

# Development and Characterization of Odogi Clay/Epoxy Nanocomposites for Electronics Packaging.

**\*Ayorinde T.O., Owa A. F. and Umunakwe, R.**

Department of Materials and Metallurgical Engineering, Faculty of Engineering,  
Federal University Oye-Ekiti, Nigeria.  
\*ayusvicas@gmail.com

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## ABSTRACT

The suitability of Odogi clay as filler in epoxy/clay nanocomposite for application in electronics packaging was studied. The calcined Odogi clay was treated with ethanol, which caused the swelling of the clay particles to improve clay dispersion. Epoxy/clay nanocomposite samples were produced using liquid-liquid techniques at 1, 2, and 3 wt% filler loadings. The clay dispersion in the nanocomposite material and the phases present were determined with a scanning electron microscope (SEM) and an x-ray diffractometer (XRD). The coefficients of thermal expansion (CTE), dielectric constants, flexural strengths, and flexural moduli of the nanocomposites were also determined. The results of XRD and x-ray fluorescence (XRF) show that the calcined Odogi clay is aluminosilicate, having a higher percentage of  $Al_2O_3$  and  $SiO_2$ . The results further confirmed that the use of ethanol to modify the clay facilitated clay dispersion in the epoxy, thereby producing an intercalated structure of the produced nanocomposite. The coefficient of thermal expansion and dielectric constant for the developed nanocomposite showed that Odogi clay disperses well in epoxy. The results show that Odogi clay can be used in place of montmorillonite (MMT) as reinforcement in epoxy for electronic packaging applications.

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## 1.0 Introduction

Pure polymeric materials are considered to be one of the best insulating materials in the field of electronic packaging. However, pure polymer shows moderate mechanical, thermal, and dielectric properties, which can limit its application as a packaging material for electronics. Pure polymer matrixes are rarely frequently employed, due to their inability to meet the required mechanical, thermal, and dielectric properties. Hence, it becomes necessary to reinforce the pure polymer with fillers or reinforcements, such as clay, graphene, silica, fibers, and other materials to make nanocomposites, which can meet the required properties for desired applications [1]. Polymer composites (polymers mixed with inorganic/metallic fillers) became famous for packaging applications as a result of advancements in technology [2]. However, difficulties abound in the dispersion of clay in epoxy. Due to the hydrophobic nature of clay particles, they tend to agglomerate in the composite, which leads to phase separation in the microstructure. As a result of this agglomeration of clay particles, the dispersion of clay in epoxy remains a challenge. Moreover, surface modification of clay, which will give intercalated or exfoliated structures, has been reported in the literature [3]. Ethanol and deionized water can be used to modify montmorillonite according to [4]. In this research, ethanol was used for surface modification of Odogi clay, which enhances the dispersion of clay

in epoxy leading to intercalated structure and consequently, improves the thermal, electrical, and mechanical properties of the nanocomposites. Developments of Odogi/clay nanocomposites were not reported and this paper addresses the research gap.

## 2.0 Materials and Methods

The clay was obtained from Odogi in Kabba Bunu L.G.A of Kogi State. A Bisphenol-A, epoxy resin parts A and B, and Ethanol (purity 98.8%) were purchased from 'GZ-Industrial Supplies' Nigeria. All chemicals were analytical reagent grades and were used as supplied.

### 2.1 Preparation of Odogi clay

The clay, which was mined from a depth of 1 m below the overburden of about 2 m thickness, was crushed, washed, sieved, and open-dried for 2 days. The sample was then calcined at 750°C for 3 hours and sieved with a 0.3 nanometers sieve. The clay was thereafter, treated with ethanol to cause the particles to swell. The mixture was stirred with a sonicator to break the particles and further prevent their agglomeration at room temperature [4].

### 2.2 Production of clay epoxy nanocomposite

The prepared clay solution was added to epoxy resin and diluent and the slurry was mixed using a sonicator for 40 minutes. The

slurry was washed three times to remove debris and centrifuged. Thereafter the slurry was stirred at 650 rpm for 1 hour at 45°C using a magnetic stirrer. In all cases, clay solution was dispersed in the epoxy at levels of 0, 1, 2, and 3 wt % filler loadings. Thereafter, the hardener was added and stirred for 5 minutes before degassing for 20 minutes at 50°C. Finally, the mixture was cast into molds and cured for 24 hours at room temperature. It was post-cured for 1 hour at 65°C [5]. This method is termed the Liquid-Liquid method.

