Morphological and Dynamic Mechanical Analyses of a Local Clay/Plantain Fiber Filled Hybrid Polystyrene Composites

K. P. Odimayomi, A. G. Adeniyi, S. A. Abdulkareem, F. M. Oladipo Emmanuel, C. A. Adeyanju, M. A Amoloye

Abstract**—**The abundant availability of the local clay/plantain fiber coupled with the various renewable and sustainability advantages has led to their choice as co-fillers in the development of a hybrid polystyrene composite. The prime objective of this study is to evaluate the morphological and dynamic mechanical properties using Scanning Electron Microscopy and Dynamic Mechanical Analysis. The hybrid polystyrene composite development was developed via the hand-lay-up method. All processing including the constituent mixing and curing were achieved at room temperature (25 ± 2 °C). The mechanical characteristics of the developed composites via Dynamic Mechanical Analysis (DMA) confirm an indirect relationship between time and storage modulus, this pattern becomes more evident at higher frequencies. It is clearly portrayed that the addition of clay and plantain fiber in the polystyrene matrix increases the stiffness of the developed composite.

Keywords**—**Morphology, DMA, Akerebiata clay, plantain fiber, hybrid polystyrene composites.

I. Introduction

THE usage of waste plastics for the fabrication of plastic composite materials has been gaining ground in recent times due to their qualities such as high strength, low specific gravity, biodegradability, renewability, and low cost. Composites are novel materials consisting of two or more components combined at a macroscopic level and are not soluble in each other [1], [2]. A composite is a material made from two or more distinct materials that when combined are better (stronger, tougher, and/or more durable). It consists of the reinforcing or discontinuous phase (metal, ceramic, fiber) embedded in the continuous phase or matrix (Thermosets and Thermoplastics). Wood is a naturally occurring composite containing cellulose fibers in a matrix of lignin [3], [4]. Reinforcing materials provides strength and rigidity to help and support the structural load while the matrix acts as a source of composite toughness and also a load transfer medium between the fibers. Hybrid plastic composites are produced when two fillers are used to reinforce a given plastic matrix. This has resulted into the development of new composite materials tailor made for specific application as the societal need changes along the pressure of economy and population [5].

Natural fibers, readily available and abundant in nature, are used to reinforce polymers to obtain materials with low density and specific strength [6], [7]. Due to their low cost and renewability, they serve as a viable alternative in polymer reinforcement compared to synthetic fibers which are expensive and non-renewable in nature [8]. Natural fibers such as wood, abaca, banana leaf and stem fibers, hemp, cotton, flax, coir (coconut fiber), wheat straw, kenaf, jute, bamboo, sisal or other fibrous material have warranted interest because of eco-friendly properties which support their potential across a wide range of applications. [9]

Plantains are of *Musa* species, they are perennial plants, whose fruits remain starchy at maturity. They are widely cultivated in Nigeria and different countries of the world [10]. The cultivation and utilization of the plant in the country generates a large amount of agro-residues/wastes which are potential resource of natural fibers used as reinforcement in composites [11]. Plantain fiber is a bast, lingo-cellulosic fiber which can be extracted from the pseudo-stem after the utilization of the fruits and leaves [12].

Expanded Polystyrene (EPS) also known as Styrofoam is a low-cost and high-performance thermoplastic with applications mainly for construction materials and packaging for consumer products. Polystyrene wastes are generated in large quantities, domestically and industrially [13], [14]. However, polystyrene is non-recyclable and non-biodegradable and it takes 500 years to decompose. Polystyrene and polystyrene products are the fifth largest source of hazardous waste and fill up to 30% of landfill space in the United States [15], [16]. The production, use, and disposal of polystyrene cause adverse health and environmental effects and these impacts being of great concern led to its alternative use as a matrix in development of composites.

