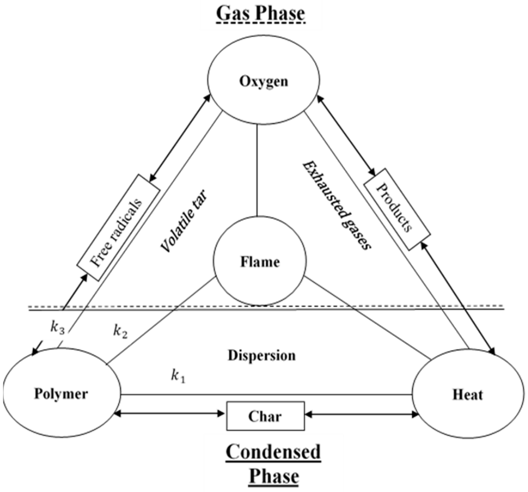

Figure 2. Concept of the combustion Emmons triangle modification [19]; kinetic points (k_1, k_2, k_3).

Although cellulose is often overlooked as a flame retardant for polymers due to its low thermal stability, its ability to charring can be beneficial in reducing calorific value as fuel and reducing peak heat release in the event of a real fire [20]. No report has been found on the concept of "flame volume" regarding cellulose thermal decomposition; some articles present the concept of ignition of solid (cellulosic) fuel and flame spread independently; however, there is no revelation of "flame volume". The concept of "flame volume" based on the volume of cellulose exposed to heat and to flame, consequently, is important to fire safety. Nonetheless, the primary goal of this literature review was to investigate the promising pathways and methods of improving the flammability properties of Cellulosic Material (CellMat)–with the use of expandable graphite (EG).

Recent investigation on intumescent base fire retardants points that it is efficient to create a physical barrier between the possible exposed material and the flame. The development of EG-based flame retardants for several different materials is the new trend in distinguished research projects.

3. Expandable Graphite (EG)

EG is first reported in the literature in 1841 by Schafhautl while analyzing crystal flakes of graphite in a solution of sulfuric acid [21]. The flame retardant performance of EG in a polyurethane coating has been previously reported. The oxygen index increases from 22 to 42 vol.% at 25 wt.% loading. It has been demonstrated that EG is an efficient additive, which acts as a blowing agent as well as a carbonization agent. EG is an intumescent additive known to improve fire retardancy properties in various materials and, in particular, in polyurethane (PU) foam [20]. EG is achieved through flake graphite intercalation derived when flake graphite is exposed to concentrated sulfuric acid (H_2SO_4) in combination with other strong oxidizers, such as nitric acid (NH_3) or potassium permanganate ($KMnO_4$). Flake graphene is synthesized from graphite or other sources of carbon by a top-down method [22]. The oxidation of graphite in protonated solvents leads to graphite oxide, which consists of multiple layers of graphene oxide, with hexagonal carbon structure, which includes hydroxyl group, alkoxy, carbonyl, and acids group. At the industrial scale, the production methods of EG is similar to that of graphite oxide (GO). Due to its economic and environmental advantages, this novel product is attracting attention in many areas of research. However, none of the reviewed papers has assessed the environmental and health hazards of expandable graphite. EG is only presented as a novel and promising alternative flame retardant. EG is not classified according to European Countries (EC) regulations, and no data except the Chinese market about effects on health and environment have been found in the literature [23]. The raw material (graphite) is not classified according to EC regulations. Data about health aspects indicates that there is a risk of physical effects, such as dust bronchitis, in workers engaged in the graphite industry. Sulfuric acid, for example, is a strong acid and can cause severe burns when used in a concentrated form. None of these sparse data indicates any negative health and environmental effects from the use of expandable graphite as an FR component in polyolefin plastics [24]. EG is one of the materials at the forefront of environmentally friendly novels. As an excellent platform to remove oil from the aqueous medium, EG/manganese ferrite composite is used to remove heavy oil from the aqueous medium, and it can be used in oil spills catastrophe as a form of crude oil removal material [25].