### 2.3 Characterization

X-ray diffraction analysis was performed on RigakuD/Max-IIIIC with CuK $\alpha$  radiation for structural examination of the clay sample and composites. SEM was used to examine the surface morphology of the nanocomposites. A Joel JSM-840 scanning electron microscope (SEM) was used. Images were taken at 15 kV. The surface was coated with silver to prevent electrostatic charges. Flexural tests were conducted on a universal testing machine, according to the American Society for Testing and Materials (ASTM D7264). The coefficient of thermal expansion measurements was carried out using a dilatometer heated from -5 to 300°C, at a heating rate of 10 °C/min. The measurements were performed on 3 different samples and the average value was recorded. The dielectric constant ( $\epsilon$ ) of the clay/epoxy nanocomposites was evaluated using the equation,  $\epsilon = \frac{C}{C'}$  where  $\epsilon$  is the dielectric constant,  $C$  is the permittivity of the nanocomposite and  $C'$  is the permittivity of free space. An X-ray fluorescent (XRF) spectrometer was used to determine the elemental composition of the clay.

### 3.0 Results and Discussion

#### 3.1 X-ray diffraction Analysis

The XRD pattern for the Odogi clay sample is shown in Figure 1. The X-ray diffractogram shows the dominance of Al and Si. The X-ray fluorescence XRF was further used to determine the elemental composition of Odogi clay as shown in Table 1, which further confirmed that the clay is aluminosilicate according to [6].

Table 1. XRF for Odogi clay sample

Element	Percentage
SiO <sub>2</sub>	55.45
Al <sub>2</sub> O <sub>3</sub>	18.67
Fe <sub>2</sub> O <sub>3</sub>	9.65
TiO <sub>2</sub>	0.72
CaO	0.75
P <sub>2</sub> O <sub>5</sub>	0.32
K <sub>2</sub> O	1.80
MnO	0.04
MgO	1.29
Na <sub>2</sub> O	0.46
LOI	10.85

There is a change in the d<sub>111</sub> spacing of the neat epoxy in Figure 2 as the angle increases as shown in Figure 3. This means that the epoxy is dispersed in between the clay layers. This is an indication of the intercalated structure of the Nanocomposites. The intercalation of the epoxy chain decreases the basal spacing from 1.472 to 0.736, causing a shift in the diffraction peak [7]. Epoxy is intercalated between the clay layers as shown in Figure 3, resulting in a composite of epoxy chains between alternating clay layers.

