CHARACTERISATION OF CALCINED KAOLINITE KUTIGI CLAY AS AN ADDITIVE FOR HYBRID POLYMER COMPOSITE APPLICATION

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Abstract: This paper is centered on the characterisation of calcined kaolinite kutigi clay, with the view of establishing its suitability as a reinforcing filler component for hybrid polymer composite production. The micro-structural properties that were analysed include the elemental composition, morphology and functional groups of the kaolinite kutigi clay sample. Clay sample was collected from kutigi deposit in Niger state. This was cleaned and beneficiated and reduced to a particle size of 75 µm. The beneficiated clay sample was calcined in a furnace at 500 ^oC for 2 h. The physicochemical property shows that it is a non-plastic kaolinite clay with low swelling- shrinking ratio. Result from the elemental composition analysis of the clay reveals that silicon (Si) and aluminium (Al) are present in appreciable amount. Further observation on this clay reveal that it has a pozolanic property, since the sum total of the weight concentration of Si, Al and Fe is ≥ to 70%. Upon calcination, there was decrease in the silicon content and increase in the aluminium content of the clay. This structural transformation caused by the calcination process changed the raw kaolinite clay sample into metakaolin. There were reduced OH group in the calcined clay due to dehydroxylation. The use of clay as a filler for hybrid polymer composite is to impact good strength through hardness, as well as to serve as a flame retardant.

Keyword: Kaolinite Kutigi clay, Calcination, Elemental composition, Morphology, Functional group.

Introduction

Most clay materials are crystalline, that is, they have a definite repeating arrangement of atoms of which they are composed. The majorities are made up of planes of oxygen atoms with silicon and aluminium atoms holding the oxygen together by ionic bonding (Nku, 2004). The three to four planes of oxygen atoms with intervening silicon and aluminiun ions depending on the clay, makes up a layer. Clay is composed of many layers stacked like a deck of cards. A clay particle is called micelle (Ugye and Malu 2017; Nku, 2004).

There are different types of clay which include: montmorilonite. Kaolinte, illite group and chlorolite group. Calcination of some clay is known to increase the whiteness, hardness, improves the electrical properties and alters the shape and size of clay particles. It usually carried out a temperature of at 400^{o}C - 700^{o}C (Aliyu *et al.*, 2014; Nku, 2004).

Kaolinte has one silica tetrahedral per sheet of alumina octahedral per layer. Thus, it is ratio 1:1 type clay (Shehu *et al.*, 2017). Almost no substitution of Al^{3+} for Si^{4+}, Mg^{2+} for Al^{3+} has occurred in kaolinite; so the net negative charge (cation exchange capacity) is low. However, each layer has one plane of oxygen (O_2) replaced by hydroxyl (OH), which results in strong hydrogen(-H-) bonds to oxygen. These planes of adjacent layer kaolinite limits, have such strong hydrogen bonding that do not allow water to penetrate between the layers and have almost no swelling. These are the types of clay used porcelain pottery works because they do not shrink or swell (Aliyu *et al.*, 2014; Raymond, 1990). The chemical formular of kaolinite minerla clay is given as, $Al_2Si_2O_5(OH)_4$. Interestingly, clay finds application in different fields of endeavour (Shehu *et al.*, 2017).

Mineral fillers or additives such as clay are used to improve strength and performance in composites. They are of different sizes, types and shapes. In composite formulation, the need to select suitable filler that will provide the needed chemical and physical performance property, at a low affordable cost, is of great importance. A sound understanding of the role and application of filler will go a long way in saving material cost and creating value addition with a difference (Tang *et al.*, 2016; Kotal and Bhowmick 2015). Nowadays, the application of fillers is tailored towards a particular purpose. For example, resins that are reinforced with fillers have better dimensional shrinking control than unreinforced resins. Some other impacting properties of mineral filler are surface smoothness, strength, temperature resistance, water resistance, hardness, conductivity and colour. Furthermore, filler improves the workability of resin during product manufacturing. Some common available fillers in use include titanium oxide, clay, calcium carbonate, alumina trihydrate (Liu *et al*., 2017; Tang *et al.*, 2016; Shehu *et al.*, 2017).

Materials and Method

Sample collection and preparation of clay

The clay sample used was collected from a clay deposit in Kutigi, Niger State. The clay material was crushed, cleaned and beneficiated to remove organic particles. The clay sample was later reduced into fine particle size of 75 µm, after which it was heated in an oven at a temperature of 80 ^{o}C for 24 h to achieve constant weight. This prepared clay sample was then calcined in a furnace at 500 ^{o}C for 2 h. The calcined clay was stored for further application as additive filler in hybrid polymer composite production (Olowokere *et al*., 2012). The pictorial view of the raw and calcined clay sample is presented in Plate 1.

