

Comparative Cone calorimetric analysis of the fire retardant properties of natural and synthetic additives in banana peduncle fibre reinforced polyester composites.

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Abstract

This research investigated the Cone calorimetric analysis of the fire retardant properties of cow horn ash particles (CHAp) bio-additives and aluminium trihydrate (AH) in banana peduncle fibre reinforced polyester composites. Cone calorimeter was used to obtain combustion information of CHAp and AH control formulated composites. The analysis presented similar fire properties with CHAp incorporated composites exhibiting delayed ignition time of 25%, increased end of burning time of 14.24 per cent, and reduced total heat release rate of 9.07% for the developed composites. The developed BPF/CHAp/polyester produced composites of justified fire retardancy, which would find relevance in the engineering industries. CHAp incorporated in the developed composites presented valid fire-retardant properties compared with AH fire retardant additive composites used as the control and would suffice as an alternative to the expensive, non-environmental friendly fire retardants.

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1. Introduction

Fibre-reinforced composites are used in a wide range of applications such as automobiles, aircraft, ships, boats, pipelines, sports equipment, storage tanks, etc. The traditional polymeric and metallic materials have been replaced successfully by fibre-reinforced composites [1]. This is as a result of their high strength-to-weight ratio, lightweight, good chemical and corrosion resistance, fatigue resistance and low maintenance requirements. The unique properties achieved depend on the fibre reinforcing material, and the polymer matrix. The fibre reinforcing material is mainly responsible for the strength and stiffness of composites while the polymer matrix material is responsible for the load distribution applied on the fibres and the protection of the fibres from the effect of environmental harm conditions [2]. Generally, the reinforcing materials are high-performance fibres such as glass, carbon, Kevlar etc., whereas the matrix material can be either thermoplastic (polyetheretherketone, nylon 6, polystyrene, acrylic, polyester, polyethylene, etc.) or thermoset polymer (unsaturated polyester, phenolics, epoxy, vinyl ester, polyimide, melamine-formaldehyde, etc.). Amongst thermoset resins, the unsaturated polyester (UP) is one of the widely used thermoset resin matrices for fibre-reinforced composite, owing to its excellent mechanical properties, good moisture resistance, good corrosion and chemical resistance [3]. Despite these advantages, poor flame resistance, the evolution of smoke and emission of styrene during the burning of UP based composites are the major limiting factors for applications where fire safety is important [4]. To mitigate the high flammability and thermal decomposition of polymers, there is a strong need to reduce their flammability [5,6]. The intrinsic flammability property of UP can be altered either by chemical modification of the resin or by adding flame retardant chemicals into it. In the chemical modification of the resin, flame retardant elements such as halogen or phosphorus [7] are introduced in the UP resin backbone. The presence of halogen or phosphorus in UP resin significantly improves the flame retardancy of UP, but when it burns the presence of halogen raises environmental issues [8]. On the other hand, commonly used mineral fillers such as alumina trihydrate (ATH), magnesium hydroxide and calcium carbonate can be used, however, to be effective, they are required in high concentration (typically >30 wt.%), which can deleteriously affect the mechanical properties of the composite [9,10]. An alternative method to improve the fire resistance of the composites is to coat the surface with ceramic or intumescent coatings. When exposed to heat, the surface coatings protect the composite by forming a thermally insulative ceramic layer or intumescent char [11]. However, this method has its limitations, mainly of additional weight. Presently, there have been developments in the area of polymer/ nanocomposites, where nanoparticles such as nanoclays and carbon nanotubes are dispersed into a resin matrix to enhance the fire retardancy and mechanical properties of the composites. Nanoclays are used at low loading levels (2-5 wt. %). Even 5 wt. % clay loadings can reduce the peak heat release value by 70 % for polymers such as polybutylene terephthalate, co-polyester elastomer [12,13]. However, the use of nanoparticles dispersed in the uncured Unsaturated Polyester (UP) may cause an increase in resin viscosity and so decrease the ease of processing. Considering these drawbacks, a different approach to improve the fire retardancy of polymers with bio-based fire retardant additives that will be human and environmentally friendly as well as not impact negatively on the engineering properties of the composites is required [14]. With this in mind, UP will be blended with cow horn ash particle to give composites that are green and sustainable with fire retardancy and mechanical properties that will compete favorably with other fire retarded polymer composites as well as address environmental and human health concern. In the prevention of fire-induced loss of lives and properties, bio-sourced fire retardant additives will provide a valuable preventive and control measure to reduce the risk of fire initiation and flashover. This will become an attractive class of fire retardant material as a result of their human and environmental friendliness, low cost and availability.