Considering graphite, a relatively stable substance at environmental temperature, their expandable property is significantly important to fire retardants' formulation design. When EG is used as flame retardant, its dilatability and thermal stability are very important parameters. In terms of thermostability, EG can be divided into three kinds: low (between 80 and 150 °C), middle (between 180 and 240 °C), and high (between 250 and 300 °C) [26]. At temperatures ranging between 280 and 438 °C, high thermostable graphite will expand, creating a porous physical barrier between the material to be protected and the flame [6]. Moreover, during the char formation, void spaces are formed within char, allowing airflow, and this cool down the fire environment (atmosphere), increasing the time to ignition of protected cellulosic material. In general, the kinetics of fire-protected cellulosic materials are still under investigation [27]. The effectiveness of these flame retardants depends on the heat-induced decomposition of the organic components and the creation of a char layer that insulates the substrate from the heat source. However, as intumescent is required to address more severe and diverse applications, new approaches are needed that provide improved performance over conventional systems. EG flake is a different intumescent additive. As a blowing agent, EG expands up to 100 times its original thickness [4]; it has an isolative layer larger in thickness more than many intumescents. Unlike the carbon char layer formed with chemical intumescent, the graphite-based char formed from expandable flake retains the superiority heat resistance in comparison with other IFRs. In addition, graphite flake is the only intumescent that expands with sufficient force to allow its use in rigidized systems, such as those employing cured phenolic resins [28,29].

4. Expansion Mechanism of EG

The actual cause of expansion/exfoliation is the increase in volume and resultant pressure, caused by the rapid heating of the intercalant. A simplified way to view the process is to model the intercalant as a liquid or solid phase that is fixed between the graphene layers. Heating of the treated graphite results in the conversion of the intercalant from a liquid or solid phase to a gas phase. Gas formation results in an increase in the volume of the intercalant by approximately 100 times [30]. The pressure generated by this volume increase forces the adjacent graphite layers to separate. Figure 3 shows a schematic of the expansion agent in their metastable residence between adjacent graphene layers. The interlayer dimensions are equal to approximately 3.355 Å (6.7 Å/2). The interlayer spacing, post exfoliation, is some value greater than 3.35 Å [21]. An increase in graphene layer spacing is a result of the protection process.

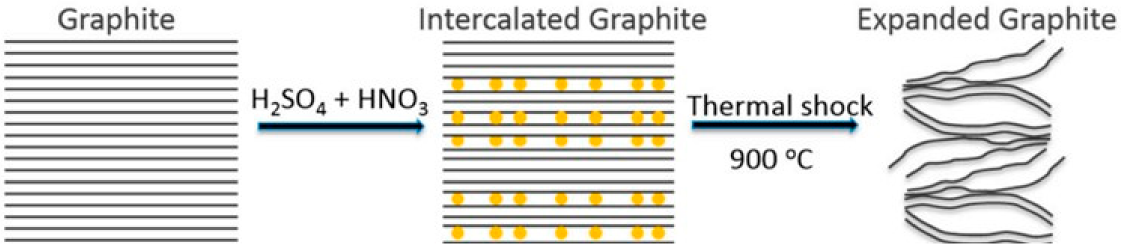

Figure 3. Schematic of expandable graphite (EG) expansion [31].

5. EG as Fire Retardant Additive in Different Materials

The FR performance of EG in a PU coating has been previously reported, where oxygen index increases from 22 to 42 vol.% at 25 wt.% loading. It has been demonstrated that EG is an efficient additive, which acts as a blowing agent as well as a carbonization agent [20].

In the work of Camino et al. [8], thermogravimetric analysis of the EG was carried out through pyrolysis. The unit raising the temperature was 10 °C/min, and, step by step, the density of residue was measured.

Similar tests were performed by Zheng et al. [27], with a temperature increase of 5 °C/min. The course of EG thermal decomposition is represented by the thermogravimetric (TG) (Figure 4) and derivative thermogravimetric (DTG) (Figure 5) curves.

