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REVIEW

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# Advancements in traditional and nanosized flame retardants for polymers—A review

Ghazal Vahidi[1] | Dilpreet S. Bajwa[1] | Jamileh Shojaeiarani[2] | Nicole Stark[3] | Amir Darabi[1]

[1]Department of Mechanical and Industrial Engineering, Montana State University, Bozeman, Montana, USA

[2]Mechanical Engineering Department, Western New England University, Springfield, Massachusetts, USA

[3]Engineered Composites Science, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin, USA

**Correspondence**
Dilpreet S. Bajwa, Department of Mechanical and Industrial Engineering, Montana State University, Bozeman, MT 59717, USA.
Email: dilpreet.bajwa@montana.edu

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**Abstract**

Synthetic polymers are ubiquitous materials widely used in construction, automotive, electronics, and countless commercial products. With the growing trend of polymer applications in everyday life, upholding the rigorous fire safety regulations has become a matter of concern. In this regard, numerous studies have been conducted for improving the fire retardancy of polymers, mainly through incorporating a diverse group of fire-retardant compounds into polymer-based composites. This review article aims to present a comprehensive overview of recent advances in the fire-retardant categories for polymeric materials especially emphasizing the nanosized fire retardants. Along with an attempt to focus attention on the consumption of conventional and possibly harmful fire retardants, potential eco-friendly alternatives are represented. A detailed discussion on the flame retardation mechanisms and conventional fire characterization techniques are also discussed.

**KEYWORDS**

flame retardance, thermal degradation, thermal properties, thermoplastics, nanosized flame retardants

## 1 | INTRODUCTION

Commercial plastic production has enjoyed an impressive growth nearly 200-fold from 2 million tons in 1950's to over 350 million tons in 2015.[1] Today, polymers are ubiquitous materials with applications in automobile industry, packaging, textiles, and biomedical devices, due to their light weight, corrosion resistant structure, and unique behaviors.[2,3] However, the specific structure of the synthetic polymers limits their applications when they are exposed to heat.[4] Most of the thermoplastic polymers undergo significant thermal degradation,[5,6] which has a substantial effect on their performance and service life, limiting their applications in different fields. In particular, polymers need to be qualified for long-term services under variable thermal conditions in hostile environments.

### 1.1 | Fire hazard losses

Fire hazard is a general term that is a combination of different factors, including ignitability, amount of heat release, ease of extinction, weight-loss, flame spread, smoke index, and toxicity.[7] Modern life is surrounded by a wide variety of readily combustible materials, such as, cellulosic materials and man-made polymers.[8] Synthetic polymers alone may not be a fire hazard, but they are factors that contribute to ignition and the rapid spread of fire in vehicles, residential buildings, and other facilities.[9]

According to the U.S. Fire Administration annual report,[10] during 2017 in the U.S. alone there were more than 1 million residential fires, injuring 14,000 people, and killing more than 3000 individuals along with billions of dollars financial loss. Unfortunately, statistics did

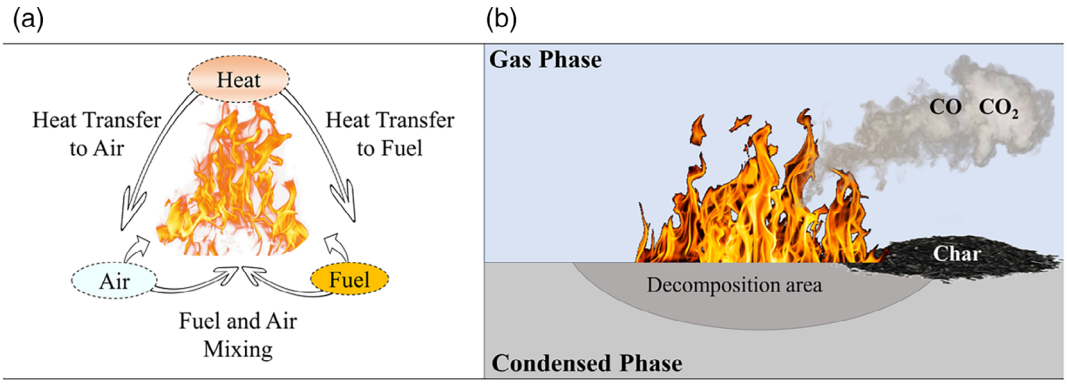



**FIGURE 1** (a) Schematic of Emmon's fire triangle (b) polymer pyrolysis products [Color figure can be viewed at wileyonlinelibrary.com]

not change much in 2018, where public fire departments responded to 1,318,500 fires, only 1000 fewer than 2017.[11]

## 1.2 | Flame retardants

Life cycle of fire is a fundamental step in understanding polymer pyrolysis and it has been described using Emmon's fire triangle (air, heat, fuel) shown in Figure 1 (a) and how it explains the mechanism of combustion of polymers have been explained in previous literature by Laoutid et al.[12] A combustible polymer, in the presence of heat and oxygen, generates combustible volatiles, causing a mass loss. Then, usually a char layer is formed in the condensed phase during the decomposition (Figure 1 (b)). Interference or absence of one or more of these steps will result in fire termination.

In order to meet fire safety requirements and diminish fire hazards, different solutions have been developed. Various chemical and physical strategies have evolved to prevent polymers from burning or to lower the heat release amount.[13] Recently, flame retardants (FRs) have been widely recognized as fire safety tools capable of lowering the number of fire injuries and death. The term flame retardant refers to a diverse group of chemicals that are added to synthesis materials, such as, plastics to prevent or slow down the combustion process. Adding flame retardants to polymers, fibers, and papers are an expanding trend that can protect the final product from burning.[14] Therefore, it is clear that flame retardants are an important part of polymer composite formulations. Role of FRs is significant for those cases that polymers have a high chance of being exposed to the ignition source (like in electronics and electrical applications), and those where polymers can ignite and spread fire quickly (like in residential and industrial buildings, limiting evacuation, and transportation).[15]

## 1.3 | Flame retardancy mechanisms

According to their specific mechanisms, fire retardants interrupt polymer pyrolysis in one or more steps. (Laoutid et al[12]) Three of the most common flame retardancy mechanisms are described in previous studies.[16,17] Gas phase inhibition mechanism, where the FRs react with the polymer under combustion in the gas phase with hydroxyl or oxygen agents at the molecular level and extinguish the combustion. Halogenated and phosphorous FRs are common in this category. Hydrated minerals (halogen free) decompose in an endothermic reaction when exposed to fire, using a cooling mechanism. They release water molecules that cool down the combustion environment of polymers. Char forming polymers (e.g. cellulose or carbon family FRs) react to combustion in a solid phase.[18] these FRs crosslink to the polymer matrix in elevated temperatures and create a barrier layer that hinders the heat transfer and release of additional gasses. They react to form a porous carbonaceous 3D-char layer that insulate the polymer surface and slow down the pyrolysis.[19,20] Intumescent FRs, such as, melamine compounds and phosphorous compounds are from this category.