2. Materials and methods

2.1 Preparation of banana peduncle fibre

The reinforcement material is banana peduncle fibre. This was collected from banana sellers at Ogbete Main market in Enugu state Nigeria, at no cost. The banana peduncle was subjected to water retting process for 25 days to extract the fibres from the peduncle. The peduncle was chopped at the inter-node and beaten gently with a mallet in order to loosen and to separate the fibre. Water retting enhanced the production of more identical and high-quality fibres. The fibres were removed from the water-retting tank; hand robbed and rinsed in sufficient water. The resulting fibre bundle was scrapped with a knife and combed. The process of combing and scrapping was repeated until individual fibres were separated. The separated fibres were washed carefully using running tap water to remove any impurities. Finally, the banana peduncle fibre was sun-dried for one week in atmospheric air to remove the maximum moisture from the fibre [15] (Figure 1).



Figure 1: (A) Banana peduncles. (B) Banana peduncle fibre after extraction

2.2 Preparation cow horn ash particles

The proposed fire retardant additive material is cow horn ash particle. The cow horn used for this research was obtained from Artisan Market Abattoir in Enugu, Enugu State Nigeria. The cow horn was washed with water and sun-dried for four weeks. The horn was mechanically crushed with a hammer and the bony core was isolated from the keratin sheath. About 5kg was washed with water and degreased by soaking it in 5 litres of acetone for two hours. This was to remove any trace of marrow, blood and other substances that will inhibit proper bonding between the matrix and the additive. The degreased bony core was then sun-dried for 2 weeks (Figure 2A). The bony core was finally carbonized in a muffle furnace at a temperature of 1200°C in the absence of oxygen (Figure 2B). The carbonized bony core was size reduced using a hammer mill and sieved to a particle size of 125micrometer.



Figure 2: (A) Photograph of cow horn bony core (B) The sieved cow horn (bone)

2.3 Composite Fabrication

There are several methods of fabricating composites; the method employed here was the hand lay-up method. A mould having dimensions of 300 x 300 x 3mm was used. Polyvinyl alcohol and wax were used to polish the surface of

the mould; they both served as releasing agents that made it easy during de-moulding of the composite. The proper proportions of the various ingredients were blended in a laboratory mixer. Initially, the cow horn ash filler particles were added with further mixing for about 10 minutes. The resin, polyester and the hardener (MEK) were measured into a beaker in a ratio of 2:1 that is two parts of polyester against one part of the hardener. The mixture was stirred with a glass rod. Part of the resin was poured into the mould and a brush was used to distribute it across the surface of the mould. The fibres were manually distributed randomly across the mould. The resin was added in the mould while the brush was used to impregnate the fibres until they were saturated. The cast was cured using a lightweight of 8.72KN. The mould was closed for curing at a temperature of 25°C for 24 hours at constant pressure. The cast was cured again in the air for 24hours after removal from the mould. Samples were prepared according to ASTM standard for each mechanical parameter and then taken to the laboratory for the test.

2.4 Composite formulation

A basis of 302.40g total mass was used in the proposed composite composition. This was derived from the density of polyester and dimensions of the fabrication mould.

$$\text{Density } (\rho) = \frac{\text{Mass } (m)}{\text{volume } (v)}$$

1

$$m = \rho v$$

$$m = 1.12\text{g/cm}^3 \times (30 \times 30 \times 0.3) \text{ cm}^3$$

$$\text{Total Mass of Composites } (m) = 302.40\text{g}$$

Table 1: Composition of the proposed composites

Samples	A(% w/w) BPF: P	B (% w/w) CHAp: P	C (% w/w) CHAp: BPF: P	D(% w/w) BPF: AH: P
1	0: 100	0: 100	0: 0: 100	0: 0: 100
2	5: 95	5: 95	2.5: 2.5: 95	2.5: 2.5: 95
3	10: 90	10: 90	5:5: 90	5:5: 90
4	15: 85	15: 85	7.5: 7.5: 85	7.5: 7.5: 85
5	20: 80	20: 80	10: 10: 80	10: 10: 80

BPF: Banana peduncle fibre, CHAP: Cow horn ash particle, AH: Aluminium hydroxide. P = Polyester resin matrix. (author's compilation, 2019).

