Fire Behavior of 3D-Printed Polymeric Composites

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1. Introduction

Thermo-compression (including extrusion and injection molding) is a classical technique applied in the production of polymer parts. However, the utilization of thermo-compression to produce parts with complex geometry is challenging. Hence, there has been the need to adopt 3D printing methods to facilitate the production process. 3D printing (or additive manufacturing) has gained popularity owing to its highly flexible nature (Ref 1). 3D printing processes such as fused deposition modeling (FDM), stereolithography (SLA), and selective laser sintering (SLS) are the well-established techniques for plastic parts manufacturing (Ref 2). The basic operating principle is different for each process and each one has its advantages and drawbacks. The FDM process operates on the basis of melting and extrusion of thermoplastic polymer filament, which provides relatively low resolution and accuracy at the lowest cost (Ref 3). In the case of SLA, the laser cures the photo-polymeric material, which provides fine details with high resolution and accuracy (Ref 4). On the other hand, SLS uses a laser source to fuse the polymer powder and form the required shape. SLS produces plastic parts with good mechanical properties resembling injection molded parts. Additionally, high productivity and low-cost production can be possible with the SLS technique (Ref 5).

Among the aforementioned 3D printing techniques, FDM is a prevalent manufacturing method because of its low-cost printing. However, the range of feedstock materials-filament that is commercially available is limited. Nevertheless, in some specific 3D printing processes, no filaments are necessary. Polymer pellets can be directly fed into the printing nozzle thus, allowing researchers to investigate many polymeric matrices with no commercial limitation (Ref 6). Although, FDM-made polymers parts are capable of possessing acceptable mechanical strength and performance (Ref 7, 8), they generally have poor flame-retardant properties (Ref 9). The poor flammability reflects negatively on the overall performance of these 3D-printed products. Figure 1 illustrates the flame retardancy mechanism of 3D-printed parts and the role of flame retardants (FRs) during polymer pyrolysis.

Researchers have attempted to enhance the flame retardancy of numerous polymers since the past decades and significant findings were reported (Ref 10, 11). For instance, halogen-based FRs have been extensively used in the past to enhance the flame resistance of various polymeric materials, however, they are currently prohibited due to their adverse effects like environmental pollution and toxicity (through the evolved gases) toward humans (Ref 12, 13). Therefore, it was essential to develop halogen-free flame retardants to enhance the fire safety of polymeric materials. In this view, an array of FRs were developed like phosphorus-based (Ref 14, 15), silicone-based (Ref 16), metal hydroxides (Ref 17, 18), nitrogen-based (Ref 19) or carbon-family (such as fullerene, carbon nano tubes and
graphene) (Ref 20) to improve the flame retardancy of polymers. Among these, phosphorus-based flame retardants are frequently incorporated by chemical or physical methods to achieve superior flame retardancy of polymers (Ref 21, 22). For instance, Xu et al. (Ref 23) synthesized a phosphorus-containing chemical agent to cure epoxy (as a reactive flame retardant), and revealed that the 5 wt.% of phosphorus-based FR added epoxy successfully passed UL-94 test with V-0 flammability rating and the LOI value was as high as 30.8%. Elsewhere, Huo et al. (Ref 24) introduced phosphorus element into the main chains of epoxy chemically and the 1 wt.% phosphorus flame retardant added epoxy displayed a limiting oxygen index (LOI) of 38.3% and passed in UL-94 burning test with a V-0 rating (Ref 24). Das et al. (Ref 25, 26) recommended biochar derived from pyrolysis of biomass as an effective filler to enhance the fire resistance characteristics of polymers. For instance, in their investigations, the peak heat release rate (PHRR) for biochar added PP composites was 318 and 281 kW/m², which was 73% and 70% lower than that of neat PP, however, the time to ignition (TTI) for biochar added PP composites was reduced to 13 and 16 sec, which was 45 to 55% lower than that for neat PP. Consequently, the total heat release (THR) was reduced by 9% and 6% compared to neat PP (Ref 25, 26).