## 1.4 | Flammability characterization methods

Flame retardancy process can be characterized either in gas phase, by investigating present pyrolysis species, or in solid phase, by studying the morphology and composition of the char layer. There are numerous macro and micro fire characterization methods. Limiting oxygen index (LOI), UL-94, cone calorimetry, microscale calorimetry, and thermogravimetric analysis (TGA) are of the most common fire characterization methods.

LOI is one of the primary methods that has been used for many years to investigate the relative flammability of materials.[21] Material with LOI less than 21% can burn easily whereas materials with LOI greater than 21% exhibit reduced flammability after removal from ignition source.[22] LOI requires a cost-effective setup and small sample size. However, due to the high oxygen index simulation and small scale input heat, it is not very suitable for determining the real extent of fire performance.[18]

UL-94 tests have been considered for measuring burning rate and characteristics of plastics. UL94 vertical test is widely used for determination of ignitability and flame spread rate of plastic materials. In this test, the specimen is burnt using specific flame conditions for a certain time period. The time required for the fire to be extinguished (after-flame removal) is an indication of fire retardancy properties of the specimen.[12,23]

As one of the most important fire characterization methods for polymeric materials, cone calorimetry measures the reducing oxygen concentration in the combustion gasses of a specimen subjected to a given heat flux. After exposing the sample to a conical radiant electrical heater, the combustion is triggered by an electric spark. Variety of data, such as, heat release rate (HRR) as a function of time, peak of heat release rate (pHRR), total heat release rate (THR), and mass loss rate (MLR) can be reported by this test.[23–25]

Microscale calorimetry test provides a rapid, cost-effective method for academic and industrial polymer research. Studies suggest the potential of this method for quantitative determination of full-scale fire performance for milligram samples.[26,27] Figure 2 shows a schematic of the microscale calorimeter including the gasification and combustion stages. Samples are thermally decomposed at a constant heating rate. Then, combustion products from solid state pyrolysis are removed using nitrogen and then mixed with excess oxygen to ensure complete combustion. The oxygen exhaustion is measured by analyzing the remaining oxygen/nitrogen mixture after the elimination of combustion volatiles from the gas stream. The heat release rate and other flammability parameters, such as, heat release capacity and char yield are among the outcomes of microscale calorimetry.[26,27]

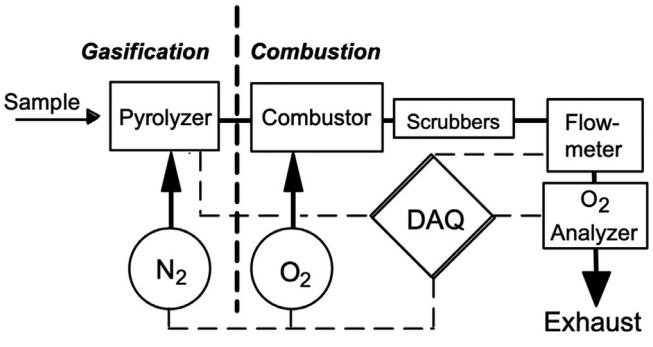



**FIGURE 2** Schematic of microscale calorimeter showing gasification and combustion stages[27]

TGA measures the changes in weight of materials as a function of temperature based on ASTM E1131 and ISO 11358 standards.[28] Weight loss at onset temperature ($T_{onset}$) and percentage of the weight that remains at the end of the heating process (including mass of char residue) are obtained by TGA. Materials with higher $T_{onset}$ produce less fuel for the combustion and therefore have better flame retardancy properties.[29]

## 1.5 | Traditional flame retardants

For decades, improvements in the flammability of materials has been achieved by using halogen-containing flame retardants, such as, tris(2-chloroethyl) phosphate, tris(1,3-dichloroisopropyl) phosphate, pentabromobenzyl acrylate, and tris(1-chloro-2-propyl) phosphate. Halogen free technologies have largely focused on phosphorus, nitrogen, silicone, boron, zinc, iron, and aluminum-containing flame retardants.

### 1.5.1 | Halogenated products

Halogenated flame retardants form the largest group of flame retardants, particularly bromine is the most effective element. They interrupt the gas phase of polymer combustion by producing free radicals in a continuous stream. High energy OH and H radicals, which are generated during combustion, react with free radicals released from halogenated FRs (RX) as per Equation 2 to Equation 5.[30]

$$R + X \rightarrow R\ + X \tag{2}$$

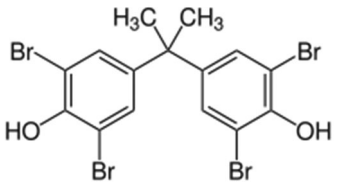
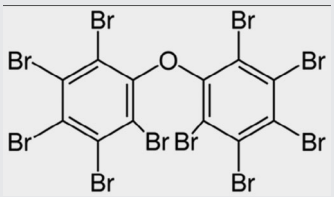
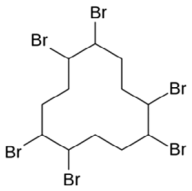
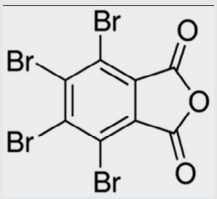
$$R'H + X\ \rightarrow R'\ + HX \tag{3}$$

$$HX + H\ \rightarrow X\ + H_2 \tag{4}$$

$$HX + OH\ \rightarrow X\ + H_2O \tag{5}$$

Type of the halogen in halogenated FRs is the key factor determining their effectiveness. Bromine and chlorine based halogenated FRs bond with polymers' carbon atoms in low bond energies. As a result, they can easily take part in the combustion process, following the mechanism discussed before. However, more thermally stable types, such as, fluorine compounds are not very common