2.5 Cone calorimetric analysis

Cone Calorimeter instrument was used for this analysis. Test samples were cut on a table saw to the dimensions of 100 x 100mm. All materials are conditioned at 23±3°C and the relative humidity of 50±5% for 24hours before testing. The samples were wrapped with aluminium foil around the back and edges before placing the samples unto the holder and then into the cone calorimeter. This was carried out to prevent any moulting material dripping from the sample unto the load cell. The samples were then backed with a non-combustible insulating refractory material (brick). All tests were carried out following ASTM E1354. All the tests were conducted on the cone calorimeter assembled by fire testing technology limited. The samples were orientated horizontally and exposed to irradiances of 25 and 50kW/m² at a temperature approximate to 600°C. The samples were pilot ignited and ran in triplicate; the average score of the three runs was taken (Figure 3).



Figure 3: (A) Photograph of cone calorimeter test sample. (B) Photograph of sample flaming inside the cone.

3. Results and Discussion

3.1 Results

Table 2: Fire properties of developed composites of polyester with BPF and CHAp

Samples	MHRR Kw/m ²	PHRR (Kw/m ²)	THR (MJ/m ²)	MASS loss(g/m ²)	TSR (m ² /m ²)	TSP (m ²)	TOC (g)	TTG (s)	ETT (s)
Polyester	223.56	556.54	308.60	14142.10	9378.20	82.90	206.30	64.00	1445.00
2.5%BPF:2.5%CHAp	223.47	534.19	308.20	13843.10	8889.20	81.40	203.90	65.00	1540.00
5%BPF:5%CHAp	222.39	516.23	301.20	13754.50	8579.40	80.60	200.10	75.00	1585.00
7.5%BPF:7.5%CHAp	206.84	501.80	280.90	13106.00	8161.50	78.90	129.32	80.00	1685.00
10%BPF:10%CHAp	207.57	505.42	207.90	12580.20	80582.00	70.90	121.16	82.00	1705.00

Table 3: Fire properties of developed composites of polyester with BPF and AH

Samples	MHRR Kw/m ²	PHRR (Kw/m ²)	THR (MJ/m ²)	MASS loss(g/m ²)	TSR (m ² /m ²)	TSP (m ²)	TOC (g)	TTG (s)	ETT (s)
Polyester	223.56	556.54	308.60	14142.10	9378.20	82.90	206.30	64.00	1445.00
2.5%BPF:2.5%AH	222.90	539.44	308.30	12274.40	8517.80	75.30	205.30	72.00	1455.00
5%BPF: 5%AH	218.24	522.21	300.00	12364.70	8438.50	73.40	203.50	77.00	1550.00
7.5%BPF:7.5%AH	215.46	515.94	297.40	12284.50	8335.20	75.20	164.60	81.00	1615.00
10%BPF:10%AH	210.52	489.9	237.80	12225.50	8282.60	72.10	125.90	83.00	1635.00

Source: Researchers compilation 2019

3.2 Analysis

3.2.1 Heat release rate with time for BPH: CHAp and BPF: AH composites

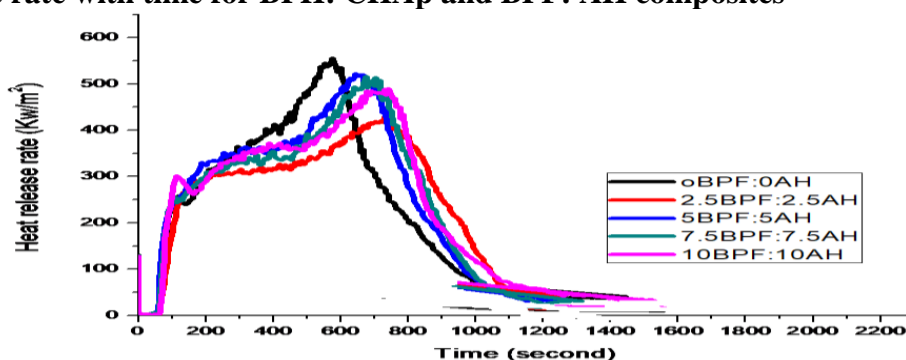


Figure 4: Variation of heat release rate with time for BPF: AH composites

3.2.2 Heat release rate with time for BPF:CHApcomposites

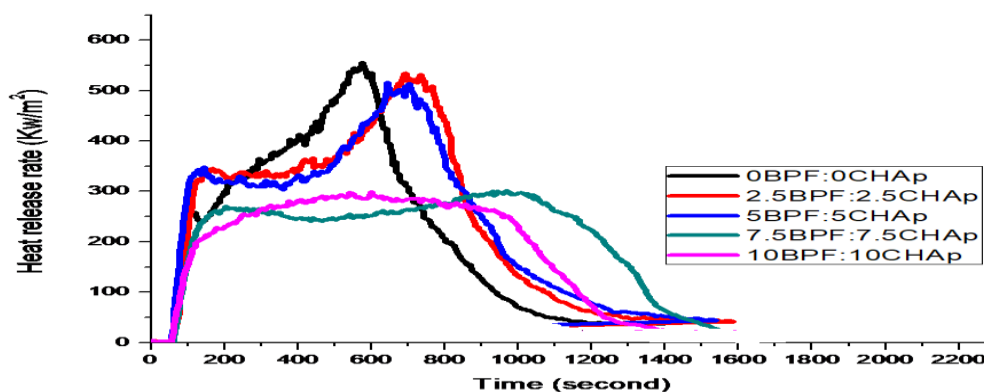


Figure 5: Variation of heat release rate with time for BPF: CHAp composites.