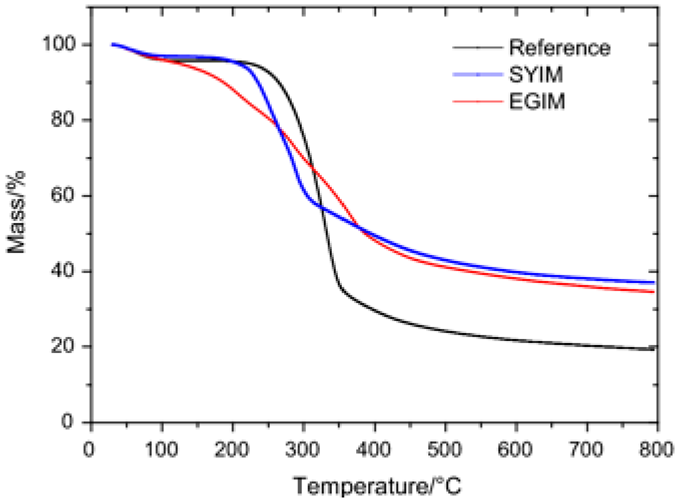

Figure 4. TG (thermogravimetric) curves of synergetic fire retardants insulating material (SYIM) and expandable graphite insulating material (EGIM) [27].

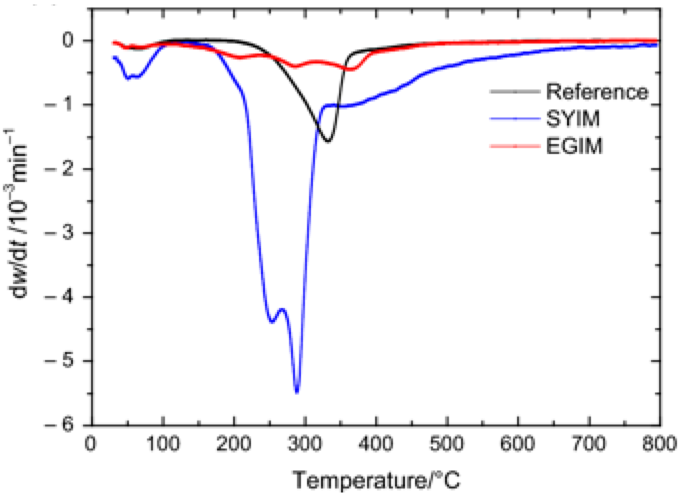

Figure 5. Derivative curves of synergetic fire retardants insulating material (SYIM) and expandable graphite insulating material (EGIM) [27].

In this experiment, the thermobalance could not be used because of the EG expansion, which was observed to expand ten times its original sample size. EG stability was lower at temperatures ranging between 200 and 350 °C, with a maximum rate of weight loss at about 250 °C. This research suggested that half and total expansion was, respectively, reached at 260 and 350 °C. In the literature, it is suggested that expansion occurs via the sulfuric acid decomposition.

The addition of EG into the polymer matrix (Polyvinyl chloride (PVC), polylactic acid (PLA)) improves thermal stability, both in an oxidizing atmosphere and in an inert atmosphere [32]. Graphene influences the thermal properties of polyethylene terephthalate (PET). An increase of graphene at 0.025% affects the thermo-oxidative resistance of the polymeric material. The addition of expanded graphite does not affect the melting point and glass transition temperature of PET [33]. Additionally, it has been observed that the addition of nanofillers does not affect the crystallization temperature, nor the degree of crystallinity of PET. In an oxidizing and inert atmosphere, the thermal degradation process of PET/EG nanocomposites has shown improved thermal stability. The mechanism of PET stabilization by graphene is associated with the transfer of free radicals on the carbon planes. Within 2% weight loss, nanocomposites containing EG, already more than 0.1% by weight, possess higher thermo-oxidative stability.

