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Investigation of Nigerian Kankara and Darazo Sediments as Synergistic Fillers in Fire Retardant Formulations

Adiat I. AROGUNDADE[1*], Ibrahim D. MUHAMMAD[1], Kafayat O. ADEYEMI[1], Benjamin I. UGHEOKE[1], Musa. T. ZARMAI[1], Saratu MAMMAN[2] and Abdulhakeem H. NURUDEEN[1]

[1]*Department of Mechanical Engineering, University of Abuja, Abuja, Nigeria*
[2]*Department of Chemistry, University of Abuja, Abuja, Nigeria*

*Corresponding Author: adiat.arogundade@uniabuja.edu.ng

Abstract

In this work, two Nigerian sedimentary deposits were characterized for material properties using x-ray diffraction analysis, thermogravimetric analysis and scanning electron microscopy in order to determine their suitability as additives in fire-retardant formulations. Results indicated that Darazo contains 88% aragonite, a calcium carbonate-based mineral, while Kankara is a layered hydrous silicate with almost equal amount of kaolinite and molybdite. Both calcium carbonate and kaolin are popularly used in the fire-retardant industries as fillers in paints and plastics for flame retardation. Thermogravimetric analysis showed Darazo to be more thermally stable, decomposing at elevated temperature between 450 °C to 650 °C to release carbon dioxide. Its flame retardation will appear therefore more active at higher temperatures. Kankara clay appeared less thermally stable, releasing surface water at around 100-200 °C. Kankara therefore has the potentials to delay ignition. The hybrid formulation however created a synergy, enabling a longer active cooling range. The highest temperature reduction of 20.56% compared to the control was achieved in the hybrid formulation using Bunsen burner test. All the coated boards recorded lower percent mass losses compared to the uncoated wood. Therefore, both Darazo and Kankara sedimentary deposits have potential to serve as additives in fire retardant paints.

Keywords: *Sedimentary deposits, fire-retardant additives, kaolin, aragonite, dihydroxylation, decarbonation.*

1.0 Introduction

Fire hazards are common occurrences in homes, offices and commercial buildings. The losses of lives and properties to fire incidents every year is a perennial problem that has led to a wide field of research into fire-rated materials including fire-retardant materials, fire-stops, and a host of others. These serve to contain the fire and buy time for the occupants to make their escapes before the arrival of the fire-fighting team. The use of fire-retardant materials is not common-spread in Nigeria and other African countries, first because of the relative novelty of the technology and secondly because most of the products are imported, therefore expensive. There is therefore, a pressing need to explore the local contents as alternative raw materials in the production of locally-made fire retardant materials. This work in response to this need examines two locally sourced fillers, one from Kankara in North-West geopolitical zone of Nigeria and the other from Darazo in North-East geopolitical zone of Nigeria for possible application in flame retardation.

Kaolin clay has a wide range of properties and uses depending on its location and age. This is due to the fact that the parent feldspars are a group of rock-forming silicate minerals having potassium as in orthoclase ($KAlSi_3O_8$), sodium as in albite ($NaAlSi_3O_8$), calcium as in anorthite ($CaAl_2Si_2O_8$) or a combination of any two of these primary forming elements as may be found in the plagioclase feldspar (oligoclase, andesine, labradorite and bytownite); the alkali feldspars (anorthoclase, sanidine and orthoclase-microcline) or the less common barium, rubidium, strontium or iron feldspars (Jongs *et al.*, 2018; Kumari and Mohan, 2021; Valentini and Mascarin, 2021) . Kaolin may have other ancillary minerals including mica and quartz, and auxiliary minerals like illite, montmorillonite, ilmenite, anatase, haematite, bauxite, graphite and halloysite among others. This varied composition is responsible for a wide range of properties necessitating the careful characterization of each deposit for optimal utilization (Kumari and Mohan, 2021; Olafadehan *et al.*, 2018).