Raw Kutigi Kaolin Clay | Calcined Kutigi Kaolin Clay at 500 ^{O}C

Plate 1: Pictorial view for raw and calcined kaolinite Kutigi clay sample

Micro Structural Analysis

The following techniques were used to determine and analyse the micro structural properties of the raw and calcined kaolinite clay.

Determination of the elemental composition and morphology of the kaolinite clay sample

SEM- EDX (Phenom ProX Generation 5) machine was used to show the morphology or surface chemistry of the raw and calcined kaolinite clay, and to determine the corresponding elemental composition of the clay sample.

Determination of the functional groups present in the kaolinite clay sample

The observations and changes in the functional group present in the raw and calcined kaolinite clay was determined and captured by Fourier Transform Infrared (FTIR) spectroscopy machine of model NICOLET 155 thermo scientific Nicolet corporation, madison USA. The FTIR spectra of the samples were analyzed in the range of 4000 cm^{-1} to 500 cm^{-1}.

Results and Discussion

The micro structural properties comprising the elemental composition, morphology and functional groups of the raw and calcined kaolinite Kutigi clay were analysed respectively, using SEM –EDX and FTIR. Table 1 present the elemental compositions of the Kutigi clay.

Table 1: Elemental Composition for Raw and Calcined Kutigi Kaolinite Clay

Elemental Composition	Si	Al	O	Fe	Cd	Ti	Na	C
Raw Weight Conc. (%)	60.37	27.44	-	3.41	2.23	0.81	0.62	-
Calcined Weight Conc. (%)	48.14	38.77	1.1	-	-	-	-	11.98

Elemental composition of Kutigi clay

The use of clay as a filler for this hybrid polymer composite is to impact good strength through hardness, as well as serve as a flame retardant. Preliminary investigation by Akhirevbulu *et al.* (2010) on the occurrence and physicochemical properties of Kutigi clay reveals that it is a kaolinite white and non-plastic residual (primary) clay, based on origin. Its non-plastic nature is a reflection of its low swelling-shrinking ratio. This is further confirmed by the elemental composition analysis on Table 1. The result reveals that silicon and Aluminium are present in appreciable amount while iron and cadmium are present in moderate quantity; but titanium and sodium are present in trace amount. This result is similar with few elemental and compositional variation with Olorungbon (2007). Further analysis on this clay reveal that it has a pozolanic property since the sum total of the weight concentration of Si, Al and Fe is ≥ to 70%. This is similar to the report by Adama and Jimoh (2011).

Result obtained from the calcined clay at 500^{o}C as shown on Table 1 presents a slight relative reduction in the silica content, while an increase is observed in the alumina content. This observation is in contrast to Hui *et al.* (2009). This contrast is due to the difference in the material composition as well as the thermal treatment process used. Some elements such as iron, sodium and cadmium which were present in trace amount in the raw kaolinite Kutigi clay, were not present in the kaolin clay sample after calcination. This is one of the effects of calcination due to volatilization of unstable components. Similar observation was reported by Kotal and Bhowmick (2015).

Morphology of the Raw and Calcined Kutigi Kaolinite Clay

The SEM image for raw Kutigi clay and calcined Kutigi clay are presented in Figure 1 and Figure 2 respectively.