From Figures 4 and 5 it was observed that there was an initial delay period before the composite released heat, and this was because the temperature of the composite was below the pyrolysis temperature of the organic matrix. Following this induction period, there was a rapid rise in the heat release rate due to the combustion of volatiles, in this case mainly low molecular weight hydrocarbons, near to the composite/fire interface. Following the peak heat release rate (PHRR), the HRR of the composites with CHAp, CHAp: BPF, and AH: BPF decreased progressively with time, due to the formation and thickening of their surface layer which slowed down the decomposition reaction rate in the underlying material. The HRR also declined as a result of the declining resin content in the samples. Eventually, the heat release rate became negligible, as the last of the resin matrix was decomposed. The heat release rate curves for the composite materials reinforced with CHAp: BPF and AH: BPF were similar in profile.

3.2.3 Peak heat release rate with varying wt% for BPF: CHAp and BPF: AH composites

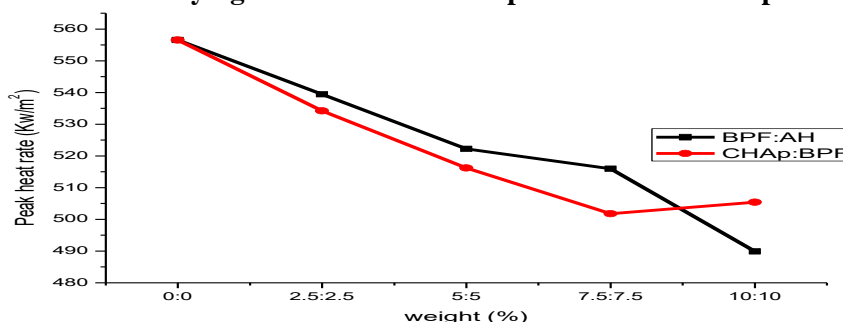


Figure 6: Variations of peak heat release rate with varying wt% for BPF: CHAp and BPF: AH composites.

3.2.4 Mean heat release rate with varying wt% for BPF: CHAp and BPF: AH composites

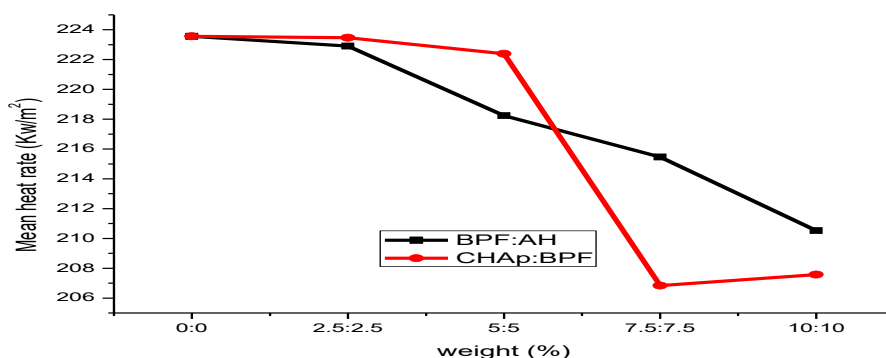


Figure 7: Variations of Mean heat release rate with varying wt% for BPF: CHAp and BPF: AH composites.

