

Fire Retardant Properties of Bio-phenolic Hybrid Composites



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Abstract Bio-phenolic based hybrid composites are used in engineering applications due of their better specific stiffness, strength, environmental resistance and thermal insulation properties. However, these composites cannot match the flammability resistance requirements for the high performance applications. Hence, numerous studies have attempted to enhance their fire retardant properties without deteriorating the physico-mechanical properties. Different approaches have been investigated to enhance the fire-retardant properties, such as the blending of phenolic resin with other polymers, addition of fillers, intumescent fire retardant coatings and chemical modification of the fibres. This article briefly presents an overview of the

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fire-retardant properties of the polymers, fibres and composites and the corresponding tests and standards involved. Recent studies on the improvement of fire-retardant characteristics of bio-phenolic hybrid composites with fillers were discussed.

Keywords Polymer composites · Bio-phenol · Fire-retardant properties · Fillers

1 Introduction

Polymeric composites reinforced with natural fibres are considered to substitute the synthetic fibres due to their lower density, low cost, abundant availability and biodegradability (Senthilkumar et al. 2018). However, the natural fibre reinforced composites are yet to find their use in high performance applications like aircraft and aerospace vehicles owing to their inferior mechanical properties (Chandrasekar et al. 2019) and poor flammability resistance to fire. Among the polymers, phenolic resin has better thermal insulation properties and fire retardation characteristic or low flammability. The superior flammability resistance or fire retardant characteristic of the phenolic resin is due to the following reasons: (i) high degree of cross-linking-in which the carbonyl linkage in the polymeric chains occur due to the oxidation of methylene groups and release of water due to the phenol-phenol condensation and (ii) release of volatile constituents such as CO, CO₂, and their ability to form char which acts as a thermal barrier (Kim et al. 2018; Mohd Asim et al. 2018a).

1.1 Fire Retardation Properties of the Natural Fibres, Polymer and Composites

Fire retardation is the ability of the material to slow down combustion, prevent flame propagation, less release of volatiles, reduction in the smoke volume, and high resistance to ignition (Kim et al. 2018; Jang et al. 2000). Thermogravimetric analysis (TGA) is the most widely used method for understanding the flammability properties of the natural fibres. In TGA, natural fibres are incinerated between 30 and 800 °C in a closed chamber filled with nitrogen. Thermograms and derivative thermograms which display the mass loss % as a function of temperature provide information on the thermal decomposition characteristic of constituents in the natural fibres. Natural fibres such as kenaf, flax, palm, jute, sisal, etc. are made up of cellulose, hemicellulose, lignin, pectin, moisture and waxes (Chandrasekar et al. 2017). These constituents are volatile compounds and decompose at elevated temperatures when subjected to fire. Thermal decomposition of the natural fibres occur in two or three stages depending on the fibre structure, fibre composition, density, etc. For a typical natural fibre, initial weight loss occurs between 80 and 100 °C which is due to the evaporation of moisture followed by decomposition of hemicellulose in the range of

200–260 °C, lignin between 160 and 400 °C and cellulose between 300 and 600 °C (Kim et al. 2018).

The fire retardant characteristic of the polymers and their composites reinforced with natural or synthetic fibres is determined from the following tests: (1) Limited Oxygen Index (LOI), (2) Underwriter's Laboratory-94 (UL-94)—vertical and horizontal burn experiments, (3) Cone calorimetry test and (4) Smoke density measurements (Table 1).

Polymers used as matrix material in the bio-composites are classified into thermoset and thermoplastic respectively. Tables 2 and 3 present the LOI % and HRR of the widely used thermoset and thermoplastic resins as matrix in the composite.