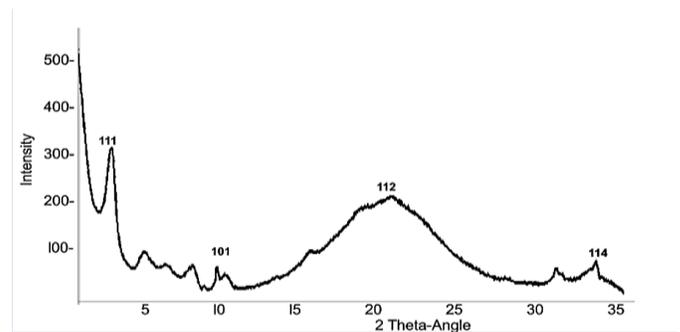


Figure 2. XRD for NEAT epoxy

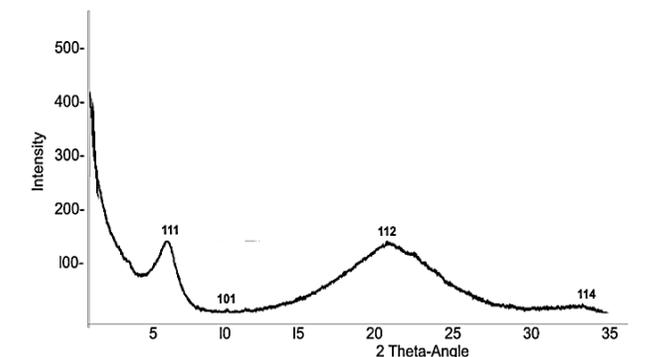


Figure 3. XRD for 1wt. % nanocomposite sample

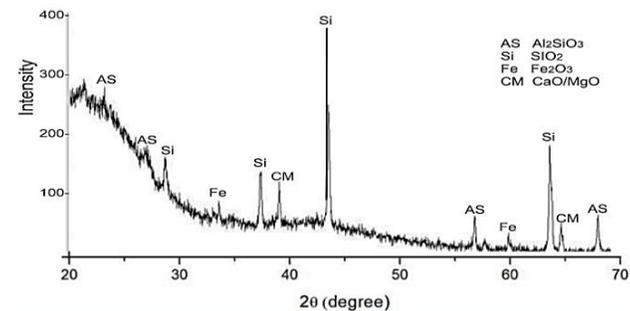


Figure 1. XRD for Odogi clay

### 3.2 Flexural properties

The nanocomposite's mechanical behavior at ambient temperature was studied through flexural properties in flexural mode since flexural properties combine the effect of tensile deformation and compression deformation. The flexural strength and modulus results in Table 2 show that flexural properties increased as the clay content increased. These can be attributed to the fact that the filler (Odogi clay particles) is stiffer than epoxy [8]. Furthermore, for high volume ratio fillers, the surface area that is exposed to the epoxy is large; consequently, the pronounced increase in modulus, with low filler contents is understandable [9]. When compared with the flexural properties of untreated clay in Table 3, the composite produced with untreated clay showed little or no increase in the flexural properties, thereby, confirming the swelling of Odogi clay when treated with ethanol (Table 2) to produce an intercalated structure. In Fig 4 it is observed that a crack mechanism occurred. It was also observed that the crack front was between the particles of the clay; hence a greater force is required under loading for crack propagation [10], thereby increasing the flexural strength.

Table 2. Flexural properties of neat epoxy and treated Odogi clay in epoxy

Wt. %	Flexural strength (MPa)	Flexural modulus (MPa)
neat	16.2 ± 2.5	296 ± 42
1	19.7 ± 3.1	365 ± 48
2	24.0 ± 2.3	400 ± 40
3	27.0 ± 3.0	442 ± 40

Table 3. Flexural properties of untreated Odogi clay in epoxy

Wt. %	Flexural strength (MPa)	Flexural modulus (MPa)
1	16.6 ± 3.1	296.5 ± 48
2	17.0 ± 2.3	296.8 ± 40
3	17.1 ± 3.0	297 ± 40

### 3.3 Coefficient of thermal expansion

The thermo-mechanical stability of electronic packaging material can be evaluated through its thermal expansion behavior. Table 4 shows the results of the CTE of neat epoxy and filled epoxy. The Table showed lower CTE for filled epoxy when compared to the neat epoxy. This is because the filler has low CTE as supported by [11]. CTE is dependent on chain stiffness [12], which means a high polymerization network will result in high material stiffness

and consequently lower the nanocomposite's thermal expansion coefficient.

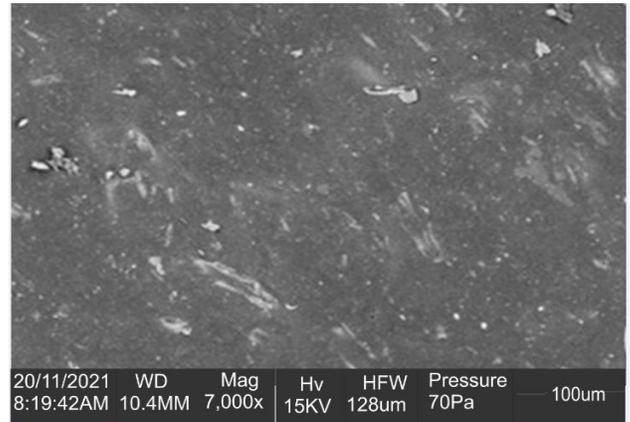


Figure 4. SEM images for 1wt% nanocomposite sample

Table 4. Coefficient of thermal expansion for filled and neat epoxy

Wt. %	CTE (ppm/°C)
neat	106.1
1	83
2	58
3	42

### 3.4 Dielectric properties

The dielectric constants for the unfilled epoxy and the nanocomposite are shown in Table 5. Although the dielectric of nanocomposites usually decreases when compared with neat epoxy [13]. This is because of the restriction of movement of polymer chain by nanoparticles, which consequently inhibits the electrical polarization [14]. This can be seen in the 1 and 3 wt % loadings. However, inorganic reinforcement has higher dielectric values than the polymer as stated by [15], and the higher values reported at 2 wt % loading are due to air bubbles, or agglomeration of the clay particles in epoxy resin [16].

Table 5. Dielectric constant for neat and filled epoxy

Wt. %	Dielectric constant
neat	2.9
1	2.5
2	3.16
3	2.7

### Conclusion

Odogi clay is confirmed to be aluminosilicate from the XRF and XRD analysis and is suitable for the reinforcement of epoxy

resin. The nanocomposites produced from Odogi clay and epoxy using the liquid-liquid method of preparation, which offers a better way of dispersing the clay particles in epoxy, show the intercalated structure, and are also confirmed to have desirable thermal, electrical, and mechanical properties that are required in electronic packaging materials. From the results, Odogi clay is a good match for the exorbitant organically modified MMT. Therefore, attention can be shifted to Odogi clay as reinforcement in epoxy for electronic packaging applications.

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