Akarebiata clay is a notable clay deposit in Ilorin. It has been used as a pottery center for local utility molding [17]. Its physicomechanical properties were also evaluated [18], [19]. The clay is found to be mainly/majorly alumina-silica based, the silica and alumina content was confirmed in the respective range of 47.30-8.50% and 32.75-34.30% [19]. Other physical properties explored, clay content, linear shrinkage, moisture content, bulk density, apparent porosity, permeability, compressive strength, thermal shock resistance, specific gravity and refractoriness, were found to be 33.80-72.20%, 6.10-9.80%, 21.00-33.00%, 1.99-2.87 g/cm^3, 21.00-37.00%, 73-94, 213-840 N/mm^2, +29 cycles, 2.18-2.52 and > 1300 ºC, respectively. Fatuyi and Samuel [20] conducted the same research in comparison of Akerebiata clay with Ikere Local Clay. Akosile et al. [21] had also studied the usage of

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Akerebiata clay in the production of ceramic filters for household water treatment in Nigeria and found it suitable. Local clays in Nigeria have been majorly deployed in the pottery and related application with less usage in plastic composite development [22], [23].

There is an increasing need for the polymer-based composite of multi-filler to achieve wider spectra of products and properties of choice. Moreover, the rising environmental problems associated with a proliferation of polystyrene and biomass wastes, and the advantages the composite possess over metal alloys are equally attractive. Evaluation of mechanical and structural properties of plantain fiber/local clay reinforced polystyrene composite using contact molding – the cold process is scarcely documented in the literature. Thus, the need to develop composites containing plantain fiber/local clay and polystyrene becomes necessary to establish a new material that can serve as a better alternative to metal alloys in an area of application where substantial structural performance is not required and to also proffer solution to the environmental menace caused by polystyrene waste.

II. Materials and Methods

A. Materials

Plantain pseudo-stem (PPS) also known as empty fruit bunch (EFB) is the branch/stem carrying the plantain fruits. EFBs were obtained from the waste stream of Ganmo market. Polystyrene is also known as Styrofoam is commonly used as packaging material for electronic gadgets to prevent them from damage. Waste polystyrene was obtained from the waste stream of the University of Ilorin central store. Akerebiata Clay was locally sourced in Ilorin, Kwara State.

1. Fiber Extraction

The fibers were extracted from the stalk the waste EFBs by the mechanical processing which involved cutting and pounding of the stalk which caused the fibers to be separated and yield juice extract. The fibers were then be allowed to dry in the open air for three days.

2. Clay Purification

The raw clay was subjected to purification treatments to eliminate non-clay substances. It was purified by mixing 10 g of clay with 500 mL of deionized water in a 1 L beaker for 24 h.

The slurry was sieved and dried in open air. It was then pounded to reduce the particle size and sieved using 100 µm mesh size.

3. Processing of Polystyrene in Solvent

A suitable solvent was used to dissolve the solid polystyrene to form a polystyrene-based resin (PBR). The solid polystyrene was dissolved in petroleum solvent [24], [25] to have it in a more suitable form for the composite molding.

4. Preparation of Plantain Fiber/Clay Reinforced Hybrid Polystyrene Composite

Solid Styrofoam (polystyrene) was dissolved in the solvent and mixed with the aid of a wooden stirrer to form a homogenous polystyrene resin. The mass equivalent of the resin concentration to be used was measured using a weighing balance and the already prepared clay and fibers were weighed according to the required concentration. The clay and fibers were poured into the resin simultaneously and the mixture was stirred to obtain a uniform and homogenous composite paste. Samples of the composites produced are indicated in Table I. After a uniform mixing is obtained, the composite paste was placed on a clean lubricated surface and molded into a slab by rolling and compressing using a metal roller. The composite preparation steps described above were repeated for composite samples. The composite samples were then allowed to cure for a period of 7 days before characterization.

TABLE I
DESCRIPTION OF HYBRID POLYSTYRENE COMPOSITE DESIGN

Sample	Description
A	100% Clay powder
B	100% Resin
C	75%Resin + 25% Fiber
D	75% Resin + 6.5% Clay + 18.5% Fiber
E	75% Resin + 12.5% Clay + 12.5% Fiber
F	75% Resin + 18.5% Clay + 6.5% Fiber
G	75% Resin + 25% Clay

B. Testing and Characterization

The prepared samples were analyzed for their physical and structural properties as presented in this section.

