



## Application of Ft-Ir and Scanning Electron Microscopy for Characterization of Modified Nanoclay Using Selected Amino Acids

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### ABSTRACT

This study was set to prepare nanoclay from locally obtained native clay commonly found in Dogon-Ruwa, opposite Maizube farm, along Minna-Bida road, Sabondaga, Bosso Local government area of Niger State-Nigeria and to investigate its chemical modification using four different amino acids; Arginine, Alanine, L-Arginine and Tyrosine. Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy were used to study the structural and morphological changes after modification. FT-IR spectral data indicated that modification was successful with all the four of amino acids used as it revealed the shift in band positions of C=O and N-H vibrations, indicating significant molecular interactions between amino acids and nanoclay occurred as new absorption bands were detected. Scanning Electron Microscopy study also indicated the presence of new morphologies on modified nanoclay which were not present in native nanoclay at its initial state.

**Keywords:** Preparation, Nano clay, amino acids, modification

### INTRODUCTION

A better knowledge of chemical composition of clay as well as its surface properties when modified is of paramount importance for industrial applications according to (Adams & McCabe, 2006). The definition of clay has been revised many times, though, the fundamentals involving plasticity, particle size, and hardening on firing were retained by most researchers (Guggenheim & Martin, 1995). Thus, clay is a naturally occurring material formed by breaking and chemical decomposition of igneous rocks with fine texture of particle size less than 0.002 mm (2 micron) (Adams & McCabe, 2006). The presence of only one tetrahedral sheet with the unshared vertex of each other forming each side of the octahedral sheet is known as layered silicates (Bhattacharya & Mandot, 2014). Layered structures are categorized as type 1:1 or 2:1 and each layer forming clay mineral particles silicates (Si-O) sheets and one octahedral metal oxide/hydroxide (M-O- or M-OH) sheet. The 2:1 layer silicates include; mica, smectite, vermiculite and montmorillonite (MMT), nontronite, saponite and hectorite species. Among these layered silicates, montmorillonite is the most widely used as re-enforcement agent because it is

environmentally friendly, readily available in large quantities at relatively low cost and its intercalation chemistry is good and well understood (Bhattacharya & Mandot, 2014).

The variation in both the chemistry and structure among clays leads to their applications in extremely diverse fields (Nwosu, Ejikene & Ebere, 2013). Clay in its natural form can only be dispersed in hydrophilic media. Example is polymer like poly (vinyl alcohol) (Manocha, Nikesh & Manocha, 2008). Cation exchange capacity (CEC) is the characteristic property of soil promoted by clay and organic matter. It is the capacity of clay to hold cations like  $Al^{3+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Na^+$ ,  $K^+$ , and  $H^+$ . It is understood as the quantity of positively charge ions held are balanced by negatively charged surface clay minerals. This phenomenon is known as isomorphous substitution which is the capacity of clay sheets to hold positive charges (Bhattacharya & Mandot, 2014). Isomorphous

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substitution within the layers by metal cations generates negative charges that are counter balanced by exchange cations such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Manocha *et al.*, 2008). However, nanoclay is nanoparticles of layered mineral such as, montmorillonite, bentonites and halloysite (Ke, Lu, Yi & Zhao, 2000). Nanoclay is derived from a mineral deposit that has a layered structure of dimension around 1nm thickness and specific surface area of 700–800  $\text{m}^2/\text{g}$ . Nanoclay is currently being used to improve modulus and tensile strength, barrier properties, flame resistance and thermal properties of many plastics (Ding, Xi & Frost, 2004). Nanoclay minerals have promising properties such as, high cation exchange capacity, swelling power and high surface areas that make clays such as smectite favorable

materials to be used for industrial applications such as rheology control agents, sorbents in pollution prevention/control, preparation of nanocomposites, fillers, food packaging and environmental remediation. Nanoclay potentials have been tremendously improved and expanded by ion exchange of organo-cation to impart hydrophobic properties. Studies have been reported that replacing the inorganic cations of nanoclay can result in a greatly enhanced capacity of these materials for industrial applications (Bhattacharya & Mandot, 2014). Sodium ions in natural clay are exchanged with amino acids such as 12-aminododecanoic acid as will be seen in this work. Equation for the reaction is indicated below:



Eq. 1: General representation of the reaction of nanoclay with amines in acidic medium

## Materials and Methods

### Reagents and Solvents

The clay used in this work was obtained from Dogon-Ruwa, opposite Maizube farm, along Minna-Bida road, Sabondaga, Bosso Local government area of Niger State, Nigeria. All reagents used were of analytical grade and were supplied by Sigma Aldrich. These reagents include: Sodium Hydroxide, Alanine, Arginine, L-Arginine, Leucine, Tyrosine, Hydrogen Peroxide, Silver Nitrate and Hydrochloric acid.