Kaolin clay, when not colored by impurities such as iron oxides and hydroxides has a white to white-pinkish coloration and find popular use in the paper and paint industries as a pigment and filler, its softness adding to the smoothness and gloss of high quality paper sheets (Raji and Bouhfid, 2020; Sanz *et al.*, 2022; Tamar-Agha, 2020). Kaolin clay, due to its good refractory properties was for centuries the traditional material for the production of high-quality porcelain and fired clays. Though kaolinite is not absorbent due to its tightly

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packed sheet structure, its large surface area makes it a good adsorbent which has found wide usage as membrane material in recent times (Marino *et al.*, 2017; Mustapha *et al.*, 2019; Yu *et al.*, 2020).

A less common use of kaolin is its application as a fire retardant. Kaolinite ($Al_2O_3(SiO_2)_2.2H_2O$) may have up to four molecules of interstitial water which is released between 300-570°C or between 400 °C – 700 °C in a dehydroxylation reaction as steam, depending on the nature of individual deposits (Tamar-Agha *et al.*, 2020; Daou *et al.*, 2020). The released steam absorbs heat from its immediate surroundings, creating a heat sink that retards the growth of flame, while the resulting heat- resistant alumina-silicate improves the thermal stability of the host system, thereby slowing down thermal degradation. Several researches have looked into the incorporation of kaolin clay and calcium carbonate as fire retardant fillers in intumescing paints, fire-rated plastics, textiles and other flame-treated combustible materials (Ou *et al.* 2021; Tang *et al.*, 2020; Ulla *et al.*, 2014).

For fire-rated plastics, flame retardancy may be improved by incorporating modified kaolin or calcium carbonate into the polymer matrix. To improve the flame retardancy of low-density polyethylene (LDPE), Ou *et al.* (2021) incorporated 3% urea-intercalated kaolin into LDPE. Loss on ignition (LOI) was found to increase from 24.1% to 27.2%. Tang *et al.* (2020) introduced 1.5 wt% glycerine-intercalated kaolin into an intumescent fire-retardant (IFR) formulation, 23.5 wt% of the IFR into polypropylene (PP) was found to decrease the peak heat/ smoke release rate. In a similar experiment, Yu *et al.* (2020) modified the surface of ammonium polyphosphate with kaolinite. Addition of this to PP led to increased thermal stability and char residue. Thus, modification of kaolin either by intercalation or grafting with a polymer moiety is found to improve the thermal stability of the fire-retardant system due to the more uniform dispersion of the kaolinite in the polymer matrix. On the other hand, calcium carbonate is an established flame-retardant filler commonly used in plastics for fire-rating.

For non-plastic materials, fire retardant components are usually incorporated via chemical impregnation or intumescing coating. Intumescing paints are passive fire-fighting materials which when used as surface coating create a physical thermal barrier to the underlying material on exposure to high temperature or flame. Intumescent formulations consist of a char forming compound, usually pentaerythritol or any of the char forming starch; an acid-based compound, most commonly ammonium poly-phosphate, which triggers the charring reaction; and a fuming agent, which releases gas into the molten char to create an expanded, insulative mass (Hu *et al.*, 2020; Lucherini and Maluk, 2019). Clays, metal oxides and hydroxides such as kaolin are often added as reinforcing filler and as synergistic additives to improve the strength and insulative efficiency of the resulting char (Aqlibous *et al.*, 2020; Ribeiro *et al.*, 2020).

Xu *et al.* (2021) grafted a phosphate ester on kaolinite surface and blended this into amino resin to prepare a transparent coating which was applied to plywood board. The coating was found to exhibit a 64.9% reduction in flame spread and 45% reduction in smoke density. Ulusoy *et al.* (2023) found a blend of kaolin, metakaolin, flyash and calcium carbonate coating to perform better than a commercial coating due to the higher proportion of macro pores displayed by the kaolin-based coating.

Nigerian clays from different deposits have been widely studied and characterized for various applications. Labiran *et al.* (2022) characterized some Nigerian clays for refractory bricks and fireclays; Maciver *et al.* (2020) and Eze *et al.* (2020) characterized some deposits for zeolites and ceramic filters; while Ofunne and Bassey [25] characterized others for paints and pharmaceuticals. Though, most have promising properties for commercial applications, blending or modification of the clay structures have been reported to significantly improve the clay properties (Labarin *et al.*, 2022; Oludolapo *et al.*, 2022). However, the idea of flame-retardant formulation is still relatively novel in the African region and no study to the best of our knowledge has been carried out on the suitability of Nigerian kaolin clay as flame retardant material despite its wide abundance. The aim of this study therefore was to determine the suitability of two Nigerian soil deposits as alternative fillers in fire retardant coatings.

