

# Characterization of fire retardant properties of cow horn ash particles and thermal behavior of polyester/ Banana peduncle fibre /cow horn ash particle hybrid composites

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## Abstract

Natural fibres thermally degrade and burn readily and their use has been restricted in applications where the heat and fire regulations are stringent. The need to enhance the fire resistance of natural fibres inspired the development of cow horn ash particles as a novel flame retardant additive for polyester/cow horn ash particles (CHAp)/Banana peduncle fibre (BPF) hybrid composites. The composites were produced by varying the ratios of CHA: BPF from 0:0, 2.5:2.5, 5:5, 7.5:7.5 and 10:0wt%. The thermal and fire properties were determined. The results obtained showed that the incorporation of CHAp played a crucial role in improving the thermal stability of the composites by acting as an effective physical barriers against thermal decomposition in the polymer composites. This work shows that at 7.5wt%CHAp: 7.5wt% composite delay the ignition time by 25, the end of burning time by 14.24% and reduced the total heat release rate by 9.07%. The research work has established that CHAp can be used to replace expensive and toxic organic and inorganic flame retarded polymer composites for structural application.

**Keywords:** cow horn ash; polyester; fire retardancy; banana peduncle fibre.

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## 1.0 INTRODUCTION

Fire is a unique destructive force, it consumes whatever it touches and leaves nothing behind but ash ( Akash *et al* ., 2017). Global fire losses are estimated to be \$500 million a year ( Kandare *et al* ., 2010). Plastics are a part of almost every component used by man but are known for their high flammability; once they are ignited a sequence of exothermic oxidation reactions take place with the evolution of heat, corrosive toxic gasses and smoke. Flammable dripping can take place: this flammable behavior can spread out the flame and complicate the fire hazards( Sarki *et al.*, 2011 ; Nayra and Javier, 2016) . For instance, the fire risk scenario in modern cars is not just from the fuel tank rupturing and leading to fire but also from the fact that there is 90-100kg of plastic (solid fuel) inside the automotive compartment where passengers are located. There is a great demand for FR products in domestic houses, transportation, aerospace, and military applications ( Boulos *et al.*, 2003).

Improving the fire retardancy of polymeric materials is a priority and also a major challenge. Research has shown that FR materials can increase the allowable escape time by a factor of 15, minimizing the heat release by 75% and evolving less smoke and toxic gasses ( Morgan , 2006 ; Morgan *et al.*, 2013). The human and economic cost of fire can be significantly reduced by the appropriate use of FR materials and fire protection systems.

There has been considerable interest in the field of flame retardancy as the demand for improved safety in domestic, public and industrial sectors increased. In recent years, fire retardant (FR) sealants have penetrated markets in building construction because of the requirement for sealing gaps in fire resisting construction applications ( Maria *et al.*, 2014). Development of ceramic forming filler compounds or combination of compounds that form an effective thermal barrier under fire conditions could provide a significant improvement in the sealant performance.

The manner in which a coherent structure is formed is important. When the polymer decomposes and vaporizes, loose filler particulates will be remaining and cause the material to disintegrate. However de-vitrification of particular fillers must occur simultaneously with loss of polymer so that the ceramic maintains its shape by fusion of the inorganic particles.

Natural fibres are becoming attractive alternatives to traditional high performance fibres such as glass and carbon fibres for reinforcement in composites ( Maria *et al.*, 2012). This is because natural fibres are from renewable sources, biodegradable and therefore are more environmentally friendly. However, unlike inherently non-flammable glass and carbon fibres, natural fibres thermally degrade and burn and their use has been restricted in applications where the fire regulations are stringent.

Also, the development of fire retardants is subject to regulations. Halogen – free, recyclable, environmentally friendly flame-retardant systems that do not release toxic gases have recently become preferable. For example, the waste electrical and electronic equipment (WEEE) and restriction of hazardous substances (ROHS) directives limit the use of bromine-based flame retardants ( Li *et al.*, 2012 ; Ali *et al.*, 2015).

The ever—increasing demand for low cost materials stimulated the interest towards production and utilization of using cow horn since they are affordable ( Abdullah and Ahmad, 2013 ; Asuke and Aigbodion , 2016). The world has a surplus amount of banana fibres and cow horn, which has a great potential that can be used as composites material. BPF and cow horn litter the entire environment which constitute nuisance to the environment, however, the right know-how (technology) to convert these into engineering materials has remained a daunting challenge to materials engineers in the country. This decision problem sharpens the focus of this research work. Based on the forgoing this work undertook a study on the possibility of using the waste cow horn as flame retarded for polymer/banana peduncle fibres composites.