**TABLE 1** Common halogenated FRs, chemical structure, and additional information[31,32]

| Halogenated FR | Code | Chemical formula | Additional info |
|---|---|---|---|
| Tetrabromobisphenol A | TBBPA |  | Most common halogenated FR, reactive FR in epoxy resins |
| Polybromodiphenylether | PBDE |  | Contains 10 bromine atoms, FR additives in styrene polymers, polyolefins, polyesters, and nylons |
| Hexabromocyclododecane | HBCD |  | Cycloaliphatic halogenated FR, expanded, or compact PS and textiles |
| Tetrabromophthalic anhydride | TBPA |  | FR additive in unsaturated polyesters, base material for other FRs |

when it comes to fire retardancy of polymers. Fluorine radicals are usually released at very high temperatures, far above the decomposition phase of most polymers. Iodine-based compounds are also not very common in thermoplastic polymers due to their weak thermal stability. They usually release halogen radicals in the processing temperature range of most polymers.[12,16,30] The most commonly used halogenated FRs are listed in Table 1.[31,32]

### 1.5.2 | Phosphorous products

Halogen-free phosphorous-based FRs are counted as the most available alternatives for halogen–containing components. Phosphorous-based FRs are found in a wide range of products, including phosphates and red phosphates, phosphines and phosphine oxides, phosphinates, and phosphonium compounds. When attached to polymer chains, phosphorous FRs utilize all three flame retardancy mechanisms to inhibit the polymer pyrolysis; they can form scavenger radicals in the gas phase, produce an insulator char layer, and cool down the combustion environment. However, in most polymers that contain oxygen, for example, cellulose or polyamides, dehydration and char formation are two major mechanisms.[33,34] With most of phosphorous products, thermal decomposition will lead to phosphoric acid condensation, and this in turn will liberate moisture and produce pyrophosphate. Water molecules cool down the combustion environment and the presence of pyrophosphate eventually result in the carbonized char layer formation. This insulator char layer protects the polymer underneath from further burning, prevents the new radical formations by limiting the volatile amount, and restricts the oxygen diffusion in the combustion environment.[12]

Qu et al reported that the incorporation of 1 wt% of phosphor-containing fire retardants in the epoxy resin resulted in a LOI value of 30.5% and V-1 rating in UL-94 tests. This inherent flame-retardant behavior of phosphor-containing fire retardants in the epoxy resin is shown in Figure 3.[35] During combustion, the phosphorous components with quenching and diluting mechanisms confirm the fire retardant effectiveness; phosphorous free radicals are formed in the gas phase to scavenge the combustion gasses, producing a diluting effect and phosphorus-rich environment promotes the formation of charring layers in the condensed phase.

It is worth mentioning that as the quenching effect of the phosphorus products can cause dilution of oxidizing

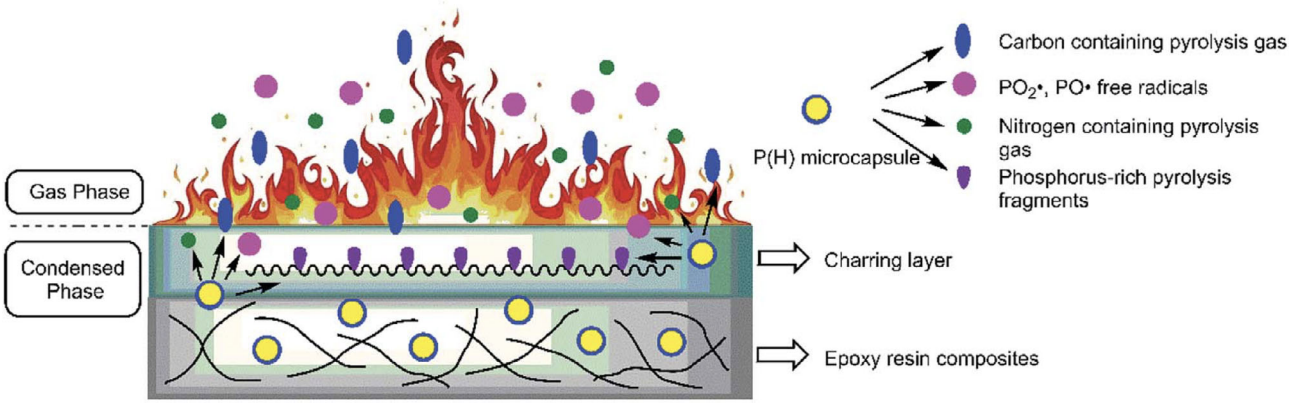



**FIGURE 3** Flame retardancy mechanism of phosphorous FR in epoxy resin[35] [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 2** List of common nano flame retardants in polymer composites

| Nanofiller | | Nanofiller loading | Polymer matrix | References |
|---|---|---|---|---|
| Metallic particles | $ZnO_2$ nanowires | 10–40 wt% | Polypropylene | 109 |
| | Aluminum tri-hydroxide (ATH) | 8–14 wt% | Polyurethane foam | 42 |
| | Zinc oxide | 1 wt% | Polypropylene-ethylene-propylene-diene monomer | 52 |
| Nanoclay | | 1–3 wt% | Polystyrene | 39 |
| Bio based fillers | Lignin | 15–20 wt% | Polypropylene | 63 |
| | Starch | 10 wt% | Polylactic acid | 69 |
| | Proteins | 20 wt% | Polyester | 70 |
| | Cellulose nanocrystals (treated) | 10 wt% | Polylactic acid | 82 |
| Intumescent flame retardant | | 20 wt% | Polylactic acid | 69 |
| Carbon family | Carbon nanotube | 0.25 wt%1 vol% | Epoxy–polypropylene | 88,85 |
| | Graphene | 2 wt% | Polyurethane, polypropylene | 95,96 |
| | Fullerene | 2 wt% | Polypropylene | 106 |

gas phase, this condensation and dehydration can induce stress concentration and crack propagation in some materials.[34] Furthermore, some studies have indicated phosphorous-based FRs as "Neurotoxicants" after they break in the environment.[12]

## 1.6 | Nanosized fire retardants

With the advent of nanotechnology in the past few decades, the prospects of nano scale fillers in polymer-based composites in the flame retardancy applications have progressed rapidly. Although nanofillers do not show excellent fire retardance inherently,[36] incorporation of low amount of them in polymer composites tend to provide drastic improvement in thermal stability,[37] smoke release amount,[38] peak heat release rate and the speed at which flames spread throughout the nanocomposites.[36] The main mechanism of fire retardancy for nanocomposites, which happens in the condensed phase, depends on different factors including structure and chemical composition of the nanofiller.[39] In general, the presence of nanofillers in polymer matrix can alter the overall response of nanocomposites during exposure to flame. A list of most commonly used nanofillers in nanocomposites with the aim of fire retardant is summarized in Table 2.