3.2.5 Total heat release rate with varying wt% for BPF: CHAp and BPF: AH composites.

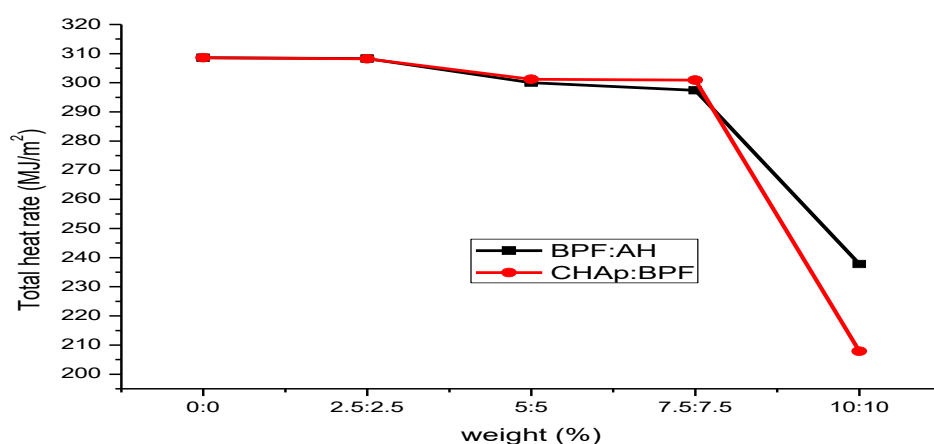


Figure 8: Variations of total heat release rate with varying wt% for BPF: CHAp and BPF: AH composites.

The results from Figures 6-8 showed that at the end of the burning period, polyester released a total heat of 306.6 MJ/m². The composites released 549.2, 303.5, 207.9 and 237.8 MJ/m² at 20wt%BPF, 20wt%CHAp, 10wt%BPF: 10wt%CHAp and 10wt%BPF: 10wt%AH respectively. It was observed that the addition of CHAp reduced the THR of the polyester. This suggested mechanism, by which CHAp acted as a fire retardant and reduced THR of the composite involved the formation of char that served as a potential barrier to both mass and energy transport between the flame and the burning polymer.

3.2.6 Time to ignition and end of test time

From Figures 9-10, it was observed that the time to ignition for the composites with BPF was shorter compared with those of the other composites. Also, the composites produced with BPF had the short end of test time, because the composites burn faster, which resulted in the lower end of test time..

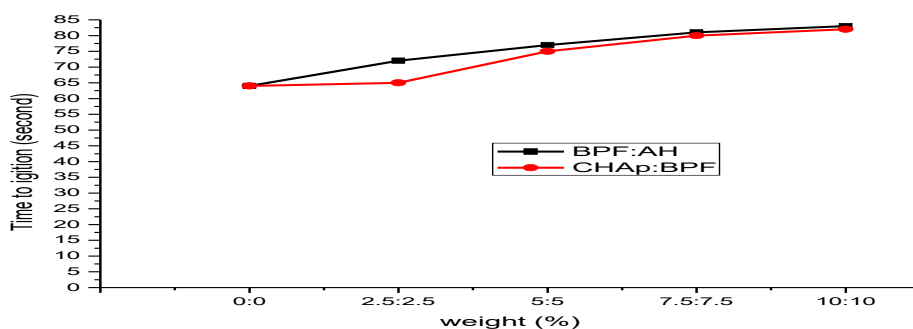


Figure 9: Variations of Time to ignition with varying wt% CHAp: BPF and BPF: AH composites.

It was concluded that addition of CHAp and AH to the polyester resin, produced a slight delay in the ignition time and reduced PHRR values. Besides, due to the action of the fire retardant (CHAp), the second peak of the HRR was less pronounced, and the total burning time was increased indicating that the fire-retarded composite of CHAp or AH burned for a longer time with a weaker flame than that of the polyester and BPF composites. However, the time to ignition (TTI) and end of test time (ETT) values of CHAp composites were increased by the incorporation of CHAp. The increased TTI value resulted from the composites containing CHAp which presented the highest TTI values. This

indicated better fire retardant property (Figures 9-10 and Table 2 and 3). This is the major reason, why the oxygen consumed and smoke release rates during burning were higher for the BPF composites than those of CHAp, BPF: CHAp and BPF: AH composites (Table 2 and 3), as a result of CHAp, BPF: CHAp and BPF: AH composite showing improvements in difficulty to-ignite