The characteristics of EG are often influenced by the modifying agent (oxidant, intercalant, and assistant intercalant) used during the intercalation process. The influence of $KMnO_4$ (oxidant agent) dosage on EG characteristics was studied by Pang et al. [34] and Zhao et al. [26]. In this research, at the range of 0.2~0.6 g/g, the influence of $KMnO_4$ dosage was detected at the mass ratio of C: H_2SO_4 (98%): $Na_4P_2O_7$ = 1.0:5.0:0.6 (g/g), the temperature conditions were 40 °C, with the reaction time of 1 h. In addition, it was observed that H_2SO_4 should be diluted to the mass concentration of 80% before the reaction. The results showed that when the mass ratio of $KMnO_4$ to C was set to 0.4:1.0, the minimum initiation expansion temperature was 160 °C. On the other hand, the insufficiency of $KMnO_4$ could lead to incomplete oxygenation of graphite and decrease expandable volume (EV) of a product. Superfluous $KMnO_4$ would cause excessive oxygenation of graphite, leading to a decrease of EG granularity and then reduced EV. In the tested dosage, the increase of $KMnO_4$ would cause an increase in initiation expansion temperature. The feasible dosage of $KMnO_4$ could be set as 0.4 g/g. Similarly, in the same work, the influence of H_2SO_4 dosage on EG characteristics was analyzed. In the range of 3.0~6.0 g/g, the influence of H_2SO_4 dosage with a mass concentration of 98% was detected at the mass ratio of C:$KMnO_4$:$Na_4P_2O_7$ = 1.0:0.4:0.6 (g/g) at 40 °C reacting for 1 h, and H_2SO_4 was diluted to the mass concentration of 80% before reaction. Results proved that when the mass ratio of H_2SO_4 to C was controlled as 5.0:1.0, EG had the lowest initiation expansion temperature of 165 °C and a maximum EV of 550 mL/g. Insufficiency H_2SO_4 would cause an incomplete intercalation reaction, leading to a decrease of expansion degree. Superfluous H_2SO_4 would cause the relative scarcity of $KMnO_4$ and incomplete oxygenation of graphite. In the tested dosage, an increase of H_2SO_4 could cause V type changes of initiation expansion temperature; the lowest initiation expansion temperature of 165 °C could be gained with EG possessing maximum expansion volume. The feasible dosage of H_2SO_4 could be set as 5.0 g/g.

In some cases, EG will work synergistically with other additives to improve the flammability properties of polymers. The synergistic FR effect between EG and modified ammonium polyphosphate (M-APP) was investigated in the case of wood floor-polypropylene composites [35]. The results from the cone calorimeter demonstrated that both EG and M-APP could effectively improve the flame retardancy of Wood Plastic Composite (WPC). The function became stronger as the EG content increased. The sample of EG:M-APP = 1:1 did have longer burning time, with lower heat rate release (HRR), total heat release (THR), smoldering test (TSP), and mass loss value. Limiting oxygen index (LOI) results of the same sample (EG:M-APP = 1:1) reached the best value. The thermal degradation analysis showed that the stability was improved with the addition of EG and M-APP, especially at the proportion of 1:1. However, the mechanical properties test results showed that EG deteriorated the mechanical properties of WPC, but when the EG:M-APP = 1:1, the mechanical properties did not decrease obviously, and flame retardancy was better than for M-APP/WPC.

As stated before, the characteristics of the char layer are significant to better FR properties of polymeric materials. The effect of EG with classical intumescent ingredients, to infer the residual weight and structure of char of EG-APP-Mel-boric, was investigated [36]. In this research, the expansion of the char increased by increasing the weight of EG at a certain limit. SEM result showed that the structure of residue char was improved by increasing the wt% of EG. X-Ray Diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) analysis showed the presence of boron oxide and boron phosphate in the residual char. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTGA) showed that EG could enhance residue weight higher than that of APP-melamine-boric acid-epoxy-hardener coating. EG is a carbon source that will create a uniform protective layer on the surface of the insulating materials. Thus, the efficiency of the heat transfer could be reduced, and this would give a better effect of intumescent into the coating formulations [36].