### 1.6.1 | Metallic and non-metallic particles

Metallic nanoparticles have received considerable attention for their applications as flame retardants in different polymer matrices. Metallic nanoparticles exhibit different reaction mechanisms against fire according to their

structure; some metal nanoparticles (metal hydroxide particles) utilize hydrated minerals and release water molecules as they decompose in the presence of fire and provide an endothermic reaction. In this case, the cooling effect would increase the self-extinguishing ability in nanocomposites. Aluminum tri-hydroxide (ATH) and magnesium hydroxide (MH) are two non-halogen fire retardant additives that undergo endothermic reaction and interfere with the combustion process when exposed to heat (Equation 6 and Equation 7).[40]

$$2Al(OH)_3 \xrightarrow{Heat} Al_2O_3 + 3H_2O. \quad (6)$$

$$Mg(OH)_2 \xrightarrow{Heat} MgO + H_2O \quad (7)$$

Incorporation of the metal hydroxide nanoparticles in polymer composites would result in a noticeable increase in limiting oxygen index (LOI). This phenomenon is due to yielding a barrier on the polymer surface, which in turn can lower the heat flux provided by flame and improve the fire retardancy. The formation of char is another mechanism in some fire retardant materials, such as, alumina trihydrate (ATH) that delays ignition and fire development.[41]

In addition, some metal hydroxide FRs release water when decomposing at elevated temperatures, which leads to the cooling the substrate below the flash point. Subsequently, water formation favors the dilution of combustible gasses, reduces the oxygen effect, and decreases the flame spread rate. Xi et al reported a flame-retardant behavior in polyurethane foams due to the endothermic decomposition and water release reaction from adding 8 to 14 wt% of ATH filler in a synergetic system. They also reported that the water released from ATH reacted with the decomposition products and formed polyphosphate, increasing the barrier effect of the char layer to heat and flame.[42] However, contradictory results were reported for release of ammonia and water owing to the incorporation of ATH in polymer matrices, which led to an earlier degradation of EVA[43] and poly(1,4-butanediol succinate) (PBS)[44] due to hot water hydrolysis.

### 1.6.2 | Zinc oxide

Zinc oxide (ZnO) is one of the most popular photocatalyst metallic compounds because of its advantages, such as, cost efficiency, numerous active sites, high surface reactivity, and low environmental impacts. In fact, it is listed as safe by the US Food and Drug Administration given that zinc is an essential trace element.[45] ZnO particles have high thermal conductivity as well as great heat capacity. Therefore, incorporating them into polymeric compounds will result in absorbing the heat transmitted from the surroundings and retarding the direct thermal impact to the polymer backbone. In other terms, they act as an inhibitor to slow down the flame spread rate.[14,46]

With recent advancements in nanotechnology, nano-sized zinc oxides are among the emerging high-value inorganic products with significant features, (such as, high catalyst effect, effective antibacterial properties, high UV absorption, high thermal and physical stability, and high heat capacity) that have many applications in different industries, such as, cosmetics, plastics, sensors, and semiconductors.[47–49]

It is common to use high concentration of inorganic mineral fillers, such as, $Al(OH)_3$ up to 20 wt% to modify flame retardancy of polyvinyl chloride (PVC).[50] However, it is reported that the addition of only 0.635 wt% of ZnO and 9 wt% of $Al(OH)_3$ combination into PVC can significantly increase the LOI value of PVC nanocomposite (up to 30%).[51] This observation was more likely due to the formation of crosslinked surface modified ZnO in polymer matrix, which accelerate the nucleation process and improve the heterogeneous nucleating ability in the cross linked polymer matrix.[48]

Intumescent flame retardant systems (IFRs) are FRs that can insulate materials during combustion through the formation of an expanded carbonized layer. These systems usually require three components: an acidic source, a carbonization source, and a blowing agent. ZnO-intumescent flame retardant (IFR) system has been reported to be effective in flame retardancy property of the polypropylene-ethylene-propylene-diene monomer (PP-EPDM) polymer blend.[52] The IFR used here was self-designed out of poly ammonium phosphate (acid source), dipentaerythritol (carbonization agent), and melamine (blowing agent). Addition of 1 wt% ZnO and 29 wt% IFR showed the best fire performance as that formulation exhibited an LOI value of 35.6% compared with 17% LOI of original PP-EPDM blend. Furthermore, a heat release peak (pHRR) appeared for the formulation containing ZnO, reflecting the better barrier effect of the char layer compared to the original polymer blend and also formulations containing only IFR. Uniformly dispersed ZnO particles assist the IFR to have a more homogenous and compact char layer. Moreover, great heat capacity of them would result in absorbing the heat transferred from the combustion and creating a more effective char layer.[52]

### 1.6.3 | Nanoclays

Nanoclays are ubiquitous nanofillers that are isolated from naturally occurring clays through energetic

stirring, followed by centrifugation and freeze-drying, centrifugation and cross-flow filtration, or ultracentrifugation. Nanoclays are composed of stacked mineral silicates layers, forming complex clay crystallites. Three main mechanisms have been reported for fire retardancy in composite materials containing clay particles, including migration,[53] barrier, and paramagnetic mechanisms.[54,55]

In the combustion process of the composites containing clay particles, the bubbles that are formed during polymer degradation push the clay nanoparticles from interior layers to the surface of the composites. The clay migration to the outer surface could be attributed to different factors; the difference in surface free energy between polymer and polymer-clay blend, the temperature and viscosity gradient during directional heating, and the formation of rising gasses during combustion process.[56] The aggregation of clay particles results in more hydrophilicity (i.e. less compatible with common hydrophobic matrices) due to the degradation of the organic treatment on the clay interlayers. Consequently, a clay-rich barrier layer will form and reduce the rate of weight loss in the composite combustion.