Table 1 Fire retardation tests (Laza et al. 2008; Marliana et al. 2016)

<i>LOI test</i>	<i>UL-94 vertical burn test</i>	
<ul style="list-style-type: none"> • ASTM D2863 • Minimum oxygen concentration required to burn 50 mm length or burn for 3 min • $LOI\% = 100 \times [O_2]/([O_2] + [N_2])$ 	<ul style="list-style-type: none"> • ASTM D3801 • V-0: burn time < 10 s per sample and sum of burn time for five samples ≤ 50 s • V-1: burn time for combustion 30 s and the sum of the after-flame times for the five samples ≤ 250 s and flame could not ignite cotton below the specimen • V-2: If flame drops and ignites the cotton 	
<i>UL-94 horizontal burn test</i>	<i>Cone calorimetry</i>	<i>Smoke density measurement</i>
<ul style="list-style-type: none"> • ASTM D635 • Flame time from 25 mm (free end) to 100 mm • $V = 60L/t$, where V is the burning rates (mm/min), L is burned length (mm), and t is the time of burning (s). 	<ul style="list-style-type: none"> • ASTM E1354 • A 50 kW/m² heat flux is applied to the sample • Heat release rate (HRR), Mass loss rate (MLR), Smoke production rate (SPR) and critical time were measured. 	<ul style="list-style-type: none"> • French Standard NF X 10-702 • Test is performed for 20 min, under flaming and non-flaming conditions in the NBS chamber • Maximum smoke density (D_{max}) and area under the smoke density vs time curve in the first 4 min of the test (VOF4) were measured

Table 2 LOI% of various polymers (Chapple and Anandjiwala 2010; Prabhakar et al. 2015)

Type of resin	Resin	LOI%
Thermoset	Phenolic	25–57
	Epoxy	23–27
	Vinyl ester	20–23
Thermoplastic	Polycarbonate	26
	Polylactic acid	21
	Polypropylene	17
	Polyethylene	17
	Polystyrene	18
	Polyvinyl chloride	23–45

Table 3 HRR of various thermoplastic polymers from the Cone calorimetry test (Prabhakar et al. 2015)

Type of resin	Resin	HRR (W/cm ²)
Thermoplastic	Polycarbonate	42.9
	Polylactic acid	27.2
	Polypropylene	150.9
	Polyethylene	140.8
	Polystyrene	110.1
	Polyvinyl chloride	42

Fibre reinforced composites to be used in interior furnishing of the aerospace and automotive vehicles are expected to fulfill their standard through the fire test. For instance, Fig. 1 shows the minimum fire retardation requirements for composites application to the interior furnishing of the Aircraft as per the Code of Federal Regulation (CFR) 25.853 (Kim et al. 2018).

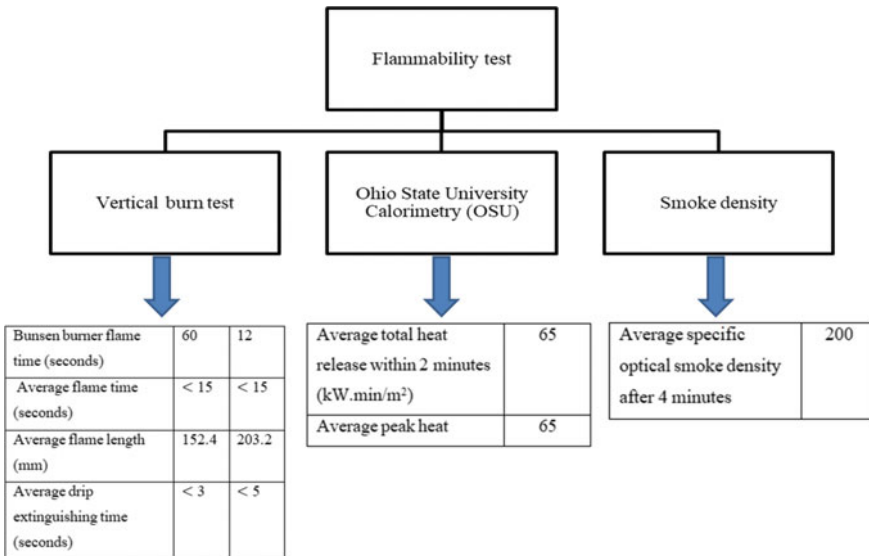


Fig. 1 Fire retardation requirements of composites in interior furnishing as per the Code of Federal Regulation (CFR) 25.853

2 Enhancing Fire Retardation Properties of the Composites

Flammability of the composites is influenced by the individual constituents such as type of fibre and matrix, density, thermal conductivity, etc. (Kozłowski and Władysław Przybylak 2008). In general, fire retardant properties of the bio-composites can be enhanced by the following methods (Chapple and Anandjiwala 2010):