### General Experimental Procedure for the Preparation of Samples

#### Collection of Samples

Native clay 500 g was weighed and oven-dried for an average period of 24 h at 105 °C (Bhattacharya & Mandot, 2014). This was done to remove moisture content. Thereafter, moisture content was determined by using the following formula:

$$\text{Percentage of moisture content} = \frac{\text{initial weight} - \text{final weight}}{\text{final weight}} \times 100 \%$$

The sample was removed from the oven and was ground using mortar and pestle until a fine

powder was obtained. The fine clay powder obtained was sieved using an 80  $\mu\text{m}$  sieve (Manocha, Nikesh & Manocha, 2008). The procedure was repeated to obtain all clay samples used.

### Preparation of Nanoclay

400 g of 80  $\mu\text{m}$  sized clay particle was weighed and dispersed in distilled water in a 1000  $\text{cm}^3$  beaker and made up to the mark. It was stirred vigorously to ensure homogeneity of the suspension and allowed to stand to undergo hydration. After which 25  $\text{cm}^3$  of hydrogen peroxide was added to the suspension with continuous stirring in order to destroy any organic matter that may be present in the suspension. The mixture was stirred continuously for a period of 3 h and it was allowed to settle for 48 h where a precipitate of the suspension was formed at the bottom of the beaker (Bhattacharya & Mandot, 2014). However, the supernatant was decanted into another container and kept still for another 48 h to precipitate. Finally, the liquid that was free from the precipitate was decanted and thus, the decanted liquid-solid slurry obtained was termed nanoclay (Bhattacharya & Mandot, 2014). However, in a similar procedure the precipitate formed i.e. the sediment formed after series of decantation is also nanoclay (Manocha *et al.*, 2008).

### **Modification of Nanoclay using Amino acids**

0.01 M of Arginine was prepared in 250 cm<sup>3</sup> beaker. Thereafter, a pH of 2 using 0.1 M HCl and 0.1 M NaOH were used to monitor the pH. 100 cm<sup>3</sup> of the nanoclay suspension was poured into the same beaker and it was stirred continuously with a magnetic stirrer equipped with a Teflon coated stirring bar after which a stoichiometric quantity of Arginine solution (100 cm<sup>3</sup>) in 1:1 ratio was added drop wise while maintaining the pH at 2. The mixture was stirred for 3 h at room temperature. The mixture was filtered with a Whatman filter paper and the residue was washed with distilled water until it was free from chloride ions. This was done by carrying out repeated silver nitrate test on the filtrate until no white precipitate due to AgCl was formed (Socrates, 2001). The mixture was air dried, ground subsequently and sieved with 80 µm micro sieve and a fine powder of modified nanoclay was obtained. This procedure was repeated for Tyrosine, Alanine, and L-Arginine (Manocha *et al.*, 2008; Socrates, 2001).

### **Fourier Transform Infrared Spectroscopy (FTIR)**

The FT-IR spectra of nanoclay and modified nanoclay using amino acid were recorded at National Research Institute (NARICT) Zaria, Nigeria. The samples were run as (KBr) pellets using FT-IR-8400S Fourier Transform Infrared Spectrophotometer in the spectra range of 4000-400 cm<sup>-1</sup>.

### **Scanning Electron Microscopy (SEM)**

The analysis was carried out in NARICT, Zaria, Nigeria. The morphology of nanoclay and modified nanoclay were examined. The powdered sample was dispersed in water and then the sediment was dried at room temperature before Gold coating. Scanning Electron Microscopy images of nanoclay and modified nanoclay were taken to show a clear picture of their morphological properties.