Barrier mechanism during the condensed phase suggests the formation of a char layer in composites containing clay particles while exposing to fire. The insulating char barrier prevents the mass transfer of degradation products to the combusting polymer surface. This, in turn, would limit further exposure to heat and oxygen and hinder the burning process.[57]

Paramagnetic radical trapping is another suggested fire retardancy mechanism of nanoclays. This mechanism proposes that structural metals in clay particles, such as, iron, can trap the radicals formed during polymer combustion and reduce the degradation rate.[54,55]

Nanoclays are widely used as flame retardant additives in polymer nanocomposites, owing to their incombustible properties. Contributions of nanoclays can result in superior fire retardancy in polymer matrices through noticeable improvement in peak heat release rate, ignition time, and fire growth index.[58] Ahmed et al observed a protective char layer on the surface of polystyrene upon the incorporation of 1 to 3 wt% nanoclays, which resulted in higher fire retardancy and lesser emission of smoke, CO, and $CO_2$ than the pure polystyrene.[39] Achieving nano-dispersion of clay in the polymer matrices is an essential parameter, which affects the fire retardancy of polymer-clay nanocomposites. Lu et al reported different methods in improving the nanodispersion of clay in LLDPE/PA6 blends. They observed that the blends with clay localized in the LLDPE phase, rather than PA6 phase, exhibited better flame retardancy.[59]

### 1.6.4 | Bio based additives

In addition to inorganic fire retardants, certain plants have developed a defense mechanism against fire invasions due to their specific molecular structure. Bio based compounds in these plants owe their intrinsic fire retardancy to the formation of a thermally stable char layer when exposed to fire. A review of bio based flame retardants has been previously published by Costes et al.[13] Briefly, char formation mechanism is initiated as the stored water in wood starts to be liberated during thermal decomposition of wood components (lignin, cellulose, etc.). This barrier char layer insulates the underlying wood from further burning by hindering the heat exposure.[13,60]

Biomass is the largest resource for bio-based materials and a massive range of chemicals and biofuels are produced based on biomass derivatives, thanks to their abundant resources and reasonable pricing. The inherent char formation ability of biomass and the resulting fire retardancy makes it desirable for FR applications.[61] Up to 75% of biomass is composed of saccharide-based products (e.g. cellulose, hemicellulose, and lignin), while the rest is mostly energy storage components (e.g. starch), proteins, and vegetable oils.

Lignin is one of the most abundant bio-based products with a high molecular weight. Thermal degradation of lignin is accompanied by a stable char formation; it first starts around 200 C with water release and condensation reaction. Lignin experiences a mass loss over a broad range of temperatures up to around 800 C, which is resulted from its structural decomposition and carbonized layer formation.[62] Chirico et al reported an improvement in fire behavior of polypropylene in the presence of 15 to 20 wt% of lignin. The pHRR and mass loss rate of the composite was generally lower compared with the virgin polymer due to the char formation mechanism of the lignin.[63]

Starch is another bio-based compound with an interesting fire retardancy mechanism. It is a polysaccharide composed of amylose and amylopectin polymers. During starch decomposition, a physical dehydration happens by releasing the stored moisture, followed by thermal condensation of hydroxyl groups in higher temperatures. Consequently, aromatic rings (e.g. furan) are formed in temperatures around 400 C as a result of above-mentioned water liberation and ether segment formations. These aromatic rings later participate in carbonization and char formation.[64–66] It is worth to mention that thermal stability of starch is highly dependent on its composition, structure, chemical modification, and extraction methods. Starch's high decomposition temperature makes it an

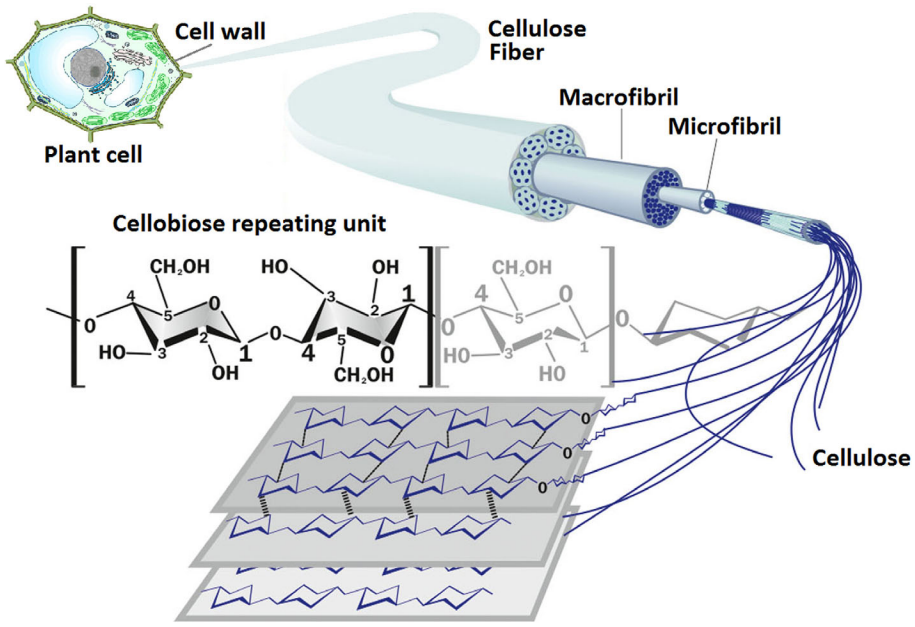



**FIGURE 4** Representation of a cellulose fiber organization found in plant cell walls[13] [Color figure can be viewed at wileyonlinelibrary.com]

interesting option for polymer composites with high processing temperatures.[67–69]

Starch is a rich carbon source and when combined with IFRs can result in flame retardancy properties for commercial polymers, such as, PLA.[13,70] Wang et al prepared a PLA composite using 10 wt% starch and 20 wt% IFR. Here, microencapsulated ammonium polyphosphate served as acid source, melamine a blowing agent, while starch as the carbonization agent. The resulting composite showed 41% LOI value along with UL 94 V-0 classification and modified dripping behaviors compared with the neat polymer.[68] It is important to note that addition of starch and IFR separately to PLA did not yield successful fire retardancy behavior compared with the neat polymer, suggesting the potential synergetic effect of starch/IFR system.[68]

Proteins also have attracted research interests in fire retardancy applications.[71,72] Casein, milk's major protein, is a phosphorous containing molecule, which is used as a coating for cotton or polyester fabrics. The fire behavior of casein-coated fabrics is reported to be improved in terms of significant reduction in total burning rate, thanks to the char formation mechanism of proteins. During the thermal decompostion, proteins like casein favor the char formation mechanism and volatile supression by releasing acidic compounds, such as, phosporic acid. Carosie et al reported a remarkable decrease of the burning rate (−70%) and an increase of limiting oxygen index (from 21 to 26%) of polyester by adding a suspension of casein with total of 20 wt% dry solid add-on.[69]