It is worth noting that 3D-printed polymers and their composites play a vital role in electronic device fabrication
27, 28), aerospace industry (Ref 29) and so on. Though beneficial for certain performance properties, these materials pose significant fire risks. Reinforcements used in polymers such as wood-based and other natural lignocellulosic materials are flammable but compared to many synthetic polymers these materials can have lower fire hazard (Ref 30-32). Fire is the major risk for most polymers and their composites since they are susceptible to combustion due to their hydrocarbon backbone. A well-designed plastic product must be safe, and for this purpose, the development of fire-proof materials is critical (Ref 33). The available manufacturing processes require 3D-printed polymers to have high strength, be thermally resistant and flame retardant. Among the aforementioned properties, mechanical and thermal properties such as tensile strength, flexural strength and thermal stability of 3D-printed polymeric materials are well documented (Ref 7, 34, 35). However, only a very few studies have investigated the fire behavior of 3D-printed polymer parts. This article, therefore, seeks to review the fire behavior of 3D-printed polymeric composites. The review article provides an insight into the various polymers and their composites used in 3D printing and the various flame-retardant treatments applicable in this field. Moreover, the contribution of the industrial sector toward the improvement of the fire retardancy of 3D printing materials is analyzed. Finally, recommendations are provided to garner further research toward comprehending the fire behavior of these 3D-printed polymeric materials.

2. Flame Retardancy of 3D-Printed Polymer Parts

In light of the above discussion, the flammability of the polymer and its composites need to be reduced to increase their use, especially in high risk applications. The flammability of polymers and their composites can be enhanced by the addition of suitable FRs. Therefore, polymeric materials’ tendency to combust upon exposure to fire must be reduced by the incorporation of different FRs (Ref 36-43). Some of the available FR strategies for polymeric materials are presented in the schematic diagram shown in Figure 2. Polymer products made from 3D printing technique are also not exempted from the problem of vulnerability toward fire (Ref 44), which warrants several FR treatments. In the following sections, the fire behavior of various types of polymers and their composites processed by AM are discussed in detail.

2.1 Poly (Lactic Acid) (PLA)

FDM is one of the frequently employed 3D printing techniques for the processing of conventional thermoplastic polymers such as PLA, Acrylonitrile Butadiene Styrene (ABS), polyamide (PA), and Polyethylene Terephthalate (PET). Among these polymers, PLA is one of the widely used materials in the FDM process. By choosing the optimal PLA grade (molecular weight, the proportion of D- or L-enantiomers, crystalline morphology, etc.), it is conceivable to achieve PLA-based polymers with satisfying mechanical and thermal properties considering the explicit application (Ref 45). PLA is a biodegradable material having excellent mechanical properties and optical transparency, which are very attractive features in several applications (Ref 46). However, PLA has high flammability that restricts their application in wide range of applications. Addition of flame retardants (in the form of nano-filler) in PLA is a viable strategy to overcome this shortcoming (Ref 47, 48). The use of nano-filler permits the simultaneous enhancement of material’s properties and processability. Drawability and processability are the two influencing parameters in FDM technology because they have roles on both PLA feedstock filament production and layer deposition during the printing of PLA. In this regard, addition of FRs

![Flame Retardant Strategies](image_url)
in precise concentration is essential to exhibit balanced flame retardancy and mechanical strength of the 3D-printed parts.

Guo et al. (Ref 49) analyzed the flame retardancy of PLA samples manufactured by melt blending and FDM. Composites were fabricated by varying the weight percentages of PLA, melamine polyphosphate (MPP) and Cloisite 30B (C-30B). The authors produced different combinations: binary phase (72% PLA + 18% MPP and 83% PLA + 17% MPP) and ternary phase (82% PLA + 17% MPP + 1% C-30B and 81% PLA + 17% MPP + 2% C-30B). PLA samples using melt blending technique and studied their flammability properties using UL-94 vertical burning test, limiting oxygen index (LOI) and cone calorimeter. In UL-94 and LOI tests, the neat PLA showed fail-rating (denoted as “NG”) and 20% LOI (vol.%), respectively, thereby showing its high flammability. On the other hand, the 82% PLA + 17% MPP + 1% C-30B sample showed V-0 rating in UL-94 test and displayed ca. 29% LOI. In addition, the 82% PLA + 17% MPP + 1% C-30B sample made through melt blending technique displayed an average heat release rate (AHRR), PHRR and THR of 198, 285 kW/m² and 84 MJ/m², respectively, during cone calorimetry test and these were 2% (lower), 1% (higher) and 1% (lower) than the similar PLA sample printed through FDM, respectively. It is interesting to note that the difference in manufacturing process did not influence the fire behavior of polymers.