To achieve this, the material characterization of the filler samples was carried out to determine their crystallinity and thermal stability. This was used to explain the behavior of the flame-retardant systems at elevated temperature. The effects of filler additives on fire-retardant paint were determined by subjecting filler-incorporated coated wooden samples to flame test and their back-side temperature recorded and compared to that of the unfilled, controlled sample. Samples of the different coatings were also subjected to thermogravimetric analysis and their residual masses at 800°C compared. A blend of the filler samples was prepared and the effect of blending on the performance of the fire -retardant coating was investigated.

2.0 Materials and Methods

2.1 Materials

Two 6 kg samples of Kankara (KK) filler and Darazo (DZ) filler were purchased from the Department of Chemical Engineering, Ahmadu Bello University, Zaria in Nigeria. The fillers were used as-received without further processing. The fire-retardant reagents were of laboratory grade. They were sourced from Aldrich Ltd, Germany. They included pentaerythritol and boric acid; epoxy resin and the curing agent.

2.2 *Characterization of Filler Samples*

The fillers were characterized for mineral composition using X-ray diffraction analysis (XRD), thermal behaviour using Thermogravimetric analysis (TGA), microstructural analysis using Scanning Electron Microscopy (SEM) and chemical groups using Fourier Transform Infra-Red Spectroscopy (FTIR).

X-ray diffraction analysis was performed on a Rigaku D/Max-lllC X-ray diffractometer. Diffractions of pelletized clay samples were collected at scanning rate of 2^{o}/min in the 2 to 50^{o} range at room temperature with a CuKa radiation set at 40 kV and 20 mA. The diffraction data (d value and relative intensity) obtained was compared to that of the standard data of minerals from the mineral powder diffraction file, ICDD which contained and includes the standard data of more than 3000 minerals.

Microstructural analysis of pelletized samples was carried out on a JEOL JSM 7600 scanning electron microscope at an accelerating voltage of 15kV and a walking distance of 12 mm to 18 mm at magnification of 9000 respectively.

For the TGA analysis, samples were used without prior preparation. 18.7 g of each powdered clay sample was put in a platinum crucible and fired in a closed furnace attached to the TGA 55 – TA Instrument from room temperature to 1000 ^{o}C at a heating rate of 10 ^{o}C/ min using nitrogen as inert gas.

2.3 *Preparation of Coatings*

The two samples were incorporated into an epoxy matrix as an additive to the main fire-retardant ingredients (FRI) of ammonium polyphosphate (APP), melamine (MEL) and pentaerythritol (PER). The powder clay samples and the FRI were blended together to achieve homogeneity before addition of the epoxy. Shear mixing of the coating slurry was carried out for 20 minutes at 40rpm before the addition of the curing agent. Shear mixing continued for additional 10 minutes to assist the dispersion of the particles in the resin matrix. The formulation of Yew *et al.* (2015) in which a blend of fire retarding fillers was used was adopted for this study. The control, B1 was without a clay additive, the hybrid sample, B2 had 5.5 wt% each of both clays, B3 had 11 wt% Darazo content while B4 had 11 wt% Kankara content. The paints were applied using a wooden spatula on one face and all edges of 10cm x 10cm x 3cm unlaminated medium density fibre boards. The paints were left to cure in open air for three days. Thin films of these formulations were also prepared in petri dishes for thermogravimetric analysis. The four formulations are presented in Table 1.

Table 1: Chemical formulations of Darazo and Kankara intumescing paints

Runs	DZ (wt%)	KK (wt%)	APP (wt%)	MEL (wt%)	PER (wt%)	EPOXY (wt%)	BINDER (wt%)
B1	0	0	18	9	9	35.33	17.67
B2	5.5	5.5	18	9	9	35.33	17.67
B3	11	0	18	9	9	35.33	17.67
B4	0	11.0	18	9	9	35.33	17.67

2.4 *Fire Performance Testing*

The heat shielding ability of the filled coatings were tested using the Bunsen burner test as shown in Figure 1. The bunsen burner test is a bench scale fire test adapted to ASTME119 for comparing the heat shielding ability of coated samples.