Figure 1: SEM Image for Raw Kutigi Clay

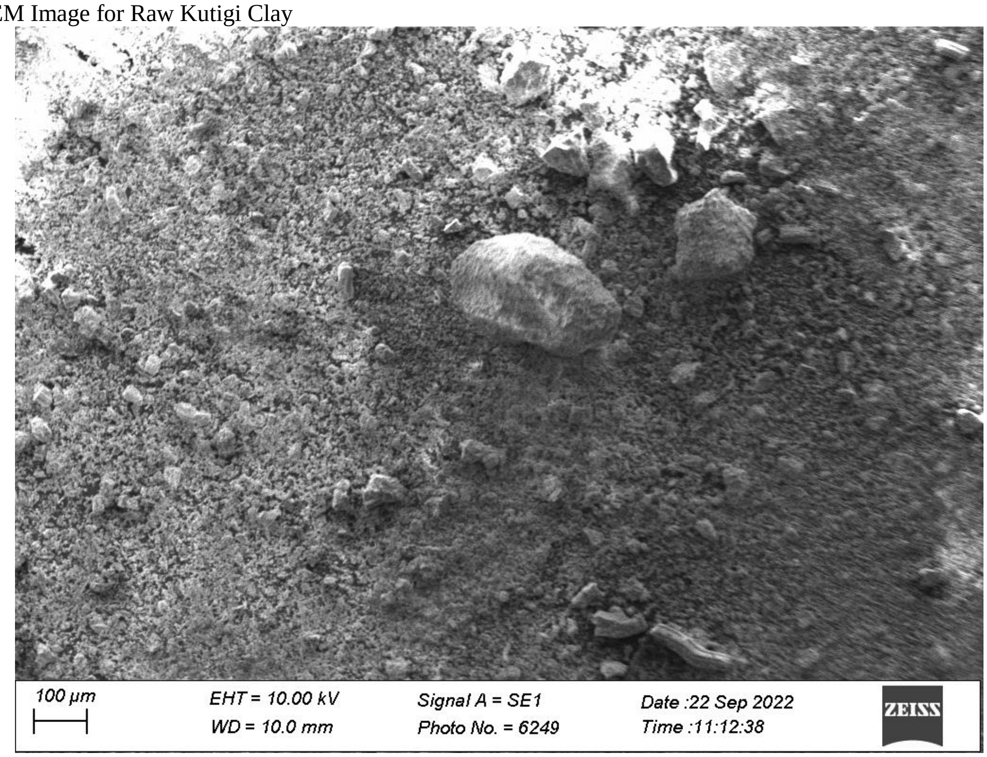

Figure 2: SEM Image for Calcined Kutigi Clay

The morphology of the raw kaolin clay in Figure 1 presents a white appearance and smooth plane surface with some few defects and impurities on the clay surface. Upon calcination as shown on Figure 2, the physical appearance of the kaolin clay changed to an off-white orange colour dehydroxylated powdery material. This structural transformation caused by the calcination process changed the raw kaolinite clay sample into metakaolin, having a specific gravity of 2.59 and bulk density of 0.36 g/cm^3. The attributes of this metakaolin clay caused by calcination is confirmed by the properties in Table 1 for calcined kaolinite Kutigi clay. Kotal and Bhowmick (2015) reported a similar observation.

Functional group of the kaolinite clay sample

Calcination at the right temperature initiates transformation in clay. The FTIR Spectra for raw and calcined Kutigi clay is presented in Figure 3 and Figure 4 respectively.