The images of transmission electron microscopy (TEM) of the sample without cloisite displayed spheroidal shape of MPP, where the high interfacial energy restricted the deformation during the melt blending followed by the extrusion processes. Addition of 1 wt.% cloisite, decreased the spherical size, however, the structure remained the same. Additionally, the addition of 2 wt.% cloisite led to an enhancement of interfacial width reducing the interfacial energy. This resulted in the formation of softer MPP domains in the sample and made the blend more responsive to applied pressure (i.e., easily deformed) during the extrusion. Therefore, it is clear that the addition of 1 wt.% cloisite is effective in reducing the MPP domains and achieving better dispersion but the addition of 2 wt.% cloisite has shown an adverse effect, where the domains have grown larger and the degree of dispersion was reduced. This is one factor that partially explains the deterioration in flame retardant performance and the cone calorimetry response when the cloisite amount was increased from 1 to 2 wt.% (see Table 1). Another factor responsible for the poor performance of the 2 wt.% of cloisite added PLA was the aggregate formation inside the MPP domains, which partially blocked the contact between polyphosphate and the PLA chains. In the condensed phase, the polyphosphate component of MPP was able to catalyze the dehydration reaction of the polymer chains, which resulted in the formation of carbo-cations and C=C bonds leading to the char formation. The excess C-30B platelets that remained aggregated within MPP domains hindered the catalysis reaction and the char formation was ineffective. In addition, it was found that the addition of MPP was essential for the formation of char, and only the chars corresponding to PLA 83% + MPP 17% and PLA 82% + MPP 17% + C-30B 1% were intumescent. The char corresponding to P17M2C was loose and powdery with no mechanical integrity. The authors also prepared PLA 82% + MPP 17% + C-30B 1% samples using Makerbot Replicator 2X - FDM 3D printer and compared the sample’s performance with the earlier measures. It was noted that the 3D-printed PLA displayed V-0 rating during UL-94 test (Ref 49). The authors produced a complete report on flame retardancy mechanism and compared the flame retardancy of the 3D-printed sample with conventionally extruded sample. The difference in HRR for the conventional sample and 3D-printed sample is provided in Fig. 3 as a guide to carry out further research on flame retardancy of 3D-printed samples with different flame retardant materials. A summary of the results from the above-mentioned research is presented in Table 1.

Kuzman et al. (Ref 50) fabricated wood (unspecified species) reinforced PLA composites and analyzed their fire behavior. The authors planned to combine the advantages of 3D printing and natural resources and hence they utilised low cost and biodegradable materials wood (30 wt.%) and PLA (70 wt.%) as the constituents. PLA composites were printed with two different types of PLA filaments having two different wood reinforcements (light brown wood and dark brown wood) at 30 wt.%. For the applied incident heat flux of 35 kW/m² (the authors used several incident heat fluxes), the PHRR of neat PLA, light brown wood/PLA and dark brown wood/PLA composites were ca. 404, 319 and 246 kW/m², respectively. At the same incident heat flux, the dark brown wood/PLA displayed shorter TTI of 65 sec. It was followed by light brown wood/PLA composite (146 sec) and neat PLA (272 sec).

| Table 1 | Comparison of flame retardant polymers made by 3D printing and conventional manufacturing |
|-----------------------------------------------|
| **Matrix** | **Reinforcement** | **Technique of manufacturing** | **LOI, %** | **TTI, s** | **AHRR, kW/m²** | **PHRR, kW/m²** | **THR, MJ/m²** | **Ref.** |
| PLA None | | Molding | 20 | 33 | 342 | 693 | 96 | Ref 49 |
| | | 3D printing | 20 | 28 | 336 | 688 | 94.8 |
| MPP (17 wt.%) and C-30B (1 wt.%) | | Molding | 28.5 | 27 | 198 | 285 | 84 |
| | | 3D printing | 28.5 | 23 | 195 | 287 | 83.3 |
| EVA None | | Thermo-compression | ... | 40 | ... | 519 | 76 | Ref 56 |
| | | 3D printing | ... | 35 | ... | 482 | 78 |
| 65 wt.% ATH | | Thermo-compression | ... | 65 | ... | 113 | 39 |
| | | 3D printing | ... | 58 | ... | 101 | 42 |
| 10 wt.% EG | | Thermo-compression | ... | 21 | ... | 156 | 63 |
| | | 3D printing | ... | 18 | ... | 217 | 75 |