#### *1.6.4.1 Cellulose nanofibers*

Cellulose is the most abundant organic polymer, which is found in cell wall of plants as well as in fungi, bacteria, and algae. Cellulose has numerous glucose units with high degree of polymerization based on its extraction method. Figure 4 represents a cellulose fiber organization in a plant cell wall, which is consisted of many cellobiose repeating units.[13,73] Char formation mechanism is very complicated in cellulosic materials. During thermal decomposition, cellulose can produce an insulating char layer under certain specifications, depending on its extraction method and surface treatment. Degradation condition and existing species in the combustion environment govern the amount of produced char and its thermal stability.[74,75]

In low temperatures, degradation of cellulose leads to the formation of anhydrocellulose. As temperature goes up, the remaining cellulose unzips into tar and further anhydrocellulose components and finally proceeds to char and gas formation. Many researches were carried out to improve fire retardancy of cellulose by chemical surface modifications or incorporation of other fire retardants (e.g. phosphorous FRs). These attempts proved to further assist the inherent char formation behavior of cellulose.[73,76]

Cellulosic nanomaterials, such as, cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs), are generally used as nanofillers for various polymers in order to tailor their physical, mechanical, and thermal properties. They typically have a diameter between 5 and 500 nm and most of them are commercially available or can be extracted via well-known methods (e.g. acid

hydrolysis).[77,78] Recently, flame retardancy potential of cellulose nanofillers has attracted a lot of interests. There are numerous reports on improved flame retardancy performance of commercial polymers in the presence of surface-modified cellulose nanocrystals or cellulose nanoparticles hybrids with other fire retardants.[49,79–81]

A 10 wt% of CNCs extracted with phosphoric acid hydrolysis has proven to increase the thermal stability of polylactic acid (PLA).[82] Phosphoric acid is well-known for its fire retardancy property.[35] Moreover, CNCs have a highly crystalline structure with well-packed chains and hard-to-break inter-chain hydrogen bonding that protects them from melting in high temperatures. Therefore, the incorporation of phosphoric acid treated CNCs in PLA matrix would enhance the thermal stability of the polymer by formation of the char layer and hindering the heat energy.

CNFs-clay nanopaper composite has been reported as an effective flame retardant coating for wood.[83] The hybrid system was prepared as a "brick and mortar" structure, where clay nanopapers represent the brick and CNFs represent the mortar. The thermal shielding provided by this system caused an 81% decrease in the heat flux of the wood as reported by cone calorimetry test.[83] The char layer formed by this hybrid acted as an oxygen barrier insulating layer and increased the oxygen diffusion length. Additionally, clay char layer hindered the diffusion of CNFs volatiles, resulting in the formation of micro voids and further decline in thermal conductivity.

### 1.6.5 | Carbon family based additives

Generally, carbon family members have attracted a great deal of attention during past decades for fabricating polymer nanocomposites, owing to their superior mechanical, and flame retardancy properties.[18]

#### *1.6.5.1 Carbon nanotube*

A wide range of studies have shown that carbon nanotubes (CNTs) either single-walled (SWCNTs) or multi-walled (MWCNTs) are among the most promising alternatives for traditional flame retardants to be used in different polymers, such as, PP, PE, PLA, lignocellulose, epoxy resin.[84–88] These studies have demonstrated that adding a small amount of well-dispersed CNTs (<5 wt%) to polymer composites can significantly improve the fire behavior due to their fascinating chemical and physical properties.[89]

CNTs have a highly elongated structure with a large aspect ratio. Their specific geometry enables them to create a strong protective network in the condensed phase to protect the underlying polymer from heat. This behavior could result in suppression of heat release rate (pHRR reduction in cone calorimetry) and weight loss rate during the combustion.[85,90] Moreover, low flame spread rate, smoke-suppression, and anti-dripping properties have been reported while incorporating CNTs in different polymers.[86,87]

Improvement in fire retardancy of polymer composites is strongly dependent on uniform dispersion of CNTs and their interactions with the polymer matrix.[84,89] There are different surface modification methods and fabrication techniques, supporting CNTs homogenous distribution in polymers. Moreover, hybridization of CNTs with inorganic compounds or covalently bonded organic flame retardants has been investigated to improve their thermal stability. It is worth noting that polymers with aromatic rings in their structures, such as, polycarbonates are known to have a good interfacial adhesion with CNTs.[91]

Chemical treatment of CNTs with concentrated sulfuric acid and nitric acid has proven to be successful when incorporated in different polymers, such as, polylactic acid or lignocellulose.[86,89] It was found that the incorporation of 2 wt% of acid-treated MWCNTs to lignocellulose/chitosan composites (LC/GC/MWCNT) can decrease the total heat release and the total smoke production by 10.7% and 45.5% compared with those of virgin polymer during cone calorimetry test. LC/GC/MWCNT composite also exhibited higher LOI values compared to neat polymers (Figure 5).[86] Moreover, Yang et al showed that addition of 1 wt% acid-treated CNTs to PLA/calcium magnesium phytate composite promoted a significant reduction in peak heat release rate up to 35% and a char residue of 18.4%.[87]

There are some studies that introduce melt-blending preparation methods without any primary treatments or modifications. Kashiwagi et al has reported a significant reduction in pHRR of polypropylene (PP) by addition of 1 vol% MWCNTs. PP/MWCNTs composites were prepared using direct melt blending without any primary modifications or additional additives.[85] Rahatekar et al demonstrated the flame retardancy effect of MWCNTs in epoxy resin through uniform dispersion of nanofillers via high shear mixing.[88] Almost 50% reduction in mass loss rate (MLR) was observed for Epoxy/MWCNTs composites compared with neat epoxy, using the gasification apparatus.[88] In another work, Kashiwagi et al has investigated the importance of uniform dispersion of CNTs in PMMA matrix in fire performance of the resulting composite.[92] SWCNTs were added to PMMA and dimethylformamide (DMF) suspension and permitted to disperse by bath sonication for 24 h. Uniform dispersion of SACNTs were controlled by their concentration in DMF. Cone calorimetric