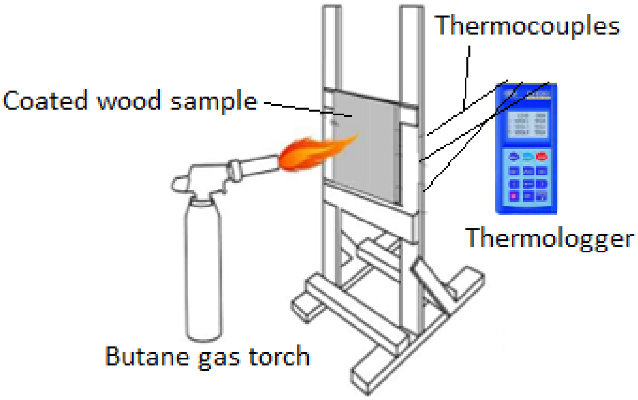

Figure 1: Bench-scale fire test set-up

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This was done by impacting flame from a butane gas burner on the coated surface and measuring backside temperature of the wood by taking the average readings of three thermocouples attached to the uncoated surface. The thermal stability of the clay-filled coatings was evaluated by obtaining residual masses of the coated film samples on a TGA 55 – TA machine.

3.0 Results and Discussion

3.1 Material Crystallinity

The XRD graphs of the samples are presented in Figure 2. The Kankara clay showed prominent peaks for kaolinite at 12.9 2θ and 27.3 2θ and a single high peak for molybdite at 27.3 2θ. Sharp peaks for aragonite (calcium carbonate) was observed at 36.6 2θ, 38.3 2θ and 46 2θ in the Darazo sample. Li *et al.* (2019) and Belmokhtar *et al.* (2018) have reported in earlier works that the physicochemical properties of soil minerals are strongly dependent on their crystallinity . Poorly crystalline soils are known to be characterized by small particle sizes, high specific surface area and excellent ion exchange rates while crystalline soils have relatively bigger particles and are more electronically stable (Castellano *et al.*, 2010; Du *et al.*, 2010). Both samples showed high degree of crystallinity, but from the diffractograms, Kankara clay appeared to be more crystalline compared to Darazo, due to the high stacking layers of both kaolinite and molybdenite.

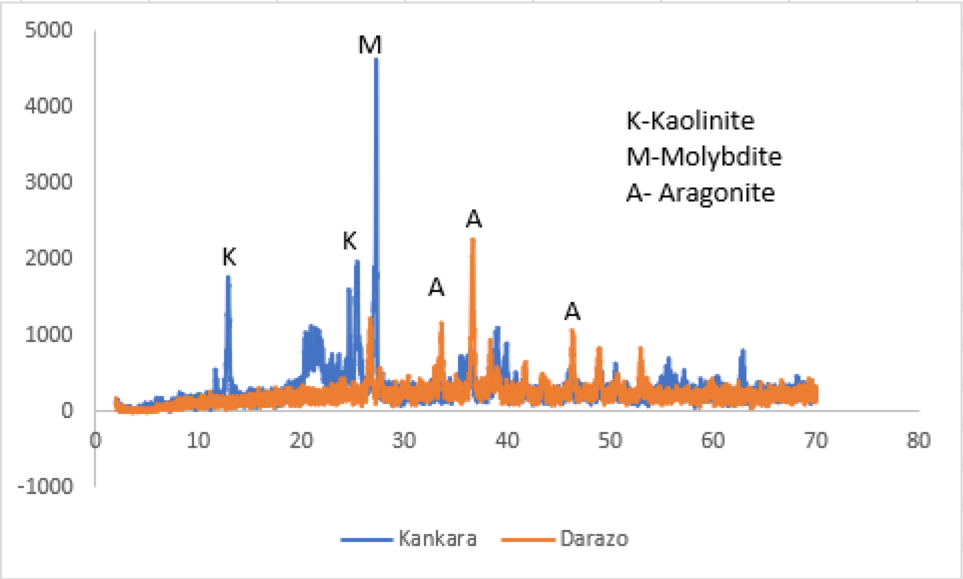
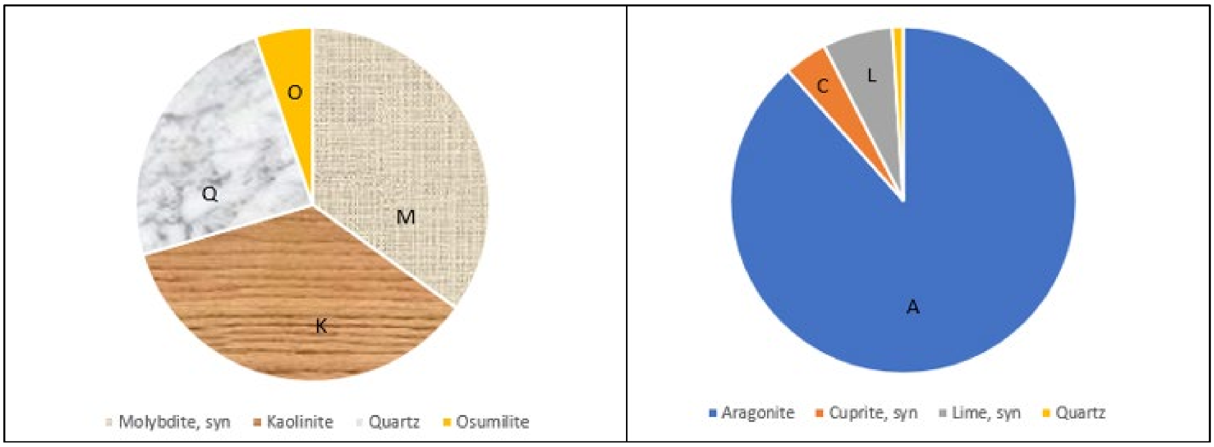