## 2.3 MATERIALS AND METHODS

### 2.1 Materials

Peduncles of *musacavendishi* bananas were collected from banana seller in Enugu State, Nigeria. With banana peduncle and cleaned with water and dried. The animal horns for the study was cow horn. The horn was obtained from abattoir at Enugu State Nigeria. Unsaturated polyester resin as matrix was used in this research. 2% solution of cobalt naphthalate and 2% solution of methyl –ethylketone( MEK) peroxide were used as accelerator and catalyst respectively.

### 2.2 Methods

**The fibres and composites were prepared as described by ( Baljinder *et al.*, 2015 ; Mohammad, 2018).**

The vinyltriethoxysilane (VTS) and 3-aminopropyl triethoxysilane (APTES) solutions was prepared at concentrations (3wt%) by adding the required type of silane (VTS or APTES) into the mixture of water and ethanol (20/80wt%), and then stirring by using a glass rod until a complete dissolution was achieved. The fibres were treated with these VTS and APTES solutions for a period of 3hours. The bony core was isolated naturally from the keratin sheath. The bony core was washed, sun dried for four weeks and degreased with water soluble stain remover (acetone) to remove any trace of marrow, blood and other substances that will inhibit proper bonding between the matrix and the reinforcement particles. The bony core was calcinated at a temperature of 1200°C in the absence of oxygen using a heat treatment furnace. The ashes were milled to the required granules and sieved to particles sizes of 125 µm.

The polyester resin was converted from a liquid to the solid state by adding hardener. Methyl ethyl ketone peroxide, symbolized as (MEKP) and in the form of a transparent liquid was added to unsaturated *polyester resin* at room temperature. Accelerator cobalt naphthalene was used to increase the rate of curing. BPF: CHAP of 0:0, 2.5:2.5, 5:5, 7.5:7.5 and 10:10wt% was produced.

Thermal stabilities of the composites were studied using thermogravimetric analysis (TGA). Heating rate of 10°C/min and high purity Argon was continuously passed into the furnace at a flow rate of 60 mL/min at room temperature and atmospheric pressure. The TG and DTA curves were obtained from TGA runs using universal analysis 2000 software from TA Instruments.

Artificial fire tests were performed on small composite panels using a dual cone calorimeter. Heat flux of 50 kW/m<sup>2</sup> was used because it caused the GRP panel to ignite after heating for 30 seconds. It was suggested that the heat flux of 50 kW/m<sup>2</sup> is about the heat energy radiated by a medium intensity room fire (see Figures 1a & b).



Figure 1a: Photograph of cone calorimeter test samples



Figure 1b: Photograph of sample flaming inside the cone

### 3.0 RESULTS AND DISCUSSION

Figure 2 shows the decomposition of the hybrid composites with polyester-CHAp/BPF. It was observed in Figures 2 that as the weight of CHAp increased in the formulation, it resulted to a rise in the thermal stability of the composites. About 20% weight char or residue remained when 7.5wt% CHAp was added to BPF (Figure 2). The increase in thermal stability of the hybrid composites was due to the fact that CHAp retarded the decomposition of the composite materials.

Figure 3 shows the derivate of weight with temperatures. It was seen that the decomposition of the materials was an endothermic process that was dominated by random-chain scission of the main polymer chain. The decomposition temperature shifted to higher temperatures for composites produced with CHAp/BPF (Table 1). The decomposition reactions of composites produced with CHAp/BPF were largely complete at around 400°C. Higher temperatures of thermal decomposition of CHAp/BPF composites than those of polyester resin demonstrated that the resin underwent substantial volatilization with most of the gases being low molecular weight combustible hydrocarbons. This behavior was determined in the initial stages by scission of highly strained portion of polyester crosslink with consequent formation of free radicals that promoted further decomposition and scission

of the polyester backbone. As a result, large amounts of low-molecular-weight volatiles (CO, CO<sub>2</sub>) were released rather than char.