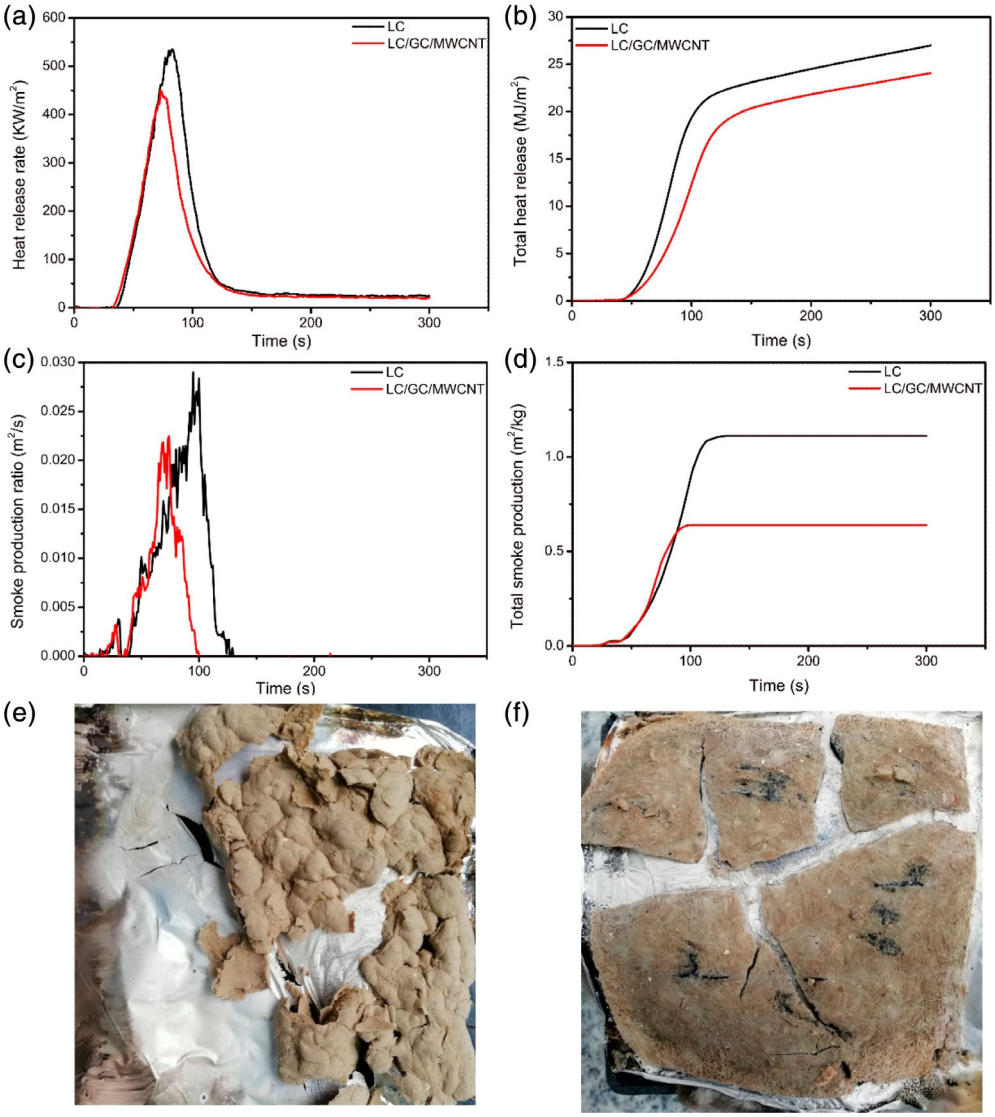



**FIGURE 5** Cone calorimetry curves of LC composite and LC/GC/MWCNT composite: (a) heat release rate; (b) total heat release; (c) smoke production ratio; (d) total smoke production; (e) residues of LC composite; (f) residues of LC/GC/MWCNT composite[86] [Color figure can be viewed at wileyonlinelibrary.com]

test results showed a significant reduction in pHRR for samples with 0.5 wt% uniformly dispersed SWCNTs in PMMA. On the other hand, PMMA containing 0.5 wt% poorly dispersed SWCNTs proved to have similar fire performance as the virgin PMMA (Figure 6).[92]

### *1.6.5.2 Graphene*

Graphene is a two-dimensional carbon nano material with outstanding physical properties, such as, electrical properties and excellent thermal conductivity due to its large surface area.[93,94] Recently, graphene flame retardants have shown promising impact on thermal stability of different polymers, mostly because of their insulator barrier effect.[95–98] Graphene is mostly prepared by removal of oxygen groups from the surface of graphene oxide (GO) or reduced graphene oxide (rGO).[99] The challenge involving the application of graphene nanosheets in the polymer matrix is to achieve a good dispersion. Graphene layers have a high tendency to restack because of their strong Van der Waals forces and π-π interactions.[95,100] Therefore, it is most common to incorporate metal oxides as a modifier of graphene compatibility with the polymer matrix.[96] To take a case in point, Wang et al prepared a rGO/cerium hybrid to reduce the fire hazards of thermoplastic polyurethane (TPU). The introduction of 2 wt% rGO/cerium hybrid into TPU led to 33% increase in char residue and a 44% reduction in pHRR. It is worth mentioning that the incorporation of sole rGO in TPU also caused a 27% reduction in pHRR when compared with pure TPU.[95] Yuan et al has also reported that the incorporation of dual modified graphene (by phosphazene flame retardant and $Ni(OH)_2$ nanosheets) in polypropylene led to an improvement in the fire performance of the polymer. Compared with neat PP, a 32.6% reduction in pHRR values were observed in the presence of 2 wt% functionalized graphene.[96] 28.6% reduction in the total smoke release and 19% reduction in

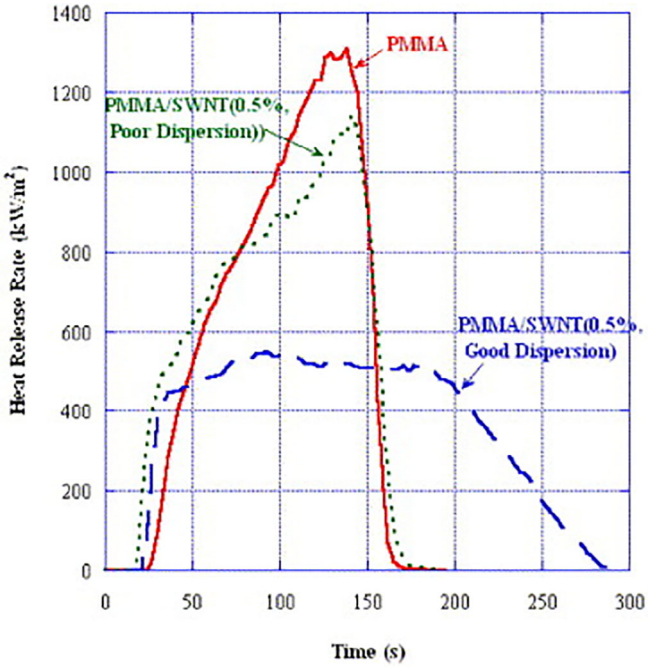



**FIGURE 6** Effect of SWNT dispersion on mass loss rate of PMMA/SWNT at 50 kW/m$^2$ in a nitrogen atmosphere[92] [Color figure can be viewed at wileyonlinelibrary.com]

total heat release of composite samples were among other promising results.