Figure 2: Comparison of the mineralogy of Darazo rock and Kankara clay

Christian *et al.* (2018) recently reported the high specific surface area and excellent ion exchange rates of Kankara clay as a promising adsorbent in the local pharmaceutical industry. The high ion exchange rate of Kankara clay will ease the incorporation of polymer ions in synthesizing organoclays necessary for the production of high performing intumescent paints. Other works have also shown that intercalation of ions is easier in more crystalline kaolinite (Dang *et al.*, SSRN 4100220). Again, both filler types may still play heat shielding roles by migration of the particles to the surface of the intumescing char to create a physical barrier and reinforce the char strength (Arogundade *et al.*, 2021). Thus, each filler type may have its own unique mechanism for improving fire retardation based on their overriding properties.

3.2 Mineral Distribution

The mineral distributions of both fillers are presented in Figure 3. Kankara clay is seen to contain almost equal percentages of kaolinite at 35.5 % and 34.9 % of molybdite. Both minerals are soft, layered sheets, leading to the prominent peaks observed in the Xray diffractogram and qualifying it as a clay deposit. Quartz has a significant presence at 24.3%, while osumilite has a minor presence at 5.24% On the other hand, Darazo is predominantly hard with a carbonite content of 88 % aragonite and other hard minerals, lime, cuprite and quartz at 6 %, 5 % and 1 % respectively.

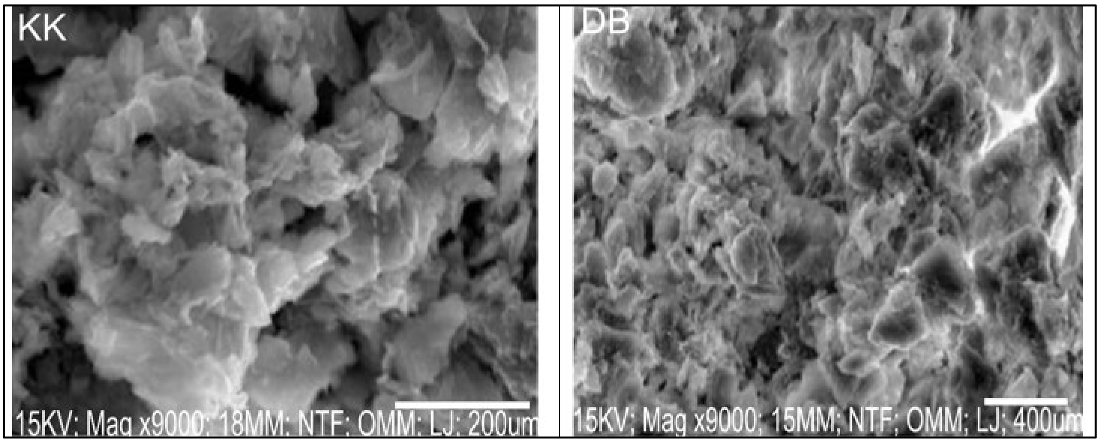


(a) (b)