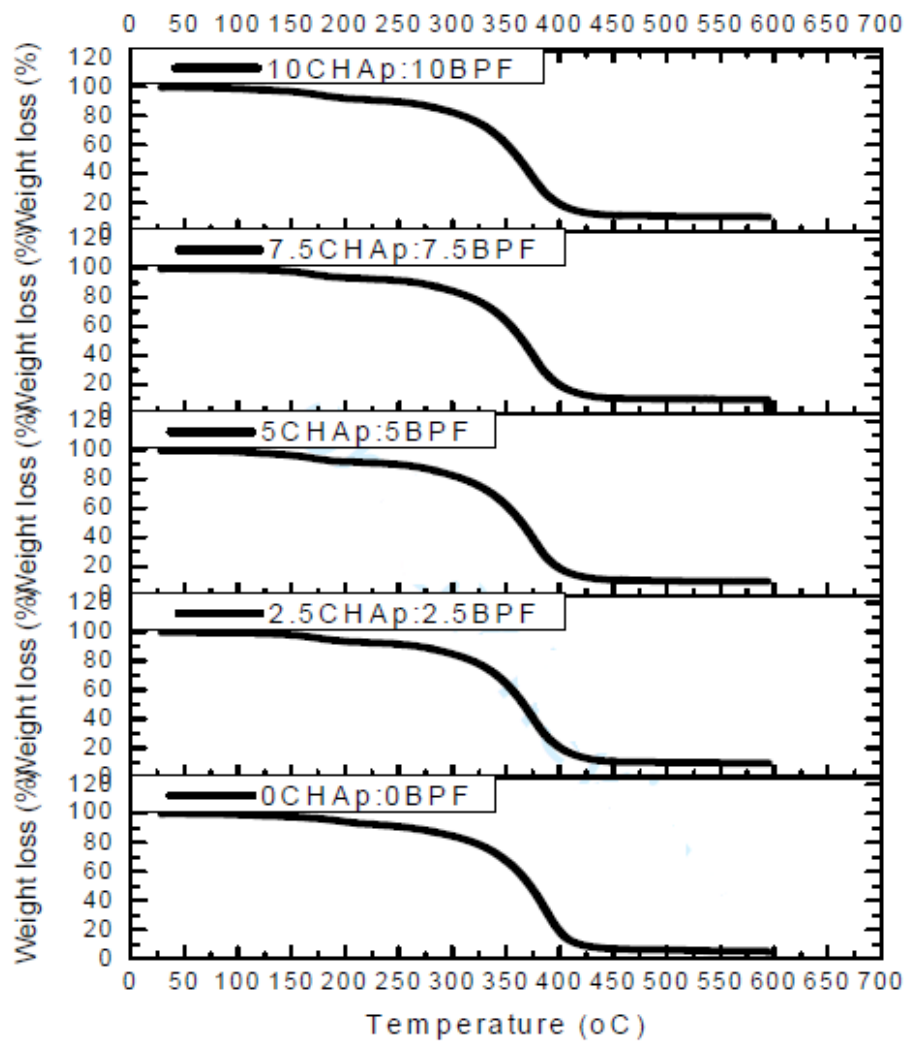


Figure 2: Variations of percentage weight loss with temperatures for composite produced with BPF/CHAp