- Blending phenolic resin with other thermoset resins that has lower flammability resistance
- Incorporation of flame retardant fillers into the polymer matrix
- Intumescent flame retardant coating on the polymer composites
- Fibre treatment with various reagents

2.1 Hybrid Composites

In a study by Laza et al. (2008), pure epoxy (E) and pure phenolic resin (P) were designated as 100E and 100P while the hybrid composite resin blend was designated as 80E/20P, 60E/40P 50P/50E, 60P/40E, 80P/20E. D_{max} and VOF4 from the smoke density experiment for 100E is 20 and 6.5 and for 100P is 289 and 682 respectively. Increasing phenolic resin in the blend led to the decline of D_{max} and VOF4 indicating improvement in the fire retardation characteristic of the hybridization effect in the composite.

Chiu et al. (2000) performed LOI test on unsaturated polyester resin (UP) blended with various proportions of phenolic resin (P) as UP0P100, UP40P60, UP60P40, UP20P80 and UP0P100. LOI was approximately 20.2% and 26.5% for the pure UP and phenolic resin. Hybrid composites possessed intermediate LOI values. As the phenolic resin% was increased in the resin blend, LOI % was found to increase in the order: UP0P100 < UP60P40 < UP40P60 < UP20P80 < UP0P100. In a recent study, Marliana et al. (2016) has shown that flame retardation of the UP/phenolic resin can be improved by the addition of kenaf into the resin blend. Cellulose, hemicellulose and lignin in the kenaf undergo thermal degradation at elevated temperatures above 200 °C unlike the UP resin which undergoes thermal decomposition at lower temperature. In particular, lignin in the kenaf fibre also adds to char and improves the fire characteristics of the composite. Similarly, UP resin burnt rapidly and did not come under V-0, V-1 and V-2 classification in the UL-94 vertical test. As the phenolic resin was increased in proportion of 10, 20 and 40%, hybrid composites came under the V-1 category.

Asim et al. (2018b) studied the effect of hybridization of PALF on the flammability properties of kenaf fibre reinforced phenolic composites. From the vertical UL-94 test, they indicated that as kenaf fibre was replaced by the PALF at 30, 50 and 70 wt%, flammability of the hybrid composites dropped to V-1 from V-0. In case of horizontal UL-94, the burn rate for kenaf/phenolic composite increased from 13.6 mm/min to 18 mm/min when the PALF was added up to 70 wt%. The significant difference in

their individual constituents such as cellulose, hemicellulose and lignin was found to be an influencing factor in combustion behavior of the PALF/kenaf/phenolic hybrid composite.

2.2 Flame Retardant Fillers

Phenolic resin based composites were widely used in thermo-structural applications due to its exceptional thermal stability and fire resistance. Nonetheless, incorporation of different additives and fire retardants would enhance the flammability of resulting nano composites. Table 4 shows the various types of fillers with the fire-retardant properties.

According to Prabhakar et al. (2015), fire retardant fillers which induce flammability resistance to the composite fall under five different mechanisms as shown in Table 5.

Table 4 Commonly used flame retardants based on their functional elements (Prabhakar et al. 2015)

S. No	Classification of retardants	Examples
1.	Mineral flame retardants	<i>Metal hydroxide</i> : Aluminium tri-hydroxide (Al(OH) ₃), Magnesium di-hydroxide (Mg(OH) ₂), Antimony trioxide (Sb ₂ O ₃) and Expandable graphite
		Hydroxycarbonates
		<i>Borates</i> : Zinc Borate
2.	Halogenated flame retardants	<i>Organochlorine</i> : Chlorinated paraffins and Antimony trichloride
		<i>Organobromine</i> : Polybrominated diphenyl ethers, Hexabromocyclododecanes and Tetrabromobisphenol-A
3.	Nitrogen containing flame retardants	Melamine, Melamine cyanurate, Melamine polyphosphate and Ammonium polyphosphate
4.	Phosphorous containing flame retardants	Ammonium polyphosphate, Chlorophosphates, Bromophosphate
5.	Silicone based flame retardants	Silicones, Silanes, Silsequioxane, Silica and Silicates
6.	Nano-sized Additives	Carbon nanotube, montmorillonite (nanoclay), vermiculite, and perlite <i>Metallic oxide</i> : Magnesium oxide (MgO), Zinc oxide (ZnO), and Ferric oxide (Fe ₂ O ₃), Titanium oxide (TiO ₂)