Figure 3: (a) Mineral distribution in Kankara clay (b) Mineral distribution in Darazo rock

3.3 Microstructural Analysis

The micrographs of Kankara and Darazo samples are presented in Figures 4a and 4b respectively. The Kankara micrographs revealed flaky, layered sheets characteristic of layered silicates while the Darazo micrograph revealed crystal platelets with sharper outlines which is more characteristic of aragonite orthorhombic structure. Both samples showed high degree of agglomeration. The particle size from the micrographs could be estimated to be in the range of 50 µm to 200 µm for both samples. Generally, particulate fillers act in the condensed phase by migrating to the polymer surface at high temperature to provide additional viscosity which reduces the release of free radicals to the flame front and encourages the thickening and strengthening of the char bulk. The Kankara clay again because of the greater surface area provided by the flaky structure may provide greater barrier and labyrinth effect, than the Darazo platelets, leading to greater delay in material decomposition and smoke generation, and inhibition of heat and mass transfer (Chen *et al.*, 2019; Liu *et al.*, 2020).

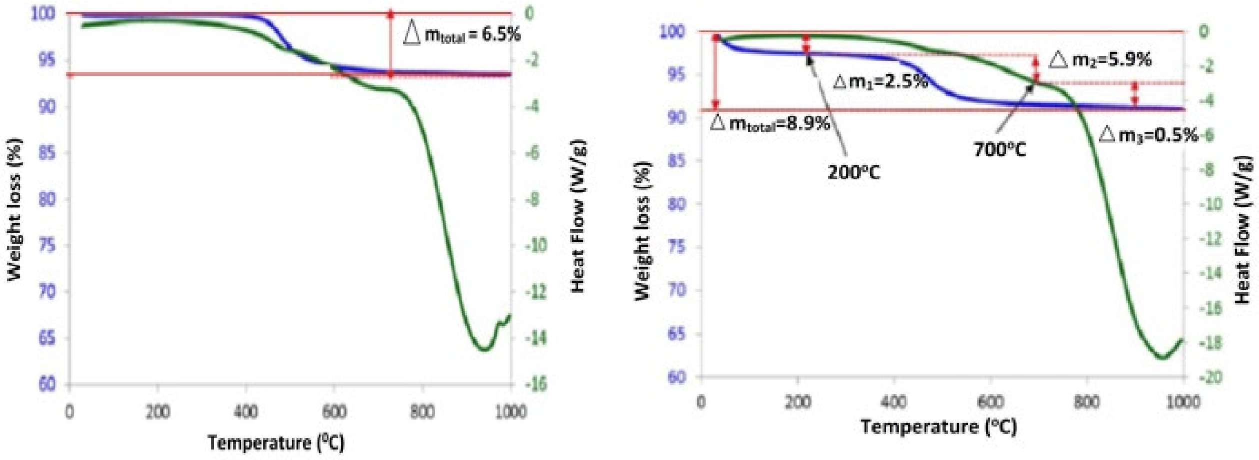


(a) (b)

Figure 4: (a) Kankara characterized by layered sheets (b) Darazo with more distinct crystalline particles.

3.4 Thermal analysis

The TGA graphs of both fillers are presented in Figure 5. The thermal analysis which was run from around 20 ^{o}C to 1000 ^{o}C showed a weight loss of about 6.5 % for Darazo occurring between 450^{o}C and 650^{o}C due to the decarbonation of the carbonate minerals with the release of carbon dioxide, a fire-retardant gas. Figure 5b showed Kankara clay had a total mass loss of 8.9 % at around the same range due to dehydroxylation initial loss of water of crystallization at 200^{o}C by the layered silicates. Kankara has the potential of a better hydrant due to about 2.5% water released around 200^{o}C. This may contribute to delaying ignition time of the treated wood material, while Darazo has the potential to interfere with burning at higher temperature given the release of carbon dioxide between 450^{o}C and 650^{o}C. Both fillers are shown to be endothermic in their reaction absorbing between 14 W/g to 18 W/g of heat at the elevated temperature of about 400^{o}C to 950^{o}C. This endothermic reaction will help draw heat away from the coated substrate creating a cooling effect that will reduce flame spread.