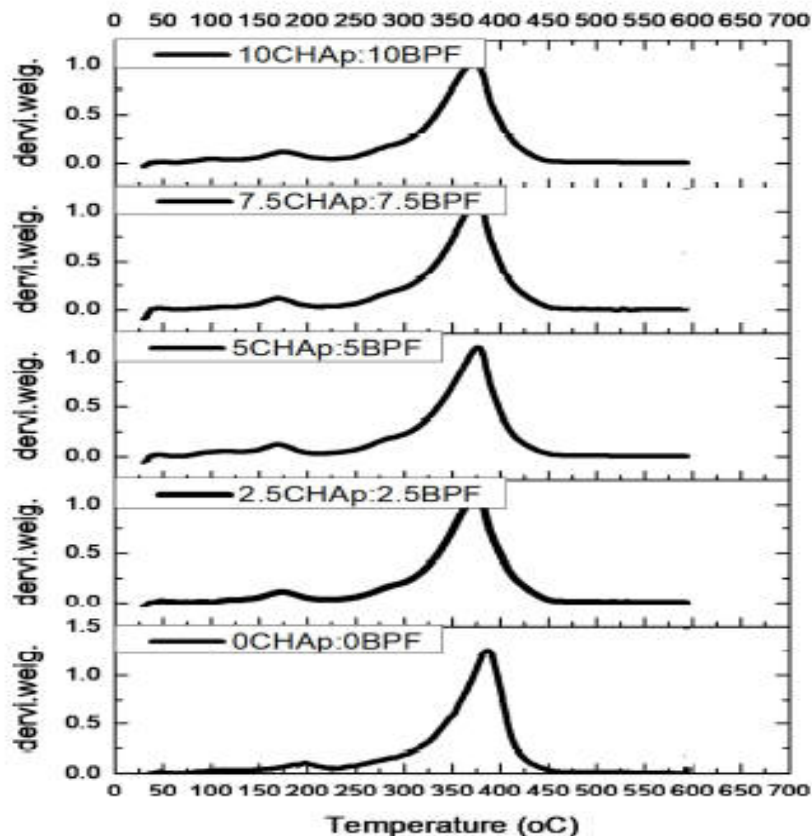


Figure 3: Variations of derivative of weight with temperatures for composite produced with CHAp/BPF

The pronounced single endothermic effects observed in Figure 2 corresponded to the oxidative degradation process and to the release of volatile matters. The presence of endothermic effects in the samples were as a results of three processes – intermolecular dehydrogenation, vaporization and solid state decomposition of some additives (e.g. plasticizer).

This conclusion was confirmed by the decreased in mass of the polymer. It was assumed that the total burning/ degradation of the residual polymer backbone(dehydrogenation polyester) took place in the temperature interval of (300-500°C), which was different for the individual composites samples. In the last temperature intervals the mass loss was minimal. This last step (accompanied by the evolution of CO<sub>2</sub> only) could be due to the degradation of the filler materials in the composite. The result indicated that the, CHAp/BPF composites biomass showed less percentage decomposition. In the CHAp/BPF composites, a slight shift of the degradation at onset and a clear evident reduction of mass loss was noticed. Within the temperature range of 150°C– 450°C, the mass loss when compared with that of the neat resin, respectively, and the final residue at 550°C was 9%(see Table 1)

Table 1: TGA results of the composites

	T <sub>10%</sub> Weight loss	T <sub>50%</sub> Weight loss	T <sub>80%</sub> Weight loss	T <sub>max</sub>	T <sub>final</sub> Weight loss	Residues weight (%)
0%CHAp:0%BPF	260.84	372.48	398.4	402.0	593.57	5.28
2.5%CHAp:2.5%BPF	267.08	376.49	400.76	402.0	593.94	9.554
5%CHAp:5%BPF	309.99	384.03	407.15	404.6	593.46	9.63
7.5%CHAp:7.5%BPF	347.1	385.85	409.15	407.0	593.04	9.811
10%CHAp:10%BPF	348.64	382.49	418.19	407.15	593.75	10.39

Figure 4 shows the heat release rate of the composites. From Figures 4 it was clearly observed that the peak heat release rate (PHRR), the HRR of the composites, decreased progressively with time due to the formation and

thickening of the surface char layer that slows the decomposition reaction rate in the underlying material. The HRR also declined as a result of the declining resin content in the sample.

Eventually the heat release rate became negligible, as the last of the resin matrix was decomposed.