A new application for EG as IFR was worked out by Batista et al. [29]. The objective of this work was the cellulose-based model material (CMM) encrusted with EG. The general aim of the research was to determine its basic fire resistance properties. The scope of the research involved measurement of the following parameters: time to ignition (Ti), time to flame out (Tf), heat release rate (HRR), and mass loss (ML). Oxygen index (OI) was also part of measurements.

The addition of EG was found to increase the flame resistance of cellulosic material. Although Ti for all CMM samples was lower than for control samples, this fact actually favored the promotion of char forming. The improved physical characteristics of char were achieved by increasing the amount of the insulating layer and reducing crack formation. This aspect allowed the combustion process of CMM, with a suitable EG, to be much longer than the combustion process of pure cellulose. Besides, the maximum HRR for CMM encrusted with EG was significantly smaller compared to that for pure cellulose.

6. Conclusions

One crucial parameter affecting the thermal degradation properties of cellulose is its crystallinity degree. It is observed that cellulose thermal degradation starts in the amorphous regions and propagates to its more crystalline domains. The structure of graphite consists of layers in which there are coupled six-membered aromatic cyclic systems. Carbon atoms within a graphite layer are covalently bonded, while layers are bound by weak van der Waals forces. Graphite is characterized by highly anisotropic properties and excellent electrical and thermal conductivities. It is stated that the char is formed during the whole combustion process rather than at the end of the combustion stage [37]. The overall role of char shall cease as soon as the carbon glows. Although research on expandable graphite (EG) has achieved great progress, its practical application is restricted due to high sulfur content and serious pollution during production. The presence of expandable graphite (EG) greatly improves the char formation rate and quality in FR systems. Based on this literature review, it can be assumed that the incrustation of cellulose with expandable graphite may be of particular importance in the context of the thermal resistance of its amorphous areas [27].

Despite many studies, there are still many gaps in fire retardants application, where innovative solutions like an extra source of carbon (cellulose, lignin, starch, graphite, etc.) might be utilized.

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References

1. Beard, A.; Angeler, D. *17 Flame Retardants: Chemistry, Applications, and Environmental Impacts*; Wiley: Weinheim, Germany, 2010; pp. 415–439. Available online: https://onlinelibrary.wiley.com/doi/abs/10.1002/9783527628148.hoc017 (accessed on 6 April 2020).
2. Jesbains, K.; Faiz, A. The study of bonding mechanism of expandable graphite based intumescent coating. *Res. J. Chem. Environ.* **2011**, *15*, 401–405.
3. Camino, G.; Costa, L. Performance and mechanisms of fire retardants in polymers—A review. *Polym. Degrad. Stab.* **1988**, *20*, 271–294. [CrossRef]
4. Zheng, C.; Li, N.; Ek, M. Cellulose-fiber-based insulation materials with improved reaction-to-fire properties. *Nord. Pulp Pap. Res. J.* **2017**, *32*, 466–472. [CrossRef]
5. Nazare, S. 14 Environmentally friendly flame-retardant textiles. In *Sustainable Textiles: Life Cycle and Environmental Impact*; Blackburn, R.S., Ed.; Woodhead Publishing Limited: Sawston, Cambridge, UK, 2009; Volume 32, pp. 339–368.
6. Wilkie, C.A.; Morgan, A.B. *Fire Retardancy of Polymeric Materials*, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2009.
7. Camino, G.; Costa, L.; Di Cortemiglia, M.L. Overview of fire retardant mechanisms. *Polym. Degrad. Stab.* **1991**, *33*, 131–154. [CrossRef]