(a) (b)

Figure 5:(a) Thermal decomposition curve of Darazo showing a continuous step of decarbonation; (b) Thermal decomposition curve of Kankara showing two-step dehydroxylation process

Also, equally important is the residual mass of the samples. Both samples are able to maintain high residual masses at the elevated temperature of 1000°C, with Kankara having a residual mass of about 90% and Darazo, a residual mass of about 93%. This is very important, since these non-combustible residues reduce the total amount of volatile elements available to the flame front, thereby thermally stabilizing the wood bulk long after the flame retardants components have degraded.

3.6 Fire Performance of Test Samples

3.6.1 Heat shielding ability

The results of the fire tests for the four coated samples without any additives (B1), with 5.5wt% of each filler type (B2), with 11 wt% of Darazo (B3) and Kankara (B4) respectively are presented in Figure 6.

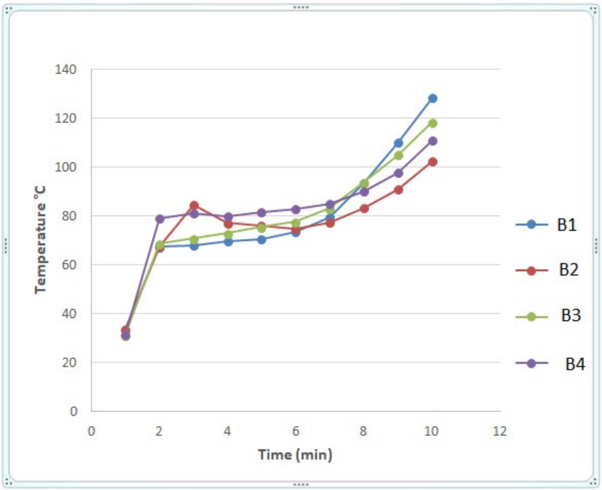


Figure 6: Comparing the heat curves for the wood samples without any additive, B1; 5.5 wt% of each filler type, B2; with 11 wt% Darazo, B3; and 11 wt% Kankara B4 when exposed to a Bunsen flame at 750°C ±50°C for 12 minutes.

At the start of the experiment, all sample temperatures rose rapidly from room temperature to about 68 °C in 2 minutes, except for B4 (containing crystalline kaolinite) which reached a higher temperature of 79 °C as surface water is released as steam. Thereafter, B4 was able to maintain a thermal plateau of 80 ± 2°C as the endothermic reaction continuously draws heat away from the wood surface. It may be observed that the rate of degradation of each sample correlates with the thermal stability of the filler as reported in the TGA analysis. Therefore, B3 which contained carbonate (Darazo) gradually rose to 80 °C in 7 minutes, while B2 which is a hybrid of B3 and B4 displayed delayed, but greater endothermic reaction due to the combined effect of the hydrates at lower temperature and the carbonate at higher temperature. The control sample, B1 maintained the initial temperature rise of 68°C for a longer time implying the immediate setting in of intumescing action. Beyond the 6th minutes, all samples showed varying increase in temperature. The filled coated samples showed slower temperature increase probably due to the diluting effect of the non-combustible residual masses. The hybrid sample, B2 showed the lowest temperature of 102 ^{o}C at the 10th minute followed by B4 with 110.9^{o}C and B3 with 118.5^{o}C. The control sample had the highest temperature increase of 128.4^{o}C after 10 minutes of flame contact. Thus, incorporation of either filler led to an improvement in the fire retardancy of the intumescing paint. 11 wt% addition of Kankara gave a greater reduction of 13.6% compared to 11 wt% addition of Darazo at 7.7% reduction. The combined effect of both fillers gave the highest cooling effect at 20.56% reduction compared to the unfilled paint.