Table 5 Fire retardation mechanism of various fillers

Description	Physical dilution	Chemical interaction	Inert gas dilution	Thermal quenching	Protective coatings
Fillers	Talc and microspheres	Organobromines	Metal hydroxides, metal carbonates and nitrogen producing compounds	Metal hydroxides and carbonates	Phosphorous containing compounds and intumescent systems
Mechanism	Acts as heat sink and increases heat capacity	Dissociates into radical species that curbs chain propagation and branching in combustion	Releases large volume of non-combustible gases during combustion and dilutes the oxygen supply	Release of water molecules due to endothermic reaction and quench the polymer during the combustion	Forms a char layer on the polymer surface, slows down pyrolysis and hinders the release of volatiles due to combustion

2.2.1 Studies on Phenolic Based Nanocomposites

Bahramian (2013) investigated the effect of graphite nano crystals (3 wt% and 5 wt%) on the flammability of graphite/novolac phenolic composites. Cone calorimetry results revealed that addition of graphite at 3 and 5 wt% exhibited 41% and 58% lower HRR (heat release rate) respectively compared to pure phenolic samples. Theoretical results were significantly closer to the experimental HRR. At 2.5×10^6 W/m² external heat flux condition the surface erosion or ablation rate for neat phenolic, 3 and 5 wt% of graphite nano-composites are 0.0184, 0.0164 and 0.0153 mm/s respectively. From the SEM analysis, it has been noticed that uniform char formation is mainly due to proper arrangement of graphite layers and thereby enhanced the thermal stability and lower the flammability at elevated temperatures.

High energy consumption in construction sector is mainly due to inefficient insulating materials with poor thermal performance. Organic thermal insulators such as phenolic foam board, extruded polystyrene foam board and polystyrene foam board were extensively used due to its thermal insulation, wear resistance and lower cost (Xu et al. 2012). Phenolic foam based insulators exhibited better thermal insulation performance compared to other wall insulators. Hence, it is termed as “King of Insulators” (Zhou et al. 2020). Neat phenolic resin is brittle in nature and the hydroxyl and methylene groups of its molecular structure can be easily oxidized. These impediments limit the application of neat phenolic resin at elevated temperature. Hence, phenolic resin can be modified with different nano fillers and fire retardants to enhance the fire resistant behavior. Most commonly used fire retardants are boron, silicones, nitrogen and phosphorous based fire retardants. Zhou et al. (2020) studied the effect of adding aluminum diethylphosphinate (ADP) and melamine on the fire performance

Table 6 Effect of fire retardants on the flammability of phenolic composites (Zhou et al. 2020)

Mass fraction (%)		UL-94	LOI
Neat Phenolic (100)		V-2	30.0
Melamine	Aluminum Diethylphosphinate		
2	–	V-1	30.8
4	–	V-0	32.1
6	–	V-0	31.6
8	–	V-1	30.4
–	5	V-1	31.0
–	10	V-0	33.1
–	15	V-0	34.6
–	20	V-0	32.3
3	10	V-0	34.6
3	15	V-0	34.8
4	10	V-0	35.8
4	15	V-0	34.4
5	10	V-0	34.1
5	15	V-0	34.0

of phenolic resin through limiting oxygen index (LOI) and vertical combustion test (UL-94) for thermal insulation applications. Table 6 shows the results of LOI and UL-94. From the results it is observed that addition of ADP (10 wt%) and melamine (4 wt%) shows higher LOI and achieved UL-94 V-0 grade. Further increase in flame retardant content declined the flame retardancy.