1. Scanning Electron Microscopy

The surfaces of composite samples were examined by Scanning Electron Microscope (SEM) Phenom Prox, manufactured by phenomWorld Eindhoven, Netherland. The sample was placed on the aluminum holder stub using sticky carbon tape, insulated using gold, and then grounded electrically. Afterward, the sample was dried in the oven at 60 ºC for 3 hours. The sample chamber was purged using nitrogen gas at a 50psi Nitrogen line. The sample holder stub was placed in the sample chamber holes and the door shut and the rotary pump picked. At about 35 minutes, a vacuum of 5 x 10^{-5} Pa is created. The filament light was switched on and the monitor too automatically switched on. At this stage, the accelerator voltage is 15 kV and the filament burned out. The lowest scan mode of 10x is picked and the TV scan is clicked. The magnification was taken to 1000x at a slow scan, 2000, 3000 to 10,000. The SEM images for the selected composite samples will then be recorded.

2. Dynamic Mechanical Analysis

The dynamic mechanical tests properties were measured by using an RSA 3 (TA Instruments) (ASTM D4092–01). The strain sweep test will be performed at a frequency of 1 Hz. The frequency sweep test will be performed at a strain of 10^{-4}, which is considered to be in the linear viscoelastic region of these materials.

III. Results and Discussion

A. SEM Analysis of the Prepared Composite Samples

The surface morphology of the composites samples produced and that of the pure resin was investigated at 500, 750, 1000 and 1500 magnifications and results are presented in Figs. 1-4. Unfilled polystyrene resin is presented in Fig. 1, hybrid polystyrene composite with 12.5% by mass each of the local clay and plantain fiber is presented in Fig. 2 while Figs. 3 and 4 have 25% each of fibers and clay, respectively. Fig. 1 is observed to have micro-particles which are the entrapped undissolved particles in the solvated polystyrene resin. This is possible because the reused polystyrene waste comes with other micro entities, entrapped in its expanded volume. Adeniyi et al. [26] observed a similar result for pure polystyrene resin. Voids are also observed as labeled in the diagram which could be as a result of trapped air previously associated with the curing process at room temperature. The unfilled polystyrene micrograph seems to have a smoother surface than the other samples.