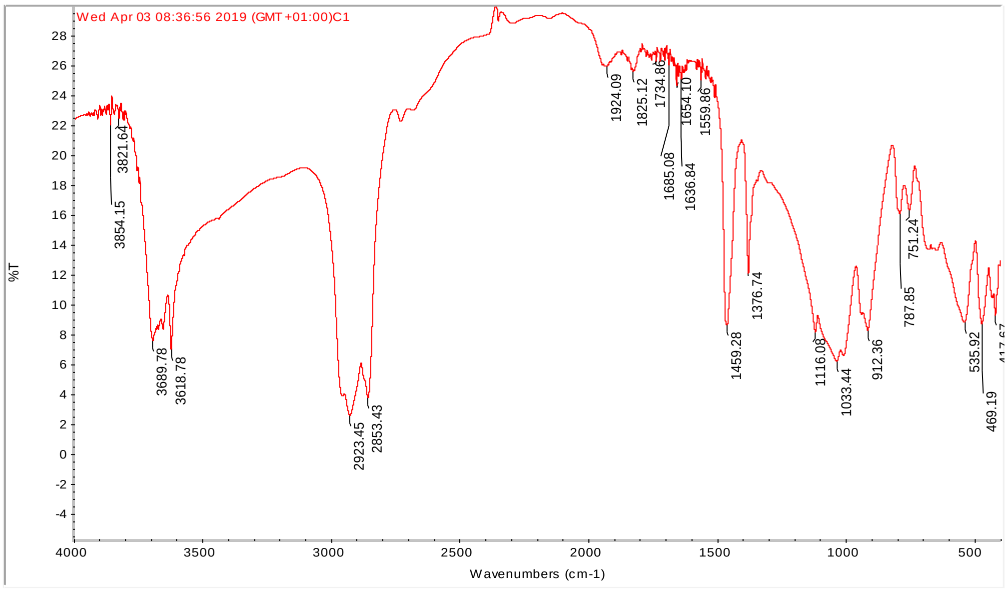

Figure 3.: FTIR Spectrum for Raw Kutigi Clay

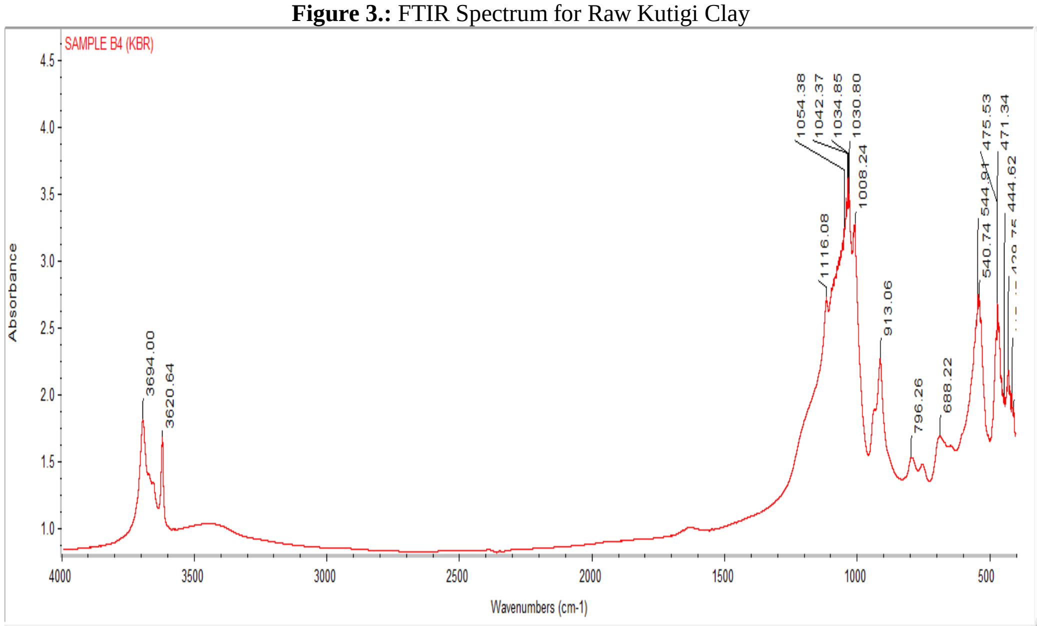

Figure 4: FTIR Spectrum for Calcined kaolinite Kutigi Clay

Figure 3 shows the presence of quartz mineral which is a property of kaolin clay, depicted by asymmetric and symmetric stretch vibrations of Si-O at 469.19 and 787.85cm^{-1} respectively. The peak at 535.92 cm^{-1} indicates the presence of Al-O-Si bend of feldspar and Si-O-Al deformation. The peaks at 751.24 cm^{-1} signifies Al-O-Si stretching in a kaolinite clay. The peak at 912.36 cm^{-1} represent Al-OH deformation band in kaolin. The band at 1033.44 – 1116.08 cm^{-1} represent Si-O stretch, normal to the planes. There exist C-H anti-asymmetric and symmetric stretch of organic materials present in the clay at 2853.43 and 2923 cm^{-1}. The peaks at 3618.78 to 3689.78 cm^{-1} represent the inner stretching surface of OH group. All these observations are further confirmed by the EDX analysis result and also by Bhaskar *et al*. (2016).

Furthermore, the FTIR spectrum in Figure 4 is presented and expressed in terms of absorbance which is an inverted presentation of transmittance. Observations from the spectrum show an absence of the C-H anti-asymmetric and symmetric stretch of organic materials which were initially present in the raw Kutigi clay. This absence may be as a result of the leaching of volatile organic materials initiated by the heat of calcination on the clay. The peaks at 3854.15 cm^{-1} and 3821.64 cm^{-1}in the raw clay are absent in the calcined clay. Peaks within 1900 – 1600cm^{-1} are absent. These are some of the effects of calcination process. These observation are similar to the report of Aroke and El-Nafaty (2014).

Conclusion

Kaolinite clay from Kutigi in Niger state was cleaned, beneficiated and calcined. The micro structural properties of the raw and calcined clay sample were analysed. The physicochemical properties of the Kutigi clay reveals that it is a kaolinite white and non-plastic residual (primary) clay, based on origin. This observation is a reflection of its low swelling-shrinking ratio. Result from the elemental composition analysis of the clay reveals that silicon and aluminium are present in appreciable amount. Further observation on this clay reveal that it has a pozolanic property Upon calcination, there was decrease in the silicon content and increase in the aluminium content of the clay. This structural transformation caused by the calcination process changed the raw kaolinite clay sample into metakaolin. Dehydroxylation leading to reduced OH functional groups occurred due to calcination. Additive fillers such as kaolinite clay impact good strength (hardness) and flame retarding property when used as reinforcement in hybrid polymer composite.

Conflict of interest

There is no conflict of interest between the authors.

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