Flame retardants together with nano filler modified phenolic resin based nanocomposites possess excellent mechanical, thermal and fire retardant properties compared to composites without nano fillers. Hassan et al. (2017) studied the influence of ammonium polyphosphate on the flame retardant behavior of nanoclay filled phenolic/polyester nano composites. Unsaturated polyester resin was blended with the phenolic resin in order to achieve superior mechanical and fire retardant properties through effective interpenetrating polymeric networks. Limiting oxygen index (LOI) and vertical combustion test (UL-94) were utilized to investigate the flame retardant behavior of the nanocomposites. Hybrid nano composites with 30 phr ammonium polyphosphate showed V-1 grade with LOI of 29.2%. Robert et al. (2015) also highlighted that incorporation of 3 wt% and 10 wt% nanoclay or MMT into the chopped silica fiber/addition curable propargylated phenolic novolac (ACPR) improved the LOI from 64 to 69%. Higher flame resistance of MMT/polymeric nano composites is due to the dispersion and exfoliation of MMT, which strengthen the polymeric network by forming a silicate barrier and protects the composite as follows: (a) obstructs the evaporation of volatile compounds during combustion and (b) inhibits the diffusion of oxygen into the composite during the combustion (Shahroze et al. 2019).

Table 7 Effect of different wt% of Tetraethoxysilan on the fire performance of phenolic nanocomposites (Chiang and Ma 2004)

Tetraethoxysilan (wt%)	UL-94	LOI
0	V-1	32
20	V-0	35
40	V-0	37
60	V-0	40
80	V-0	43

Polymeric nanocomposites possess excellent thermal and fire resistant properties compared with fiber reinforced polymeric composites due to restriction in polymeric chain movement by nano sized fillers (Leszczyńska et al. 2007). Generally, the compatibility between inorganic additives and polymeric matrix is poor. It can be improved through organic modification of additives using organic surfactants. Organically modified nano fillers play a vital role in improving the wetting characteristics with the matrix. Also, it reduces the surface energy of the inorganic host (Alexandre and Dubois 2000). On the other hand, hybridizing organic and inorganic materials combine the advantage of individual constituents and it has received much attention in recent years. The most commonly used inorganic materials are titania, alumina and silicone (Chiang and Ma 2004). These materials are termed as “Ceromers” or “Ormosils” (Wilkes et al. 1985; Schmidt 1986). The hybrid organic-inorganic nano composites can be produced through sol-gel process at the molecular level. A coupling agent is required to form a covalent bond in between the constituents. “Ceromers” are well known for their thermal and flame retardant behavior. Incorporation of nano ceromers in the phenolic resin would improve the flame retardancy (Mark and Wen 1995). Chiang et al. investigated the effect of adding Tetraethoxysilan on the fire performance of phenolic resin through limiting oxygen index (LOI) and vertical combustion test (UL-94). The hybrid phenolic/silica ceramer has been synthesized by sol-gel process (Chiang and Ma 2004). The results are shown in Table 7.

Table 7 shows that addition of tetraethoxysilan significantly improved the flame resistance. Increase in silicone content enhanced the LOI compared to neat phenolic resin. Also 80 wt% of silicone based phenolic composites exhibited UL-94, V-0 grade. Hence, this hybrid ceramer can act as a green flame retardant.

Nanoclay filled polymeric composite exhibited outstanding properties at a much lower weight or volume fraction. For instance, it was found that at less than 1 wt% of clay content, the nano- composites showed higher thermal stability and low heat release rate compared to virgin polymer (Zhu and Wilkie 2000). Nanoclay modified phenolic composites has declined the peak heat release rate. However, there is no significant effect on Limiting oxygen index and UL-94 classification (Wang et al. 2010).

3 Conclusion

The need for new structural elements motivates the research in the field of fire-retardant biocomposites. Thermal properties of biocomposites play a vital role in the usage of composites in thermo-structural applications. Many industries are aiming in the development of fire-retarded materials. For instance, in the electronics industry, there is a need for developing flame retarded and flexible, recyclable/biodegradable circuit boards. They have successfully demonstrated the use of phosphorus-based fire retardants in the instrument housings and the application of ceramers in cable coatings to prevent short circuit. Phenolic based composites have a combination of properties that make them attractive for engineering applications requiring flammability resistance. Methods to obtain phenolic based bio-composites with better flame retardant properties have been discussed and the flame retardant mechanisms have been elaborated. New multifunctional additives and processing techniques that can improve fire-retardant characteristic of the biocomposites could make them suitable for the thermo-structural applications.

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