8. Khan, M.; Ganster, J.; Fink, H. Natural and man-made cellulose fiber reinforced hybrid polypropylene composites: Effect of fire retardants. *Adv. Mater. Res.* **2007**, *29*, 341–344. [CrossRef]
9. Feng, C.-M.; Zhang, Y.; Lang, D.; Liu, S.-W.; Chi, Z.; Xu, J.-R. Flame retardant mechanism of a novel intumescent flame retardant polypropylene. *Procedia Eng.* **2013**, *52*, 97–104. [CrossRef]
10. Wladyka-Przybylak, M. Combustion characteristics of wood protected by intumescent coatings and the influence of different additives on fire retardant effectiveness of the coatings. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A Mol. Cryst. Liq. Cryst.* **2000**, *354*, 449–456. [CrossRef]
11. Hao, J.; Chow, W.K. A brief review of intumescent fire retardant coatings. *Arch. Sci. Rev.* **2003**, *46*, 89–95. [CrossRef]
12. Zhuge, J. Fire Retardant Polymer Nanocomposites: Materials Design and Thermal Degradation Modeling. Ph.D. Thesis, University of Central Florida, Orlando, FL, USA, 2012. Available online: https://stars.library.ucf.edu/cgi/viewcontent.cgi?referer=https://www.google.com/&httpsredir=1&article=3173&context=etd (accessed on 6 April 2020).
13. De Araújo, M. Fibre science: Understanding how it works and speculating on its future. In *Natural Fibres: Advances in Science and Technology Towards Industrial Applications*; Springer Science and Business Media LLC: Berlin, Germany, 2016; Volume 12, pp. 3–17.
14. Shen, D.; Xiao, R.; Gu, S.; Luo, K. The pyrolytic behavior of cellulose in lignocellulosic biomass: A review. *RSC Adv.* **2011**, *1*, 1641–1660. [CrossRef]
15. Lowden, L.A.; Hull, T.R. Flammability behaviour of wood and a review of the methods for its reduction. *Fire Sci. Rev.* **2013**, *2*, 4. [CrossRef]
16. Salmeia, K.A.; Jovic, M.; Ragaisiene, A.; Rukuiziene, Z.; Milasius, R.; Mikucioniene, D.; Gaan, S. Flammability of cellulose-based fibers and the effect of structure of phosphorus compounds on their flame retardancy. *Polymers* **2016**, *8*, 293. [CrossRef] [PubMed]
17. Mazela, B.; Broda, M. Natural Polymer-Based Flame Retardants for Wood and Wood Products. 2015. Available online: https://www.researchgate.net/publication/282156040_Natural_polymer-based_flame_retardants_for_wood_and_wood_products (accessed on 18 May 2020).
18. Shen, D.; Gu, S. The mechanism for thermal decomposition of cellulose and its main products. *Bioresour. Technol.* **2009**, *100*, 6496–6504. [CrossRef] [PubMed]
19. Emmons, H.W.; Atreya, A. The science of wood combustion. *Proc. Indian Acad. Sci. Sect. C* **1982**, *5*, 259. [CrossRef]
20. Duquesne, S.; Le Bras, M.; Bourbigot, S.; Camino, G.; Eling, B.; Lindsay, C.; Roels, T. Expandable graphite: A fire retardant additive for polyurethane coatings. *Fire Mater.* **2003**, *27*, 103–117. [CrossRef]
21. Zabel, H.; Solin, S.A. *Graphite Intercalation Compounds I: Structure and Dynamics*; Springer Science & Business Media: Berlin, Germany, 2013; Volume 14, pp. 5–6.
22. Thangamuthu, M.; Hsieh, K.Y.; Kumar, P.V.; Chen, G.-Y. Graphene- and Graphene Oxide-Based Nanocomposite Platforms for Electrochemical Biosensing Applications. *Int. J. Mol. Sci.* **2019**, *20*, 2975. [CrossRef]
23. Yang, Q.; Geng, Y.; Dong, H.; Zhang, J.; Yu, X.; Sun, L.; Lu, X.; Chen, Y. Effect of environmental regulations on China's graphite export. *J. Clean. Prod.* **2017**, *161*, 327–334. [CrossRef]
24. Kutz, M. *Handbook of Environmental Degradation of Materials*; William Andrew: Norwich, NY, USA, 2012; Volume 3, pp. 367–385.
25. Nguyen, H.D.T.; Nguyen, T.T.; Le Thi, A.K.; Nguyen, T.D.; Bui, T.P.Q.; Bach, L.G. The preparation and characterization of $MnFe_2O_4$-decorated expanded graphite for removal of heavy oils from water. *Materials* **2019**, *12*, 1913. [CrossRef]
26. Zhao, H.; Pang, X.; Zhai, Z. Preparation and antiflame performance of expandable graphite modified with sodium hexametaphosphate. *J. Polym.* **2015**, 1–5. [CrossRef]
27. Zheng, C.; Li, N.; Ek, M. Mechanism and kinetics of thermal degradation of insulating materials developed from cellulose fiber and fire retardants. *J. Therm. Anal. Calorim.* **2018**, *135*, 3015–3027. [CrossRef]
28. Krassowski, D.W.; Hutchings, D.A.; Qureshi, S.P. *Expandable Graphite Flake as an Additive for a New Flame Retardant Resin*; GrafTech International Holdings Inc.: Brooklyn Heights, OH, USA, 2012; pp. 1–6.