**RESULTS AND DISCUSSION****Transmission FTIR Spectroscopy Studies**

Table 1.1: FT-IR band Assignment for Nanoclay and Modified Nanoclay

<b>Sample</b>	<b>Band Position (cm<sup>-1</sup>) (Absorption)</b>	<b>Band Assignment (functional group)</b>	<b>References</b>
Native Clay	3602	OH bond stretching of structural –OH	(Omar & Laurent, 2008).
	1638	H-O-H deformation	(Socrates, 2001).
	1025	Si-O stretching	(Omar & Laurent, 2008; Katti, Katti & Dash, 2008) (Omar & Laurent, 2008).
	922.97	Al-OH deformation	(Omar & Laurent 2008; Katti, Turlapati, Verma, Gujjula and Katti, 2006). (Katti et al., 2008).
Peaks associated with clay due to modification	3867-3615	O-H bond stretching of structural OH groups	(Katti et al., 2008; Richards, Cram & Hammond, 1967). (Omar & Laurent, 2008; Katti et al., 2008; Richards et al., 1967).
	1141-1025	Si-O stretching.	
	926-921	Al-OH deformation.	
	784-730	Si-O stretching of quartz and silica	
	448-441	Si-O-Si deformation.	
New peaks found in modified samples		C=O stretching of intermolecular hydrogen bonding in carboxylic acids and H-O-H bending vibration of inter layer in modified Nanoclay. -N-H vibrations in modified nanoclay.	(Omar & Laurent, 2008; Richards et al., 1967).
MDBMCArgeSED	1704-1643		(Socrates 2001; Amarasinghe, Katti and Katti, 2009).

Table 1.1: FT-IR band Assignment for Nanoclay and Modified Nanoclay continued

<b>Sample</b>	<b>Band Position (cm<sup>-1</sup>) (Absorption)</b>	<b>Band Assignment (functional group)</b>	<b>References</b>
MDBTyrSUS			(Omar & Laurent, 2008; Katti et al., 2008).
MDBCTYSEDIMENT	1543-1530	-N-H symmetric stretching vibrations.	(Socrates, 2001; Katti et al., 2008; Katti et al., 2006).
MDBC <sub>CaLa</sub> <sup>+</sup>	3444-3417		(Omar & Laurent, 2008; Katti et al., 2008).
MDBMCLSUS	2410-2278	-N-H <sup>+</sup> stretching.	(Katti et al., (2008).
MDBCOMPO	1454	NH <sub>3</sub> <sup>+</sup> vibrations.	(Socrates, 2001).
	1420	RCOO <sup>-</sup> Symmetric stretching and CH <sub>2</sub> deformation vibration.	
	1364	-OH deformation of the carboxylic groups.	

The following strong absorption bands as reflected separately on the FT-IR spectra of nanoclay (untreated) and modified nanoclay (treated with amino acids) from **plate I-VII**, have been used to infer whether modification was achieved or not. The characteristics absorption of  $\text{—OH}$  bond stretching vibrations were observed at  $3602\text{ cm}^{-1}$  for MDBControl,  $3846\text{ cm}^{-1}$ , for MBMCArGSED,  $3619\text{ cm}^{-1}$  for MDBCTyrus,  $3615\text{ cm}^{-1}$  for MDBCTyrSED,  $3623\text{ cm}^{-1}$  for MDBCaLa<sup>+</sup>,  $3623\text{ cm}^{-1}$  –  $3867.40\text{ cm}^{-1}$  for MDBMCLSUS and  $3417$  –  $3846.51\text{ cm}^{-1}$  for MDBCompo (Socrates, 2001). A shift in the  $\text{—OH}$  band in modified samples was observed.

This has been attributed to strong electrostatic interactions between negatively charged Nanoclay surface and the charged Nitrogen atom of amino acids used. The band absorption at  $1600$  –  $1750\text{ cm}^{-1}$  and  $3100$  –  $1750\text{ cm}^{-1}$  are assigned to  $\text{H—O—H}$  bending vibrations and  $\text{O—H}$  stretching region of water. In addition, the band at  $1025\text{ cm}^{-1}$  has been assigned to  $\text{Si—O}$  bond stretching (Omar & Laurent, 2008; Katti *et al.*, 2008). The spectral absorption peaks also showed evidence of the successful modification of Nanoclay by amino acids due to broadening of the amino acid absorption bands which has been attributed to intercalation in between layered silicates (Amarasinghe *et al.*, 2009). A weak absorption at  $900\text{ cm}^{-1}$  –  $930\text{ cm}^{-1}$  was observed and it confirms  $\text{Al—OH}$  deformations while the absorption band at  $1530\text{ cm}^{-1}$  is characteristic band for  $\text{N—H}$ . This band was missing in control sample but appeared in all modified samples confirming the success of modification as reported by other researchers (Socrates, 2001; Katti *et al.*, 2006). Samples modified with amino acids showed a shift in band positions corresponding to the structural  $\text{—OH}$  group with pure nanoclay (Socrates, 2001).