3.2.7 End of test time with varying wt% CHAp: BPF and BPF: AH composites

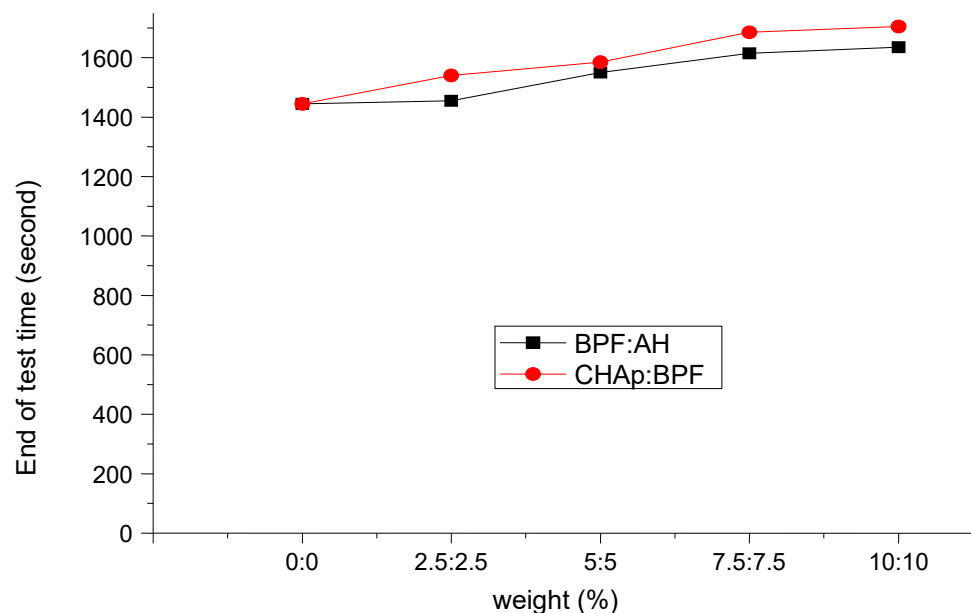


Figure 10: Variations of end of test time with varying wt% CHAp: BPF and BPF: AH composites.

3.2.8 Mass loss with varying wt% BPF and CHAp composites

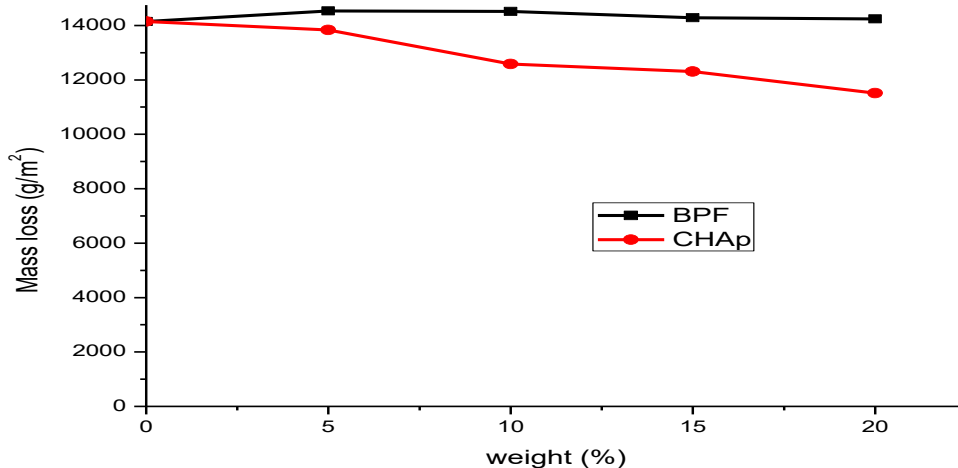


Figure 11: Variations of mass loss with varying wt% BPF and CHAp composites

3.2.8 Mass loss with varying wt% BPF: AH and CHAp: BPF composites

From Figures 11 and 12, it was observed that the mass loss of the composites with BPF increased with increase in wt% BPF addition, while the mass loss of the composites produced with CHAp, CHAp: BPF and BPF: AH decreased with increased weight% addition to the composites. This was attributed to the increased rate of char formation, which helped in slowing down the rate of burning. A similar observation was observed in the work of Nayra et al, [16]. Also, the reduction in mass loss, increased residue formation (Table 2 and 3), indicating that CHAp decomposition reduced

the rate of burning of the composite by decreasing the total heat produced as a result of char formation in the condensed phase. The char formation and the CHAp intumescent behaviour was noticed during and after the cone calorimeter test for the CHAp-based composite.

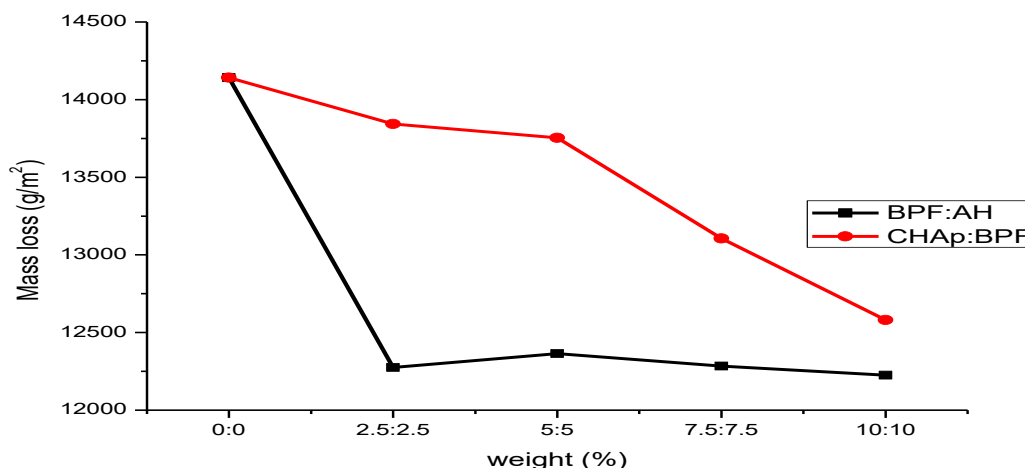


Figure 12: Variations of mass loss with varying wt% BPF: AH and CHAp: BPF composites.