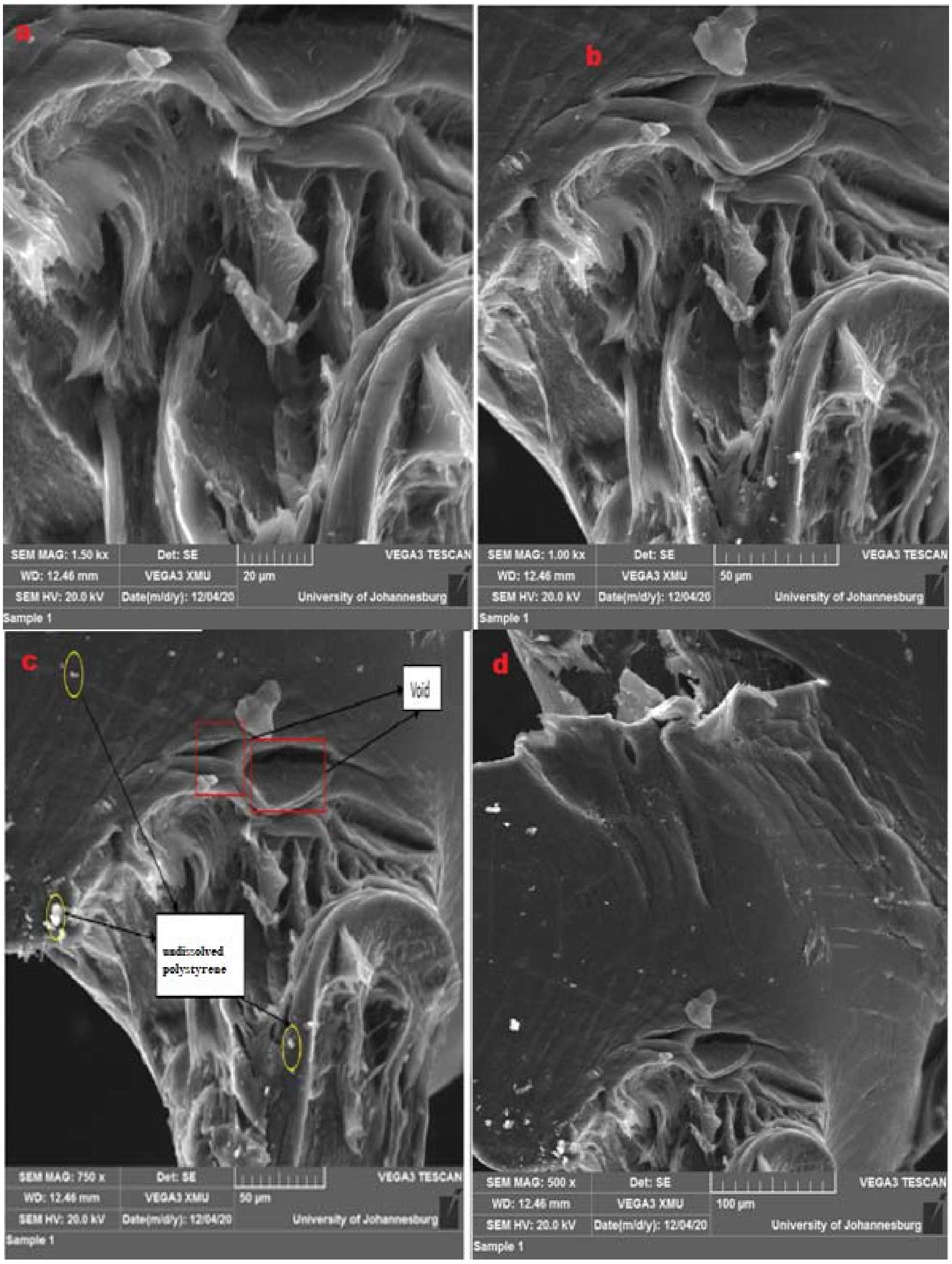

Fig. 1 SEM image of solvated polystyrene: (a) 1500x (b) 1000x (c) 750x (d) 500x

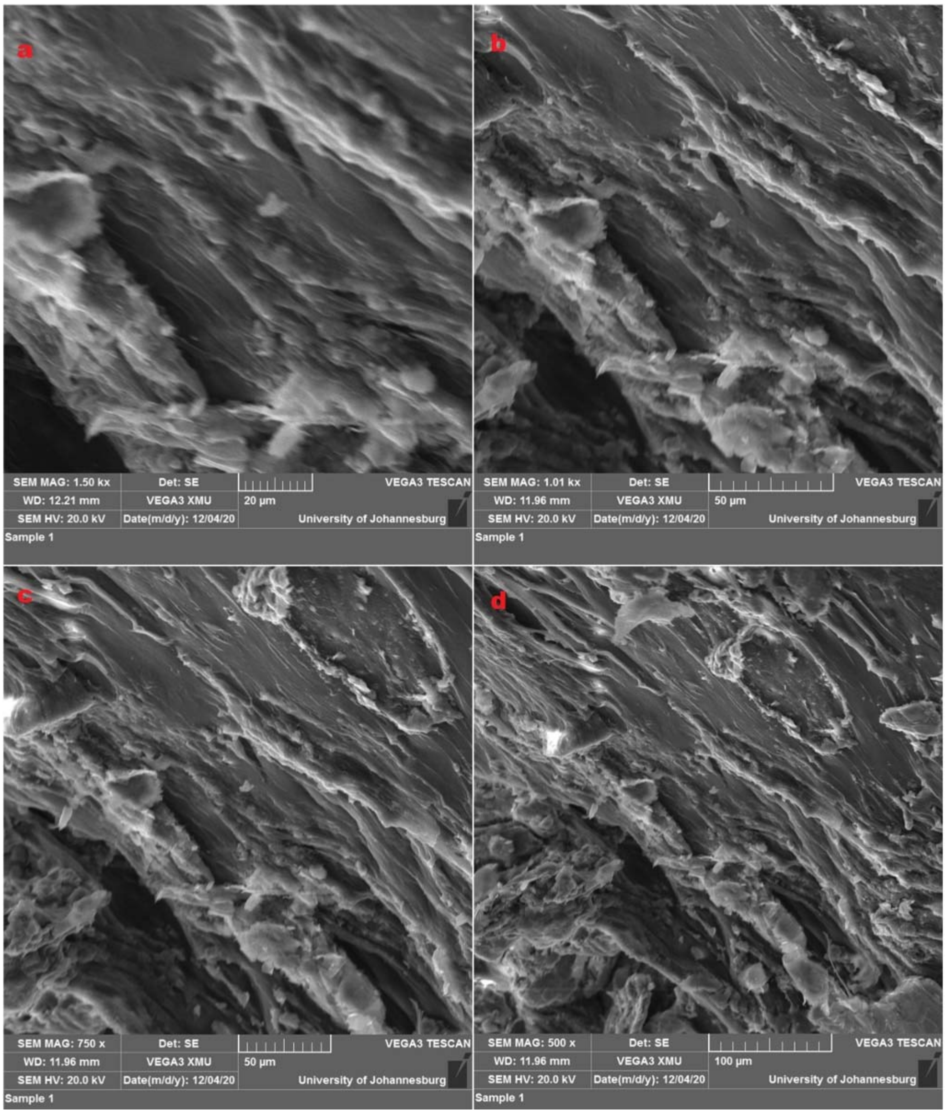

Fig. 2 SEM image of fibrillated polystyrene-clay composite containing 12.5% Clay + 12.5% Fibre + 75% Resin: (a) 1500x (b) 1000x (c) 750x (d) 500x

Fig. 2 shows striped layers of plantain fibers, which are clearly observed in Fig. 3, however, a better adhesion and good interaction between the fiber/clay to solvated polystyrene is observed in Fig. 2 when compared with Fig. 3 which contains only plantain fiber and polystyrene. Similar fiber-polystyrene adhesion has been earlier reported in the literature [26]. The possibilities were linked to viscous nature of the solvated polystyrene used as the matrix and fibrous nature of the fillers earlier reported. Moreover, the presence of clay as co-filler in Fig. 2 now gives an improved matrix-filler adhesion and interaction. The presence of clay as co-filler in the solvated polystyrene is also found to facilitate the smoothness of the composite. This is confirmed when Figs. 2-4 are compared. Fig. 3 shows strip layers of plantain fibers with few cluster portions on surface of the sample, although, Fig. 4 shows slight agglomeration of clay particles and crack is also observed in the sample, while Fig. 2 averaged the features with little observed clusters and agglomerations of clay due to lower presence of clay. This increased with clay concentration in the solvated polystyrene matrix. This is likely due to the effect of differential aspect ratio of clay/fiber fillers in the solvated polystyrene matrix. Moreover, smoother surfaces signify less flexibility which allows for elongation at break [27]. This will affect the mechanical properties as the stress field will be centered around the aggregate causing cracks to propagate easily hence leading to an untimely failure [28] as observed that the higher percentage of clay in the sample affects the mechanical properties negatively. This result is opposed to a uniform distribution of clay in HDPE matrix observed by Tanniru et al. [28] howbeit at a lower clay percent (4%).

B. Dynamic Mechanical Analysis

DMA is a characterization method that gives clear information on the visco-elastic behavior of polymers. It is a method that determines the complex modulus by measuring the strain in a material when a sinusoidal stress is applied.

This is done by varying the frequency or temperature/time of the sample which in turn leads to a variation in complex modulus [29]. The DMA was carried out for the sample in order to study the response of the material to stress and frequency as time varies. Figs. 5-9 show the relationship between the storage modulus, modulus, time and tan d (phase angle or phase lag) [30].