In the case of nanoclay modified samples, bands seen at  $1643\text{ cm}^{-1}$ ,  $1645\text{ cm}^{-1}$ ,  $1646\text{ cm}^{-1}$  indicates the presence of amino acids in modified nanoclay. These bands are due to non-bonded/ free carbonyl ( $\text{—C=O}$ ) stretching bands of carboxylic group in amino acids. There is a difference in the shift in  $\text{—C=O}$  stretching band to a lower frequency by  $2.9\text{ cm}^{-1}$  in the case of nanoclay modified with arginine and this suggests hydrogen bonding interactions

between Arginine and nanoclay (Socrates, 2001). The spectra of all modified samples gave new absorption bands at  $1543$  –  $1530\text{ cm}^{-1}$ , owing to  $\text{—N—H}$  stretching vibrations. This absorption band confirms the successful insertion of  $\text{—}^+\text{NH}_3$  ion into the clay gallery. The bands near  $1535\text{ cm}^{-1}$  region in the case of nanoclay modified with Arginine and L-arginine may be due to the  $\text{—N—H}$  deformation vibrations owing to the presence of amino acids in nanoclay (Socrates, 2001; Katti *et al.*, 2008; Katti *et al.*, 2006). The absence of  $\text{N—H}$  deformation near  $1535\text{ cm}^{-1}$  region in the case of Alanine and Tyrosine may be attributed to the presence of two carboxylic acids groups which may mask the effect of the presence of the amine group. A shift in  $\text{Si—O}$  stretching vibrations for all modified samples was observed. These shifts may be attributed to interaction between the protonated amine group and surface oxygen of silica tetrahedral structure and also that the crystal structure of nanoclay has changed due to interaction of amino acids in the nanoclay (Socrates, 2001).

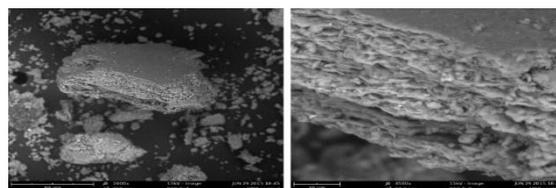


Plate I: Scanning electron micrograph of Nanoclay untreated (control sample)

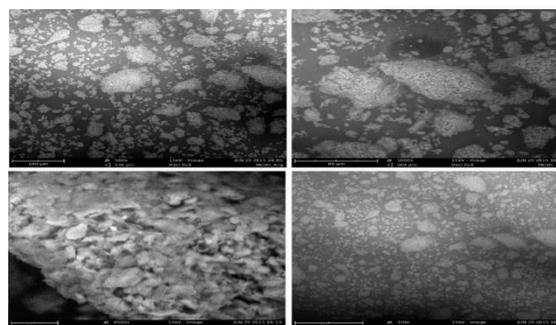


Plate II: SEM micrograph of Nanoclay particles modified with Arginine

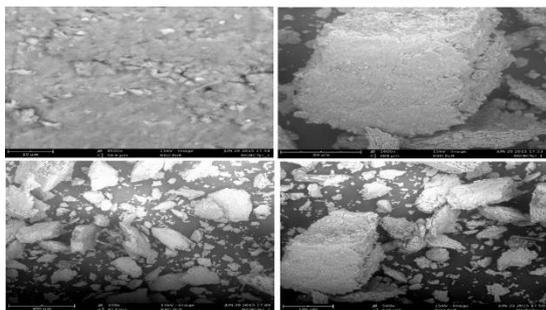


Plate III: SEM micrograph of nanoclay suspension particles modified with Tyrosine

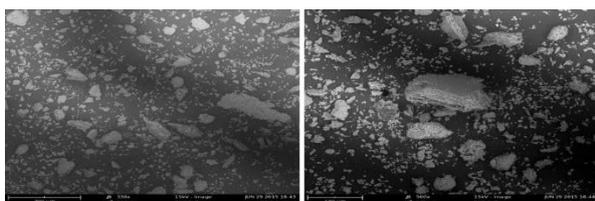


Plate IV: SEM micrograph of nanoclay sediment particles modified with Tyrosine

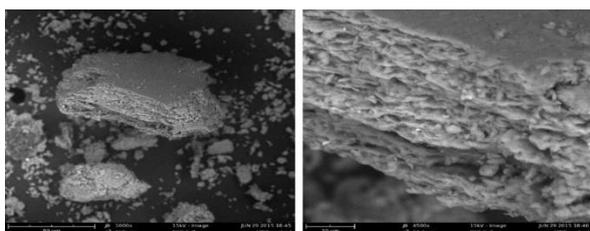


Plate V. SEM micrograph of nanoclay particles modified with L-arginine

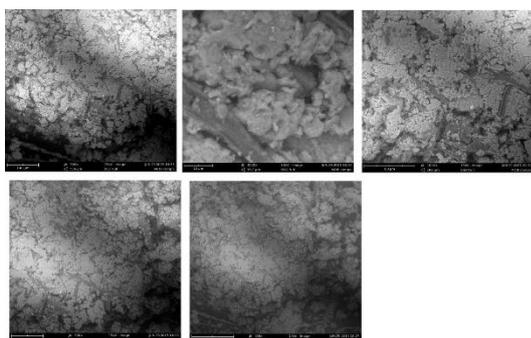


Plate VI: SEM micrograph of nanocomposites particles of modified nanoclay with nanocellulose