3.2.9 Mass loss with time for varying wt% BPF: AH composites

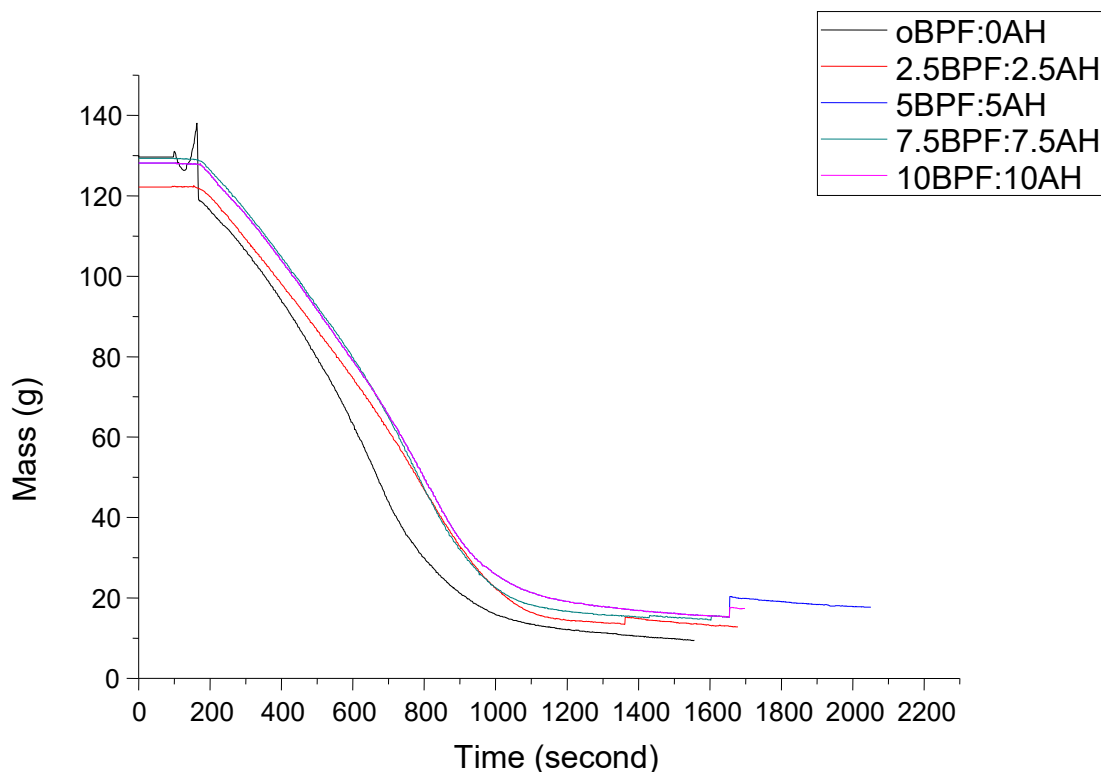


Figure 13: Variations of mass loss with time for varying wt% BPF: AH composites.

3.2.10 Mass loss with time for varying wt% BPF: CHAp composites

From Figures 13 and 14, it was observed that the mass loss of the composites with BPF increased with increase in wt%BPF addition, while the mass loss of the composites produced with CHAp, CHAp: BPF and BPF: AH decreased with increased weight% addition to the composites. This was attributed to the increased rate of char formation, which helped in slowing down the rate of burning. A similar observation was observed in the work of Nayra et al, [16].Also,