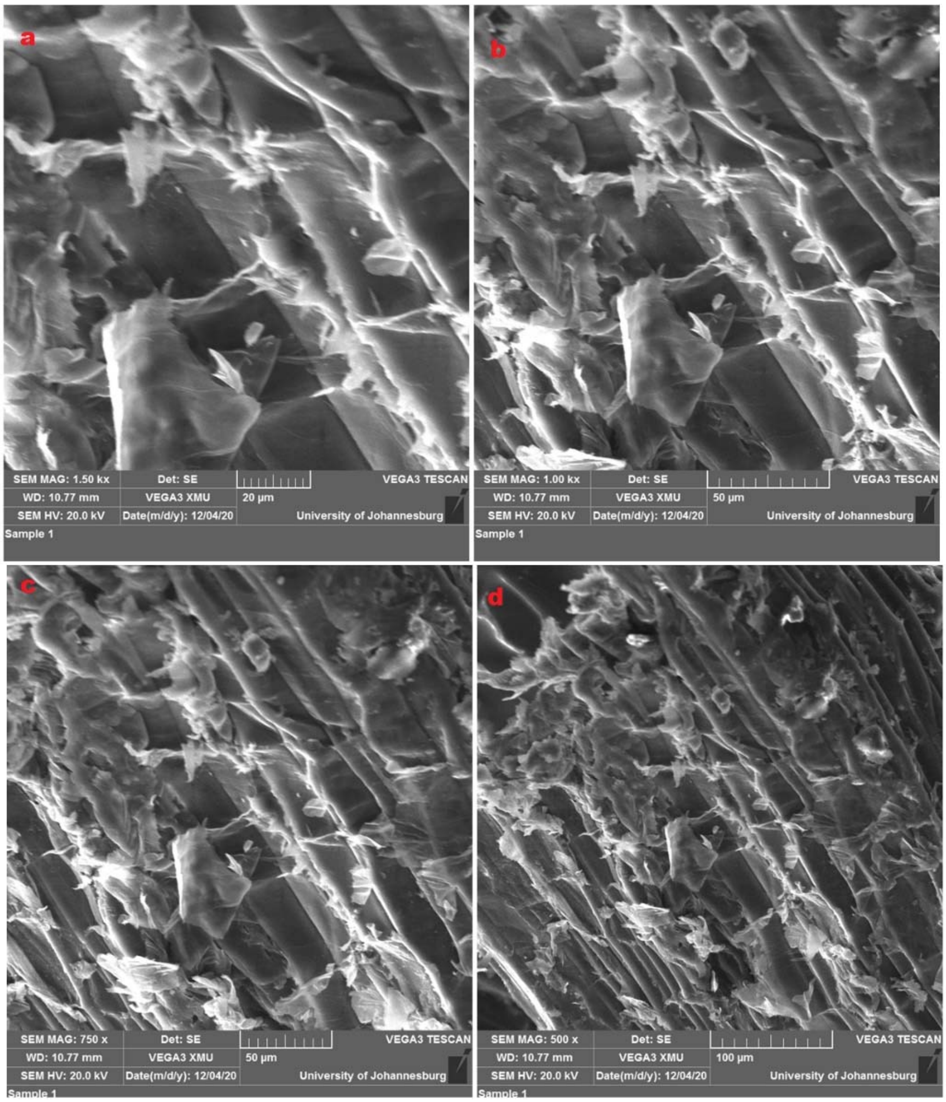

Fig. 3 SEM image of fibrillated polystyrene-clay composite containing 0% Clay + 25% Fibre + 75% Resin: (a) 1500x (b) 1000x (c) 750x (d) 500x

Figs. 5-9 generally show a stable composite under dynamic loading as time increases from the frequency of 1.666, 2.5 and 5.0 Hz. As the time was increased, the storage modulus reduces generally for all the samples with more decrease at higher frequency. Ye et al. [31] observed similar trend albeit for addition of Butylated lignin to polypropylene. For the sample containing 100% resin, a clear transition was observed after 5 min and the addition of clay filler improves the loss modulus possibly because of the increase in the surface area of the clay per unit volume. This gives rise to an increase in the constituents of the composites which transforms energy to heat when deformed under an applied load. An increase in the filler content of the clay and plantain fiber increases the force of friction until a limit has been exceeded when there might be agglomeration in the matrix [32]; however, this was not observed in the samples as there was a uniform distribution of both the fiber and the clay particles in the matrix due to the chosen composition.