### Morphological Properties of Samples

Scanning electron microscopy (SEM) micrographs of Nanoclay modified and unmodified Nanoclay are indicated in Plate I-V as well as Nanocomposites of Nanoclay in Plate VI. The surface morphology of nanoclay in Plate I above before modification indicated that untreated Nanoclay particles formed various sizes and shapes which resulted to the formation of different agglomerated particles. This was attributed to the nanosize of these particles implicated for their high tendency to agglomerate and interact due to their large surface.

The implications is that these modified particles could be used as adsorbent for the removal of heavy metals in water and wastewater effluents because of their large surface area and the presence of  $-\text{NH}_2$ ,  $-\text{CO}$  and  $-\text{OH}$  that makes the products potential metal chelators. In addition they can be used as template for growing hydroxyapatite for application in bone tissue engineering. The surface morphology of these clay samples as revealed by SEM is supported by reports on Aluminosilicates type clay consisting of silica ( $\text{SiO}_4$ ) tetrahedral bonded to alumina ( $\text{AlO}_6$ ) octahedral in a variety of ways with a sheet-like layered structure (Bhattacharya & Mandot, 2014). The local clay used in this work showed some of the basic properties of Aluminosilicates as evidenced by FT-IR and SEM analysis. Furthermore, **Plate I-V** represents surface morphology of modified Nanoclay samples with Zwitteronic amino acids. Thus, from SEM images uniformly dispersed small particles are observed compared to neat nanoclay particles.

Only slight difference in morphology was observed between modified nanoclay despite the differences in the amino acids used (Arginine, Alanine, L-Arginine and Tyrosine) in this work. This is due to the presence of amine group (which is cationic) in all the amino acids that undergoes cation exchange reaction with  $\text{Na}^+$ - nanoclay. Furthermore, modified nanoclay in Plate I indicates massive aggregates and bulk flames. Sodium Hydration in nanoclay has been implicated for the massive aggregates in nanoclay morphology. On the other hand, modified nanoclay as indicated in Plate II-V formed agglomerations of various sizes than

those of unmodified nanoclay. This may likely be due to hydrogen bonding between free amino groups on the surface and the -COOH acid functionalities on the surface of different particles (Katti et al., 2006). SEM images of modified nanoclay indicated that modified nanoclay was characterized by large amount of curled flakes particles. The SEM Micrograph in Plate VI indicates nanocomposites of modified nanoclay and acetylated nanocellulose. Thus, from the SEM images, nanocellulose rods were found embedded in the deep, surrounded by less ordered nanoclay matrix. The agglomerations of the clay particles were not lost, but they look rough and have been attributed to solvent used for composite formation. The surface was rough and the presence of fissures was observed. Nanocellulose rods intercalated into modified clay galleries inferred confinement of the nanocellulose rod-like particles in modified nanoclay particles which is an indication of the success of nanocomposites preparation (Omar & Laurent, 2008).

### Conclusion

In Conclusion, nanoclay was prepared from locally obtained native clay that is cheap and readily available in many locations in Bosso LGA, Niger State, Nigeria. The prepared nanoclay was then modified using four different amino acids and these include; Arginine, Alanine, L-Arginine and Tyrosine. FT-IR proved useful for structural identification of functional groups. Evidence of the success of modification was revealed by the presence of  $1643\text{ cm}^{-1}$ ,  $1645\text{ cm}^{-1}$ ,  $1704\text{ cm}^{-1}$  and  $1530\text{ cm}^{-1}$ ,  $1535\text{ cm}^{-1}$  and  $1543\text{ cm}^{-1}$  for  $\text{C}=\text{O}$  and  $\text{H}-\text{N}$  vibrations respectively. SEM morphological properties indicated the molecular interactions in both nanoclay (untreated) and modified nanoclay. Thus, the SEM image of both untreated nanoclay and modified clearly indicated that the samples formed various sizes of particles with different agglomerates due to their nanosize and large surface area. A change in morphology of modified nanoclay was observed.

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