the reduction in mass loss, increased residue formation (Table 4.8), indicating that CHAp decomposition reduced the rate of burning of the composite by decreasing the total heat produced as a result of char formation in the condensed phase. The char formation and the CHAp intumescent behaviour was noticed during and after the cone calorimeter test for the CHAp-based composite. The smoke generated by the fire is toxic and opaque and seriously endangers personnel safety. Therefore it is vital to detect the smoke production when materials burn. The TSP and TSR of CHAp decreased progressively as the wt% CHAp loading increased. This indicated that CHAp has smoke suppression performance. The MHRR is used as an indicator to measure the tendency for the fire to develop under real conditions. The MHRR of CHAp decreased unlike those of BPF which increased (Table 2 and 3). This reduction indicates that CHAp can indeed diminish the tendency for the fire to develop. As shown in (Table 2 and 3), the residue of the polyester-BPF composite after burning was mainly greyish white ash with a small amount of carbon (char) blocks. The residue of CHAp/polyester-based composites had some white ash on the surface but the carbon or char shape maintained the original shape of the composite, which indicated that CHAp was beneficial to promoting the carbon formation of composites during combustion. In particular, the residues of greater CHAp percentage composites seemed to be more complete and harder. This indicated that the uniform and dense CHAp was more favourable for carbon formation.

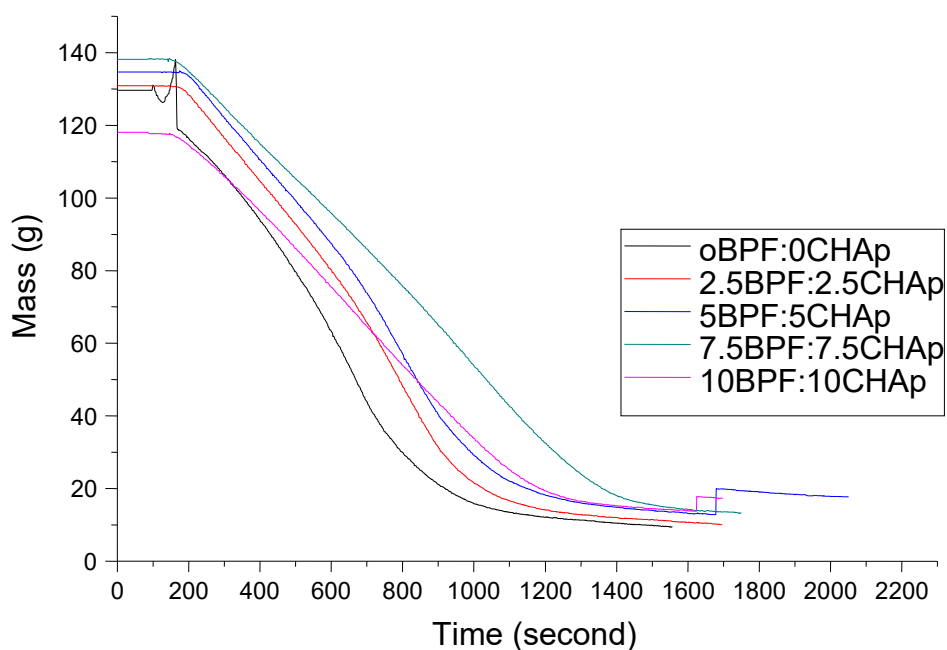


Figure14: Variations of mass loss with time for varying wt% BPF: CHAp composites.

3.3 Surface structure of test composites after the fire test

The residues of the composite sample left after fire test for the polyester /7.5%CHAp/7.5%BPF and polyester/7.5%AH/7.5% composites presented a thick and cohesive residual char. It can be seen that there were some swollen residual char (Figure 13), which acted as a barrier to prevent the transmission of oxygen and heat. The residue of the composite as shown in Figure 13 showed a compact and intumescent char layer, which was the main reason for obtaining better flame retardancy of the composite. It was observed that the residue of BPF composites was surrounded with soot, while a black swelled char characterized the residue of fire-retarded composites incorporated with CHAp or AH. This confirmed the potentials of CHAp and AH in foaming and expanding the composites surface, hence, insulating and protecting the underlying material during thermal decomposition.



Figure 13: (A) Photograph of the 7.5%CHAp: 7.5wt% BPF sample left after fire Test. (B) Photograph of the 7.5%AH: 7.5wt% BPF sample left after fire test.

4. Conclusion

Cone calorimetric analysis of the developed composites showed that CHAp was effective as a flame retardant additive. CHAp incorporation to polyester composites decreased the total heat release of the composite, as a result of char formation which acted as a barrier between the flame and the composites. It reduced the total mass lost, increased the time to ignition and increased the end of test time of the developed composites. It was observed that CHAp/BPF/ polyester composites and AH/BPF/ polyester composite had similar fire properties at the same percentage addition of 7.5wt% for CHAp and AH respectively to the polyester matrix. The polyester composites with 7.5wt%CHAp: 7.5wt%BPF additions produced the best results of fire retardancy for engineering material applications. This combination delayed the ignition time by 25%, the end of burning time by 14.24% and reduced the total heat release rate by 9.07%.

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