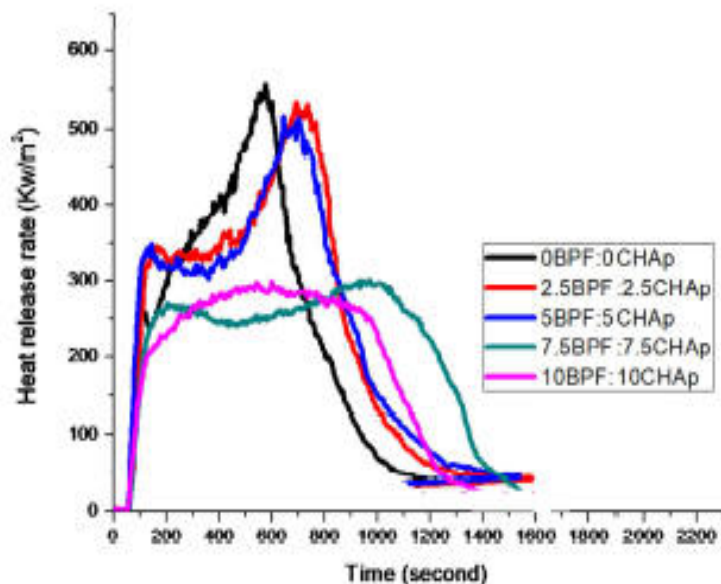


Figure 4: Variations of Heat release rate with Time for BPF:CHAp

The results of this study showed that at the end of burning, pure Polyester released a total heat of 306.6MJ/m<sup>2</sup>. The composites released 207.9MJ/m<sup>2</sup> at 10wt%BPF: 10wt%CHAp(Figure 5 and Table2). It can be observed clearly that the addition of CHAp reduced the THR of the polyester. The suggested mechanism by which expanded CHAp acted as fire retardant reducing THR, involved the formation of a char that served as a potential barrier to both mass and energy transport between the flame and the burning polymer.

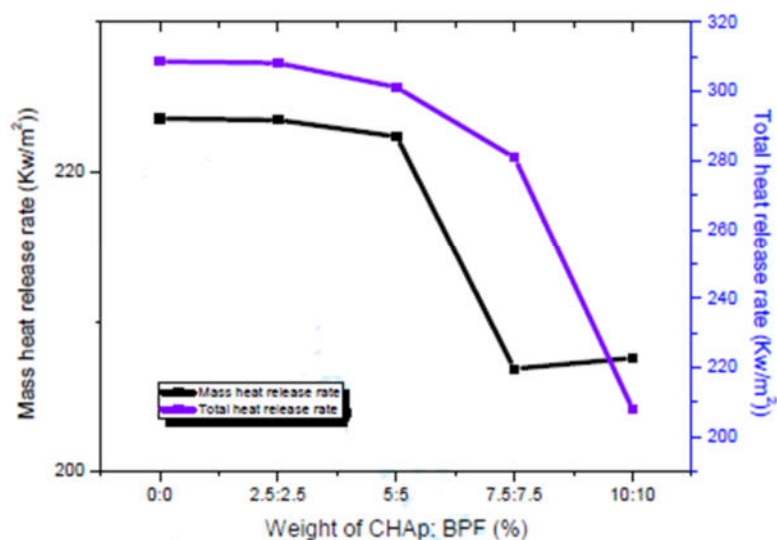


Figure 5: Variations of mean heat release rates and total heat release rates with wt% for BPF:CHAp

Figure 6 was used to validate the results obtained from the TGA/DTA. It was observed that the mass of the samples decreased as time increased.