LOI Limiting Oxygen Index; TTI Time-to-ignition; AHRR Average Heat Release Rate; PHRR Peak Heat Release Rate; THR Total Heat Release; PLA Poly (lactic acid), EVA Ethylene-vinyl acetate, MPP Melamine polyphosphate, ATH Aluminum trihydroxyde, EG Expandable graphite
This was because the wood (and other natural fibers) itself has very short TTI (Ref 51). It is to be kept in mind that for composites a longer TTI is desirable, which indicates that the material will take longer time to ignite, thereby, providing some form of safety from fire hazards. However, TTI is not the only parameter to judge the fire behavior of composite materials and other factors, such as PHRR, should also be considered. In this study, the authors observed that the dark brown wood/PLA composite had the lowest PHRR (at 35 kW/m²) whereas the light brown wood/PLA composite had considerably higher PHRR. Although not mentioned by the authors, the most probable reason for the dark brown wood/PLA sample to have the lowest PHRR is due to a dense char formation, which can be seen from the two distinct HRR peaks as opposed to a shoulder and overlapped peak in the light brown wood/PLA samples. This means that the dark brown wood containing sample formed a more rigid char than the light brown counterpart. It is envisaged that the incorporation of FRs with wood/PLA composites would further lower the PHRR, making the composites more fire resistant.

2.2 Ethylene-Vinyl Acetate (EVA)

EVA is a non-degradable, biocompatible, non-toxic and insoluble elastomer. EVA is a copolymer of ethylene and vinyl acetate (VA), which has been approved by the Food and Drug Administration (FDA) to be used as a biomaterial (Ref 52). The amount of VA in an EVA copolymer can range between 0 and 40%. The properties of the resultant EVA copolymer are dependent on the proportion of VA. High VA concentration leads to an increased polarity, adhesion, impact resistance, flexibility and compatibility of EVA with other polymers. At the same time, high VA concentration results in decreased crystallinity, stiffness and melting point of the copolymer (Ref 53). Filament buckling is the main problem associated with the processing of elastomers and this limits its application in FDM process. This buckling effect due to high flexibility making it difficult to process and extrude the elastomer via a small nozzle (Ref 54). However, various design implementations and modifications are proposed to print these flexible materials (Ref 55).

Geoffroy et al. (Ref 56) fabricated two different composites, namely, EVA copolymer with aluminum trihydroxyde (ATH) and EVA copolymer with expandable graphite (EG) using thermo-compression and 3D printing techniques and compared their flame retardancy properties. Mass loss calorimeter (MLC) was used to test the flame retardancy of the prepared EVA/ATH and EVA/EG samples. The neat EVA showed TTI of 40s and 35s for thermo-compressed and 3D-printed samples, respectively. The THR and PHRR for thermo-compressed neat EVA were 76 MJ/m² and 519 kW/m², respectively; whereas for 3D-printed neat EVA these were 78 MJ/m² and 482 kW/m², respectively. The THR and PHRR were reduced by 49% and 78%, respectively, when 65 wt.% of ATH was added in EVA and TTI was increased by 72% compared to neat EVA. The 65 wt.% ATH added EVA composite showed better flame-retardant performance than the 30 wt.% ATH added EVA composite. This was majorly due to an endothermal dehydration that took place upon heating, resulting in the formation of the aluminum oxide (Al₂O₃) ceramic residue. A critical amount of ATH is desirable to generate an effective homogenous residue, which acts as a fire barrier layer. This barrier formation was not accomplished at low ATH concentration (i.e., 30 wt.%) (Ref 56). The research (Ref 56) reported the flame retardancy of two different composites but the mechanical properties were not revealed by the authors. In addition, the research (Ref 52)
dealt with a single combination of 3D-printed polymer composites. In order to obtain balanced mechanical strength and flame retardancy, further optimisation studies have to be carried out.