*1.6.5.3 Fullerene*

Fullerene (C60, aka. buckybull) is a carbon allotrope, which has a spheroidal-shaped structure. Combination of magnificent thermal stability and unique physical and electrical properties of fullerene with popular advantages of polymers has attracted a lot of research interests.[101–103] However, only a few studies have focused on fullerene flame retardancy effect of polymers. Fullerene has a high reactivity against free radicals. It can act as a free radical scavenger to trap radicals produced during combustion in the gas and/or condensed phase and delay thermo-oxidative degradation of polymers.[104–108]

Fullerene nanoparticles have a tendency to agglomerate due to their strong Van der Waals forces and significant specific surface area. This, in turn, can result in poor fire performance of the polymer composite. To this extent, it is important to assure uniform dispersion of fullerene nanoparticles in polymer matrix. Song et al reported successful incorporation of pristine fullerene nanoparticles in PP matrix via melt compounding technique.[106] Cone calorimeter recorded a 46% reduction in pHRR for fullerene containing samples at the maximum fullerene loading (2 wt%) compared with that of neat PP. Meanwhile, TGA analysis have demonstrated that in 2 wt% loading of fullerene, $T_{onset}$ and $T_{max}$ were 20 C and 62 C higher than those for PP, respectively. This could be assigned to the role of fullerene as a free radical sponge in slowing down the thermal oxidation of PP. Flame retardancy mechanism of fullerene is also believed to involve trapping PP free radicals during the burning process in order to form a crosslinked network structure. This structure is called "gelled-ball", owing to its high gel content and complex viscosity.

## 2 | CONCLUSION

A broad range of flame retardants including commercial inorganic FRs along with bio-based and mineral FRs at nanosized scale are under development and investigation. Since some of the traditional halogenated FRs are in the process of being prohibited due to their deleterious effect on human health and the environment, understanding the functionality of green bio-based, and nanosized alternatives is of the utmost importance. It is worth mentioning that the complexities in the fire-retardant systems for different polymers and lack of systematic studies on various parameters (materials, mechanisms, methodologies, and techniques) have mostly led to only qualitative observations.

Recently, advancements in nanotechnology is playing important role in improving the fire retardancy of polymers; there has been an emerging trend on using various nanofillers in the polymer networks to modify their fire behavior. Thanks to significant surface area of nanoparticles and their boosted effectiveness, they are capable of enhancing the flame retardancy of the host polymer, even in relatively small concentrations. However, homogenous dispersion of nanosized FRs in the polymer network is the major challenge, especially because it influences their efficacy. Most of the time, due to the differences in the inherent characteristics of nanofillers and the matrix, achieving a uniform dispersion requires some kind of chemical and physical modification, or a distinctive manufacturing technology.

It has been confirmed that the flammability of polymeric materials is a matter of convolution for which no sole solution can be found; especially considering the wide variety of polymer matrices. However, advancements of fire characterization techniques and a better understanding of the flammability phenomenon have facilitated the selection of the most promising additives for fabrication of safe and fire-resistant polymers.

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## CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

## ORCID

*Dilpreet S. Bajwa* https://orcid.org/0000-0001-9910-8035

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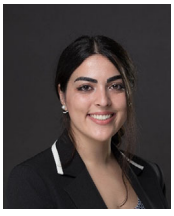

**Ghazal Vahidi** is a PhD student in Mechanical Engineering Department at Montana State University-Bozeman, working on biomechanics and multiscale material characterization. She received her MSc. in 2019 and BSc in 2015 degrees both in

mechanical engineering from North Dakota State University and University of Tehran, respectively. Her MSc project was focused on fire retardancy of polymer nanocomposites under the supervision of Dr. Dilpreet Bajwa.

**Dilpreet S. Bajwa** is a Professor in the Department of Mechanical and Industrial Engineering at Montana State University, Bozeman, MT. He received his PhD in 2000 from the University of Illinois, Urbana-Champaign, USA. He worked in various R&D leadership roles in wood products industry. His current research is focused on development of multifunctional materials from nanocellulosic feedstocks and fiber-polymer composites. He has authored over 125 research papers, technical articles, in various journals and books. He is associate editor of Industrial Crops and Products (Elsevier Journal) and serves in the editorial board of several other journals.

**Jamileh Shojaeiarani** is currently working as an Assistant Professor in Mechanical Engineering Department at Western New England University (WNE), Springfield MA, USA. Prior to joining WNE, she worked as a research fellow at North Dakota University where she received her PhD in 2018. Her research, centers around manufacturing, processing, and advanced characterization of nanocomposites with potential application in biosensing and biomedical fields. She has authored numerous research papers in various journals and books.

**Nicole Stark** is a Research Chemical Engineer in the Engineered Composites Science Group at the USDA Forest Products Laboratory (FPL) in Madison, Wisconsin, USA. Her research focus is to combine forest-based resources with other polymers to develop novel composite materials. Her program includes examining the influence of raw materials and additives on natural fiber-plastic composite performance and incorporating cellulose nanomaterials into films for packaging applications. Nicole has degrees in Chemical Engineering and Mechanical Engineering from the University of Wisconsin-Madison, and PhD from Michigan Technological University.

**Amir Darabi** is a second-year PhD student in Mechanical Engineering at Montana State University-Bozeman. He received his MSc. in Mechanical Engineering from North Dakota State University, where he was focused on the material characterization and FEA of thermal spray composites. He also received his BSc in Mechanical Engineering at University of Tehran. His current research involves surface engineering and multiscale characterization of bio-inspired polymer composites.

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