3.6.2 Resistance to flame propagation

Flame spread may be described as the extent of travel of the flame point over the surface of the combustible solid. The area of the uncharred, coated wood samples could be taken as a measure of the coating resistance to flame spread. Measured with a scale ruler to the nearest millimeter, the length of the uncharred region in B2 representing the hybrid formulation was found to be 12mm while that of the control, B1 was found to be 5mm. B3 had an uncharred length of 8mm while B4 had an uncharred length of 10mm. This is seen to correlate with the heat shielding ability of the systems, where the highest temperature reduction is observed in the hybrid sample. These are shown in Figure 7. The presence of the minerals improves the fire-retardant ability as they increase the non-combustible component of the system.

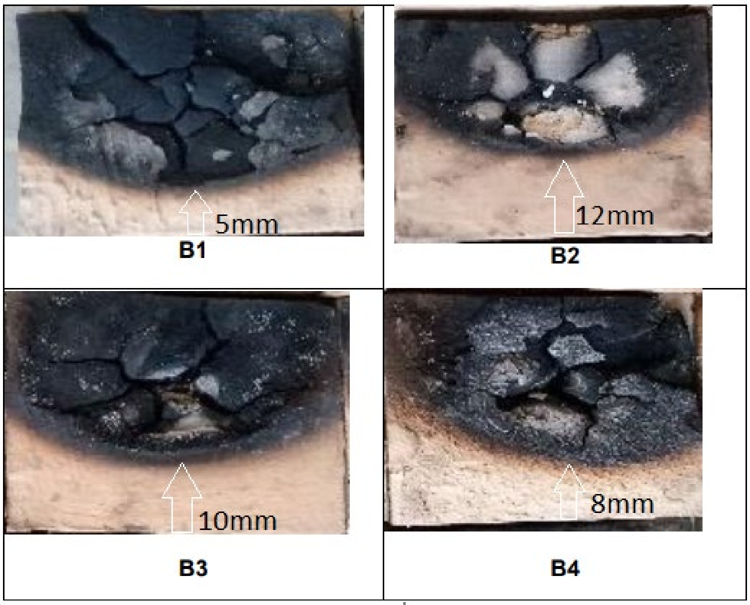


Figure 7: Test samples after fire test showing extent of flame propagation

3.6.3 Percent Mass Loss

The weights of the samples taken before and after the fire test were used to compute the percent mass loss during burning. B0 represents the uncoated wood, B1, the coated wood without filler, B2, the coated wood with hybrid filler; B3, Darazo clay-filled coating and B4, Kankara clay-filled coating. The uncoated wood had the highest mass loss of 31.55 %, confirming that the fire-retardant paints improved the fire-resistance of the wooden material. The filled samples both had a mass loss of approximately 21%, the hybrid formulation had a slightly higher mass loss of 23.36%, while the unfilled sample B1 had a mass loss of 23.67%. From this, it can be seen that incorporation of the fillers slowed down thermal degradation of the coated wood.

4.0 Conclusion

This work investigated the suitability of two of the numerous Nigerian sedimentary deposits as fillers in fire retardant paints.

1. It was found that Kankara clay consisted of crystalline kaolinite while Darazo rock is predominantly aragonite.
2. Kankara clay displayed a 2-step dehydroxylation process with the first endothermic reaction occurring at around 200 ^{o}C and the second one beginning at around 450^{o}C. Darazo experienced decarbonation between 400 ^{o}C to 650 ^{o}C. Thus, Darazo exhibited greater thermal stability while Kankara clay showed greater tendency to decompose and release more water of dehydroxylation thereby delaying ignition.
3. The material properties of each filler type affected the overall performance of the paint when incorporated as additive. The performance of the Kankara-filled paint appeared to depend majorly on thermal cooling as the endothermic reaction drew heat away from the wood surface creating a

thermal plateau on the wood surface. For the Darazo-filled paint, performance appeared to depend more on the thermal stability created by the decarbonation at higher temperature.

4. The addition of both fillers led to improvement in the heat shielding ability, flame propagation and thermal degradation of the coated wood, while the combined effect created even greater synergy allowing cooling over a longer range of temperature. The high percentage of non-combustible residual masses found in both clays also added to the thermal stability of the system.

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