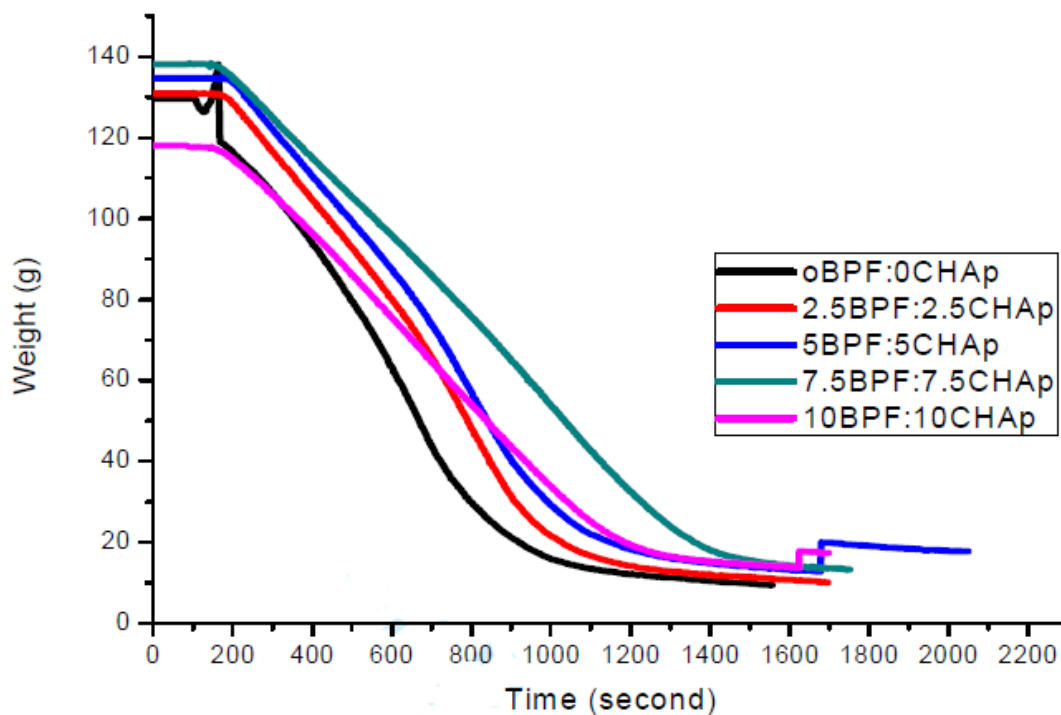


Figure 6: Variation of weight loss with time for wt% BPF:CHAp

From Figure 6 it was observed that the mass loss of composites produced with CHAp: BPF decreased with increase in with weight% of the reinforcement. This was attributed to the increase in the rate of char which helped slow down the rate of burning. Similar observation was reported in the work of . Also the reduction of mass loss, enhanced residue formation (Table 2) indicated that CHAp decomposition reduced the composite burning by decreasing the total heat production due to the char formation in the condensed phase. The char formation and the CHAp intumescent behavior was clearly noticed during and after the cone calorimetric test for the CHAp-BPF based composites.

**Table 2: Results of the Cone calorimeter test**

	MHRR (kw/m <sup>2</sup> )	PHRR (kw/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	MASS loss(g/m <sup>2</sup> )	TSR (m <sup>2</sup> /m <sup>2</sup> )	TSP (m <sup>2</sup> )	TOC (g)	TTG (s)	ETT (s)
0%BPF:0%CHAp	223.56	556.54	308.6	14142.1	9378.2	82.9	206.3	64	1445
2.5%BPF:2.5%CHAp	223.47	534.19	308.2	13843.1	8889.2	81.4	203.9	65	1540
5%BPF:5%CHAp	222.39	516.23	301.2	13754.5	8579.4	80.6	200.1	75	1585
7.5%BPF:7.5%CHAp	206.84	501.80	280.9	13106	8161.5	78.9	129.32	80	1685
10%BPF:10%CHAp	207.57	505.42	207.9	12580.2	80582	70.9	121.16	82	1705

MHR= mean heat release rate, PHRR = peak heat release rate, THR= total heat rate, TSR= total smoke release, TSP = total smoke produce, TTG = time to ignition, ETT = end of test time.

Time-to-ignition is the minimum exposure time required for the specimen to ignite and sustain flaming combustion. The spark igniter to the cone calorimeter was used to induce ignition. Time-to-ignition is an important fire reaction property because it defines the time that a composite material can withstand the heat flux radiated by a fire before it experiences sustained flaming combustion.

From the Figure 7, it was observed that the time for ignition for the composites was higher than those of the polyester. The time to ignition increased from 64 to 82 second at 0%CHAp: 0%BPF and 7.5%CHAp: 7.5%BPF respectively. Also the composites produced took a longer end of test time, because the composites burnt slower

which resulted to longer end of test time. In addition, due to action of the CHAp as a fire retardant, the second peak of the HRR was less pronounced, and the total burning time was increased indicating that the fire-retarded composite burnt for a longer time with a weaker flame than the polyester and BPF composites.

This was the major reason, the oxygen consumed and smoke releases rate during burning was lower for the composites (see Table 2 and Figure 8). This was because the CHAp: BPF composites reduced the rate of ignitability.