29. Anielkis, B.; Wojciech, G.; Bartłomiej, M. Expandable graphite flakes as an additive for a new fire retardant coating for wood and cellulose materials—Comparison analysis. In *Wood & Fire Safety*; Springer Science and Business Media LLC: Berlin, Germany, 2020; pp. 120–124.
30. Kim, J.; Oh, S.; Kim, H.; Kim, B.; Jeon, K.-J.; Yoon, S.-H. Expanding characteristics of graphite in microwave-assisted exfoliation. In Proceedings of the Scientiic Cooperations International Workshops on Engineering Branches, Istanbul, Turkey, 8–9 August 2014.
31. Seredych, M.; Mikhalovska, L.; Mikhalovsky, S.; Gogotsi, Y. Adsorption of bovine serum albumin on carbon-based materials. *C J. Carbon Res.* **2018**, *4*, 3. [CrossRef]
32. Paszkiewicz, S. Morphology and thermal properties of expanded graphite (EG)/poly (ethylene terephthalate) (PET) nanocomposites. *Chemik* **2012**, *66*, 26–30.
33. Paszkiewicz, S.; Nachman, M.; Szymczyk, A.; Špitalský, Z.; Mosnacek, J.; Rosłaniec, Z. Influence of expanded graphite (EG) and graphene oxide (GO) on physical properties of PET based nanocomposites. *Pol. J. Chem. Technol.* **2014**, *16*, 45–50. [CrossRef]
34. Pang, X.Y.; Song, M.K.; Tian, Y.; Duan, M.W. Preparation of high dilatability expandable graphite and its flame retardancy for LLDPE. *J. Chil. Chem. Soc.* **2012**, *57*, 1318–1322. [CrossRef]
35. Guo, C.; Zhou, L.; Lv, J. Effects of expandable graphite and modified ammonium polyphosphate on the flame-retardant and mechanical properties of wood flour-polypropylene composites. *Polym. Polym. Compos.* **2013**, *21*, 449–456. [CrossRef]
36. Sami, U.; Faiz, A. The effect on expansion and thermal degradation of 63um expandable graphite on intumescent fire-retardant coating composition. *Res. J. Chem. Environ.* **2011**, *15*, 944–951.
37. Sun, L.; Xie, Y.; Ou, R.; Guo, C.; Hao, X.; Wua, Q.; Wang, Q. The influence of double-layered distribution of fire retardants on the fire retardancy and mechanical properties of wood fiber polypropylene composites. *Constr. Build. Mater.* **2020**, *242*, 118047. [CrossRef]