A design modification was demonstrated by Geoffroy et al. (Ref 57) compared to the previously discussed literature (Ref 56) to accomplish light-weight 3D-printed parts with better flame retardancy. The design contains a core part, which was covered with an outer shell part. Firstly, the authors fabricated two different grid-patterned cores by varying infill density of either 30 or 50 wt.% and demonstrated the performance of two flame retardants (i.e., ATH and EG) used in the EVA. Secondly, the effect of biphasic materials containing air, water, solubilized or powdered potassium carbonate (K$_2$CO$_3$), sodium carbonate (Na$_2$CO$_3$) on the flame retardancy of 30 wt.% of ATH added EVA materials were evaluated. It was observed that 65 wt.% ATH/EVA and 10 wt.% EG/EVA materials displayed better flame retardancy than the 30 wt.% ATH/EVA, irrespective of the design studied. The PHRR of standard design plate (containing 100% polymers) consisting of 30 wt.% ATH/EVA was 88% and 150% higher than that of materials with the standard design containing 10 wt.% EG/EVA and 65 wt.% ATH/EVA, respectively. Furthermore, a remarkable improvement of flame retardancy was noticed in sandwich designs containing voids compared to 100% filled standard design plates irrespective of the material used. This was due to the presence of lower polymeric material in sandwich design compared to the standard design plates and consequently less fuel available for combustion. On one hand, there was no significant improvement in THR and PHRR when voids in the sandwich design were filled with H$_2$O or powdered K$_2$CO$_3$ compared to 30 wt.% ATH/EVA material, which was filled with 70% air. Therefore, no benefit was achieved when air was replaced by H$_2$O or powdered K$_2$CO$_3$. Instead, a significant decrease of PHRR (by 80% and 72%), THR (by 75% and 71%), and increase in TTI (by 31% and 42%) were displayed when solutions with a same mass concentration of K$_2$CO$_3$ or Na$_2$CO$_3$ were used. The material with K$_2$CO$_3$ in liquid phase revealed the fastest flame extinguishment (due to H$_2$O and CO$_2$ emission and the release of K and KOH into the flame) and hence, this material showed the lowest HRR and THR when exposed to heat (Ref 57).

In the previous design, leakage of H$_2$O-based flame retardant was the major issue due to porosity of the polymeric matrix. To address this issue, Geoffroy et al. (Ref 58) introduced a novel multi-material sandwich incorporated with three different liquid hydrogels mixed with vermiculite (VMT) and vermiculite/K$_2$CO$_3$ and assessed their flame-retardant performance using mass loss cone calorimeter test. The material was composed of (as shown in Figure 4) EVA/ATH (the square-shaped hollow cells at the middle, which is covered with two skin plates made of same polymer) and the hollow space in the cell zone filled with commercial fire extinguishing additive of saturated solution (K$_2$CO$_3$). The incorporation of alginate hydrogel (HA) and HA+VMT both displayed longer TTI (6.5 and 7.5 times higher) as compared to air-filled 3D part. However, there was no significant improvement of THR and PHRR as compared to air-filled 3D part. For the 3D-printed multi-materials sandwich containing HA+VMT+K$_2$CO$_3$, the addition of K$_2$CO$_3$ led to a drastic reduction of THR and HRR. The THR of HA+VMT+ K$_2$CO$_3$ system was reduced by 88%, 66% and 88%, compared to the air-filled reference part, K$_2$CO$_3$ saturated liquid-filled 3D part and 3D sample filled with HA+VMT, respectively. In addition, a decrease in PHRR by 86%, 38% and 84% was also observed for sample with HA+VMT+K$_2$CO$_3$ compared to air-filled 3D-printed part, and the sample filled with K$_2$CO$_3$ in liquid phase and HA+VMT, respectively. However, the sample containing a saturated K$_2$CO$_3$ solution showed 1.9 and 1.5 times higher TTI than the sample with air and K$_2$CO$_3$ saturated liquid. However, when compared to the sample HA + VMT the TTI was 3.9 times lower. The physical barrier formed by VMT platelets during the fire test, as well as the condensed phase mechanism of K$_2$CO$_3$ were found to be responsible for the excellent flame retardancy, as determined by confocal microscopy observations, electron probe micro analysis and x-ray diffraction experiments (Ref 58). This study developed routes for potential future research as there are opportunities to develop new 3D-printed composites using alternate flame retardants such as graphene quantum dots, graphene and carbon nanotubes.