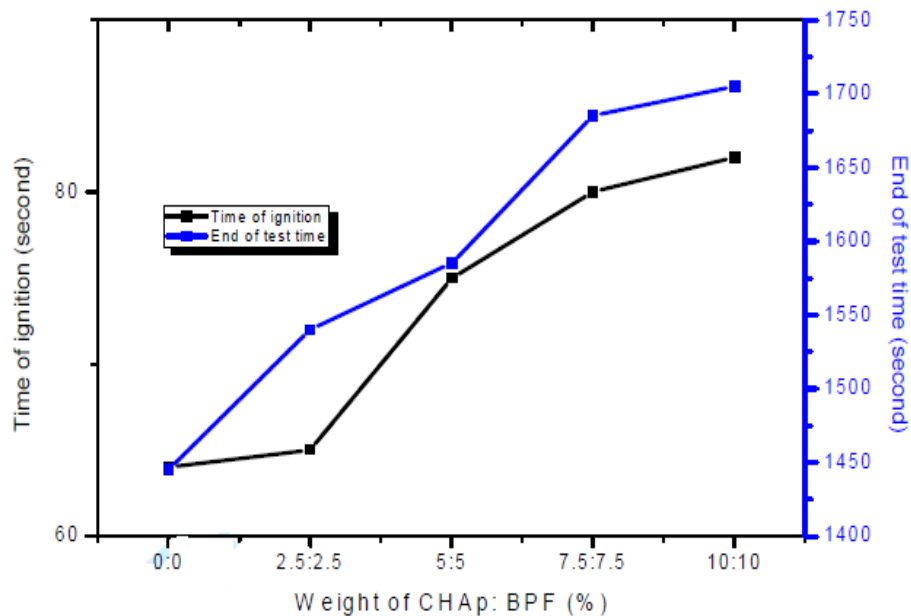


Figure 7: Variation of Time to ignition and end of test time with wt% CHAp :BPF

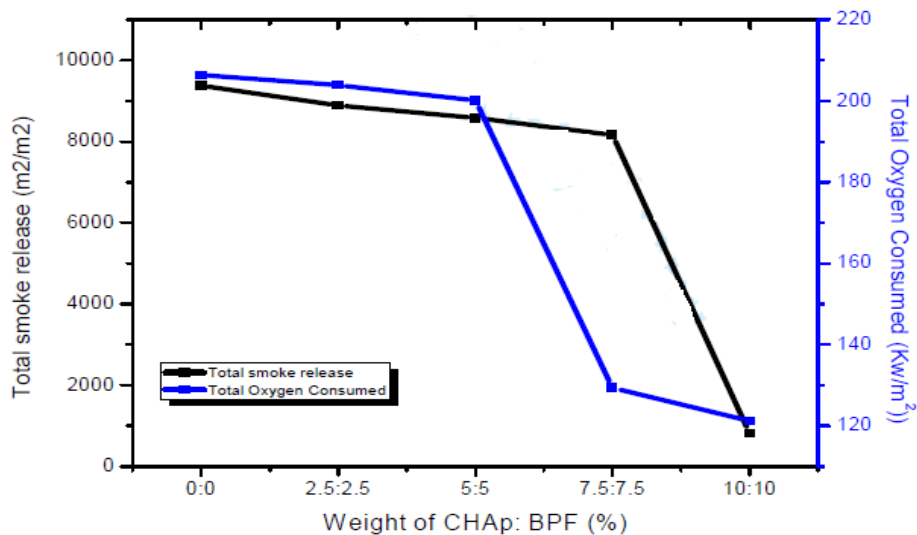


Figure 8: Variations of total smoke release and total oxygen consumed with wt%CHAp:BPF.

This work shows that at 7.5wt%CHAp: 7.5wt%BPF , there was a very high flame retardancy in the sense that the composite delayed the ignition time by 25%, the end of burning time by 14.24% and reduced the total heat release rate by 9.07%.





Figure 9a: Photograph of the polyester sample left after fire test



Figure 9b: Photograph of the 7.5%CHAp:7.5wt%BPF sample left after fire test

Figures 9 (a&b), shows the photo graphs of the residues after the cone calorimeter experiment. It was observed that the polyester showed little or no residue after burning (Figure 9a). The residue of composite as shown in Figure 9b shows a compact and intumescent char layer, which was the main reason for obtaining better flame retardancy for the composites. The residue of the polyester was surrounded by soot, while a black swelled char characterized the residues of the composites, confirming the effectiveness of CHAp in foaming and expanding the composite surface, hence insulating and protecting the underlying material.

#### 4.0 CONCLUSIONS

From this work and the discussion above the following conclusions were made:

1. The incorporated CHAp played a crucial role in improving the thermal stability of the composites by acting as effective physical barriers against the thermal decomposition in the polymer composite
2. The maximum endothermic peak shifted to higher temperatures with increase in weights of CHAp in the composites reflects improved thermal stability.

3. This work showed that at 7.5wt%CHAp: 7.5wt%BPF, CHAp served as an effective flame retardant by delaying the ignition time by 25%, the end of burning time by 14.24% and reduction of total heat release rate by 9.07%.
4. Waste cow horn can be used as a flame retardant materials for the development of polymer composites.

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