### 2.3 Polyetherimide (PEI)

PEI belongs to the special engineering thermoplastics with very good strength and thermal stability. PEI is an amorphous
polymer, which has primarily been used to manufacture high-
performance electronic parts and biomaterials (Ref 59). Pro-
duction of new materials with thermal stability has good 
potential (Ref 60) and is highly sought after for the design of 
thermal protection systems (TPS) used on space vehicles. The 
performance of these vehicles depends on TPS during hyper-
sonic flight to guard against aerodynamic heating in atmos-
pheric re-entry. Currently, the manufacturing of TPS is labor 
tensive and overall production costs can be high. However, 
the aerospace industry (both commercial and military areas) is 
already utilizing the benefits of 3D printing. For aerospace 
applications, 3D printing can significantly lower cost and 
production time when compared to conventional polymeric 
material processing methods (Ref 61). Developing materials 
that can be used to 3D print the heat shields for TPS will save 
both time and costs (Ref 62).

In this light, Wu et al. (Ref 63) developed novel high-
temperature polymer composite filaments through extrusion 
process for application in FDM. Filaments were developed by 
altering PEI (ULTEM™ 1010 resin) with the incorporation of 
functional fillers, namely hollow glass microspheres (HGMS), 
nano clay (NC), and non-halogenated flame-retardant fillers. Three different filaments were extruded at varying proportions 
of fillers (PEI + 10 wt.% HGMS, PEI + 10 wt.% HGMS + 5 
w t.% NC, PEI + 10 wt.% HGMS + 5 wt.% NC, 10 wt.% flame 
retardant) and their flame retardant properties were compared 
with neat PEI. The flame retardant (OP 1312) was a non-
halogenated additive composed of organic aluminum phospho-
nates. After burning, the PEI filament consisting 10 wt. 
HGMS, 5 wt.% NC, and 10 wt.% flame retardant fillers 
produced higher char yield of 62% than other filaments, which 
was 11% higher char than the neat PEI filament and exhibited 
low heat release capacity (HRC) of 119 J g⁻¹ K⁻¹ (52% lower 
HRC than the neat PEI). In addition, the same filament 
composite showed 52% reduced PHRR (W/g) and 30% 
reduced THR (W/g) than the neat PEI during microscale 
combustion calorimetry (MCC) test. The majority of the 
HGMS broke during combustion and the broken pieces acted 
as reinforcement to the already solid char layer, resulting in 
even lower flammability. The synergistic benefit of two 
manufacturing processes (extrusion and 3D printing) was 
simultaneously utilised in this study to demonstrate the 
performance of TPS. The results presented in this preliminary 
study will direct future optimisation and characterizations of 
FDM printed parts, which will provide a better understanding 
of the performance of PEI composite materials (Ref 63). For 
this purpose, composites with different fillers and filler effect 
on various polymers like PLA, EVA need to be investigated. 
Moreover, there are more opportunity to study flame retardancy 
of recycled 3D-printed polymer parts that will lead to increased 
reuse of waste polymers and cause reduced environmental 
pollution (Ref 64).

2.4 Polyamide

Polyamide-6 is one of the major polymeric material used in 
engineering applications due to its good fiber-forming ability, 
biodegradability and biocompatibility (Ref 65). 3D-printed and 
electrospun polyamide polymers are potentially used in tissue 
engineering application due to its biocompatibility (Ref 66, 67). 
The printability of the material is highly dependent on the melt 
flow index (MFI), which conveys a measure of the ease of 
thermoplastic melts. MFI quantifies the weight of a thermo-
plastic (in grams) melt in 10 min via a die of specific diameter 
and length with the application of pressure at a given 
temperature (Ref 68). Materials with an adequately high MFI 
(i.e., >10 g/10 min) display good flow properties with no 
clogging at the nozzle (Ref 69) that lead to good finished 
printed part. Therefore, measurement of MFI of the polymer 
before and after the addition of flame retardant is highly 
informative to estimate its printability.

With this prospect, Wu et al. (Ref 70) fabricated flame-
retardant polyamide-6 (PA6) nanocomposites through FDM 
process. The MFI of both neat PA6 and the 15 wt.% of flame 
retardant added PA6 nanocomposites was tested as per ASTM 
D1238. A drastic reduction in MFI was observed on the 
addition of flame retardant to the PA6 polymer. The neat PA6 
showed an MFI value of 21.5 g/10 min, which was significantly 
higher than the MFI of flame retardant added PA6 (6.8 g/10 
min). This was due to the increased viscosity of the flame 
retardant PA6 compound, developed as a result of reduced 
chain movement induced by the formation of a nano-filler 
network. However, the increased melt viscosity of the 
nanocomposite sample did not significantly affect the filament 
processability, which means the flame retardant added PA6 
nanocomposite was still found to be suitable for FDM printing. 
In addition, the thermal combustion properties of the printed 
PA6 and PA6 composite were tested according to ASTM 
D7309-2007 using the combustion calorimeter. The test was 
conducted at the combustion temperature of 900 °C and the 
heating rate of the pyrolysis was 1 °C/s. The heat release 
capacity and total heat release of the composite (ca. 900 J/g-K 
and ca. 60 kJ/g) was lower than the neat PA6 (ca.1300 J/g-K 
and ca.63 kJ/g), which demonstrated the reduced flammability 
of the PA6 flame retardant composite.

2.5 Silica Aerogels

Silica aerogel is a porous and transparent solid material (Ref 
71). Machining of silica aerogels is a challenging task due to its 
low density and high brittleness (Ref 72). Therefore, 3D 
printing of silica aerogels is a highly useful method to widen its 
applications. Maleki et al. (Ref 73) synthesized silk fibroin (SF) 
biopolymer, extracted from silkworm cocoons and added it to 
neat silica aerogels. In order to form stable covalent bonds 
between silica and SF structure at a molecular level, a 
carboxylic acid functional group-containing silane coupling 
agent as co-precursor was incorporated. The prepared hybrid 
silica-SF aerogel displayed an admirable printability in the wet 
state using a micro-extrusion-based 3D printing method. A 
significant enhancement in the mechanical strength (three-fold 
increase in stiffness) compared to the neat silica aerogel was 
achieved with minimal or almost zero compromise on the 
density and thermal insulation performance (Ref 73). Most 
importantly, the developed silica-SF aerogel had fire retardancy 
behavior and hence, did not require any additional flame 
retardant. Compared to halogen-based FR materials, silica 
aerogels are well-known fire-retardant materials that are 
considered to be innocuous toward human health (Ref 74). 
This innocuous nature of silica aerogel allows its utilization as a 
FR in composite preparation. In addition, hybrid form of silica-
SF aerogel exhibited fire retardant behavior due to the 
homogeneous mixing of silica-SF network in the overall 
aerogel composite. The vertical burning experiment displayed 
some form of fire retardancy since the self-propagation of the 
flame did not happen and resulted in a carbonized residue with
a retained shape and dimension as the original aerogel upon burning. However, the test for fire behavior was not conclusive since the authors did not report the rating of vertical burn test. In fact, it is not clear if they used proper standard for UL-94 test. Furthermore, the authors did not determine the LOI values as well as reaction-to-fire properties using cone calorimeter. The 3D-printed hybrid silica-SF aerogel composites have potential for a wide range of applications such as designing anisotropic thermal insulation materials. The simultaneous presence of micron and nano-sized pores provides an opportunity to develop scaffolds for bone-based regenerative medicine (Ref 73). However, it is important to study their flammability properties extensively to enhance their application in fire resistant applications.

2.6 Contribution of Industries Toward Increasing Flame Retardancy of 3D-Printed Parts

In this section available FR polymer filaments developed by industries are discussed. Research groups from well-known industrial 3D printer manufacturers are working to develop flame retardant reinforced plastics. For instance, the nylon-based carbon fiber filaments (trade name Onyx and Onyx FR) were developed by Markforged, Massachusetts, United States. The designed Onyx filament consisting of nylon mixed with chopped carbon fiber (Ref 75) showed tensile modulus, tensile stress at yield and tensile strain of 1.4 GPa, 36 MPa and 25%, respectively. Onyx FR is plastic composite filament composed of flame retardant mixed continuous micro-carbon fiber and nylon. Compared to Onyx filament, the Onyx FR showed tensile modulus, tensile stress at yield and tensile strain of 1.3 GPa, 29 MPa and 33%, respectively. In addition, the Onyx FR filament obtained V-0 rating in UL-94 burning test down to a filament thickness of 3 mm. The V-0 rated flame retardant 3D printing plastic filament had good strength, high print quality with excellent surface finish and high resistance to fire. This combination of qualities makes Onyx FR fit for a wide range of applications in the aerospace clips and brackets, automotive, welding fixture, laser marking fixtures and defense industries, which often require non-flammable materials. The material was also designed to enable users to easily switch between different materials on the same 3D printer. This provides opportunity to examine the flame retardancy performance of various plastic composites (Ref 76). Recently, CRP technology, Modena, Italy introduced flame-retardant material known as Windform FR1 for additive manufacturing. It is carbon fiber reinforced flame retardant (UL 94 V-0 rated) material for additive manufacturing. The Windform FR1 underwent several tests such as Federal Aviation Regulations (FAR) 25.853 test, 12-second vertical and 15-second horizontal flammability tests. The 45° Bunsen burner test and the smoke density test have also been conducted that the material successfully passed. The Windform FR1 contains halogen-free polyamide-based material that combines good mechanical properties with lightweight nature. Owing to its flame retardancy performance, this high-performance polyamide-based composite material is suited for aircrafts and aerospace applications such as interior parts, cockpit, cabin components, air conditioning piping, air ducts, air outlet valves; automobile and transportation components such as vehicle interiors, housing and enclosure assemblies; consumer goods and electronics such as lighting, appliances and in general for any components demanding flame retardant standards (Ref 77).

The same company developed and introduced Windform FR2 composites, which contain polyamide-based material filled with halogen-free flame retardant and glass fiber and polyamide composites were fabricated by SLS process. Windform FR2 composites appear in white color and are electrically non-conductive. Windform FR2 combines high wear resistance and good temperature resistance. It allows for high detail resolution with a smoother surface finish than the Windform FR1. Similar to Windform FR1, this material also underwent series of flammability tests such as UL 94 horizontal burning of 1 mm and 3 mm rating, the FAR 25.853 12-second vertical and 15-second horizontal flammability tests as well as the 45° Bunsen burner test, smoke density test with successfully passing all of them (Ref 77, 78). These investigations by leading manufacturers of the 3D printers highlight the importance of the fire retardancy in 3D printing feedstock materials.

3. Summary and Scope for Future Research

This review article deals with the flammability characteristics of 3D-printed polymer and polymer composites. It is well known that 3D-printed composites have been studied in detail for their mechanical strength, and the available literature is also adequate in this area. Since, polymer and polymer composites are flammable, there is sufficient literature available to understand and address the flammability of polymers and their composites. However, there is dearth of studies on the fire behavior of 3D-printed polymers. This paves the way for the research community to develop flame retardant 3D-printed polymer composites and was the driving force behind this review article. From the review it is found that the available results are not enough to highlight the flammability behavior of 3D-printed materials. Following are some significant findings from the literature review:

- It should be noted that the variation in the printing parameter could have an effect on the flammability of 3D-printed materials, which has not been investigated in detail. For example, critical FDM printing factors such as infill density, layer thickness and layer orientation, could alter the flammability of 3D-printed polymers and composites. However, some of the studies reported insignificant differences in flammability between 3D printing and conventional manufacturing process.

- Investigations on the flammability of 3D-printed polymer fiber composites are also inadequate. Most natural fiber reinforcements (except for wool) are expected to enhance the fire resistance of the polymer through an additive effect. Furthermore, the flammability properties of 3D-printed materials could also vary due to the variation in fiber orientation and the reinforcement percentages, which need to be investigated in future research.

- The addition of a flame retardant could lead to a reduction in the strength of 3D-printed polymers, which should be studied in an interrelated approach between the flammability and the mechanical strength of the flame retardant added polymers and composites. Selection of a suitable matrix and fire retardant could warrant a balanced mechanical performance and flammability of the 3D-printed polymer and its composites.
Apart from the flame retardant, the addition of nano fillers mainly carbon-based nano fillers such as graphene, carbon nanotubes, fullerene can provide effective mechanical strength and fire resistance, which should be studied in detail. Recent studies have examined the use of biochar reinforcement in polymers to increase fire resistance. Furthermore, biochar-based composites are sustainable and the development of biochar-based composites through FDM can simultaneously increase composite strength and fire retardancy with low production time and cost.

Unlike conventional manufacturing methods, in 3D printing there is a chance for the development of pores and the loss of bonding of the layer, which lead to a reduction in the mechanical performance of the resulting components. The comparison of the flame retardant performance of the 3D-printed part with the conventionally produced should be performed comprehensively in future investigations.

Most of the available literature did not report details such as PHRR, time to PHRR, THR, etc. It is therefore essential in the future, to report complete fire parameters, which would generate a holistic idea regarding the materials’ flammability.

In conclusion, the available information for the aforementioned aspects are not sufficient to define, understand or presage the flammability of 3D-printed polymeric materials. Incentivising research into the issue will create mechanically sound and fire retardant 3D-printed parts and facilitate their foray into various engineering applications.

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