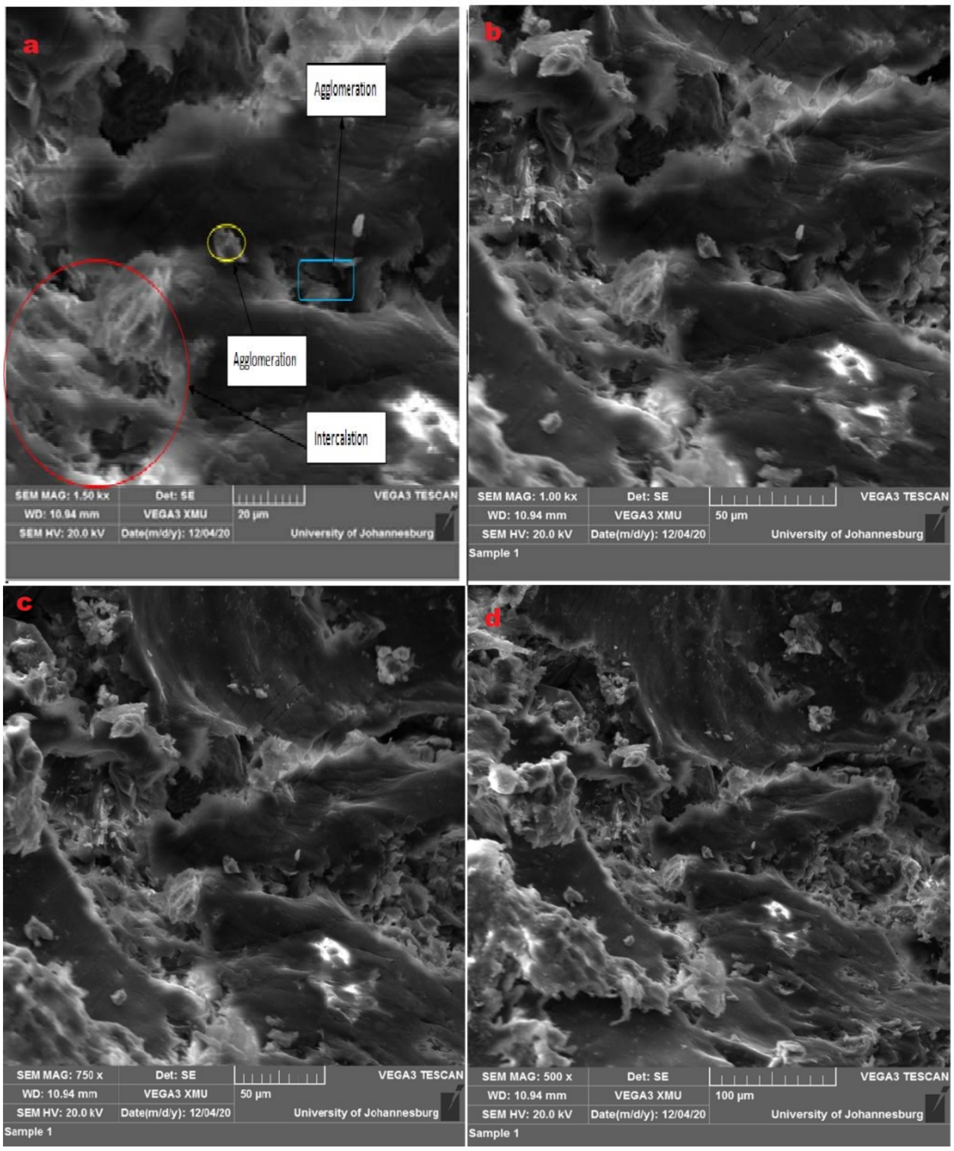

Fig. 4 SEM image of fibrillated polystyrene-clay composite containing 25% Clay + 0% Fibre + 75% Resin: (a) 1500x (b) 1000x (c) 750x (d) 500x

The result clearly shows an increase in the stiffness of the material and a decrease in *tan d* as the clay and fiber filler are added to the matrix. The storage modulus values clearly show an enhancement in the rubbery plateau as the fillers are being added. Liu and Wu [29] and Kodgire et al. [33] observed a similar result for polypropylene clay nanocomposite. The curve for polystyrene resin shows about 18% loss of stiffness from 110 MPa to 90 MPa at 5 min. The transition occurs rather faster before 2 minutes when 25% of the fiber was added to the resin sample and an increase in the frequency reduces the transition time as stated earlier with a constant loss modulus (Fig. 6). This could be as a result of the cellulose, lignin and hemicelluloses present in the fiber. On the other hand, at a reduced fiber content with the addition of small clay filler (Fig. 7: 18.75 fiber + 6.25% clay + 75% resin), about 16.7% loss of stiffness from 3.6 MPa to 3.0 MPa was observed at 4.5 min. However, when equal amount of clay and fiber (Fig. 8: 12.5% each) were added to 75% resin, about 10.4% loss of stiffness from 5.58 MPa to 5.0 MPa was recorded. As fiber filler was added to the sample, the relaxation peaks become more obvious and about three relaxation peaks are observed for sample containing 75% Resin + 25% Fiber. These peaks disappear gradually as clay filler increases and fiber filler reduces however it became more evident again in Fig. 9 (for the sample composition of 75% resin + 18.75% Clay + 6.25% Fiber).

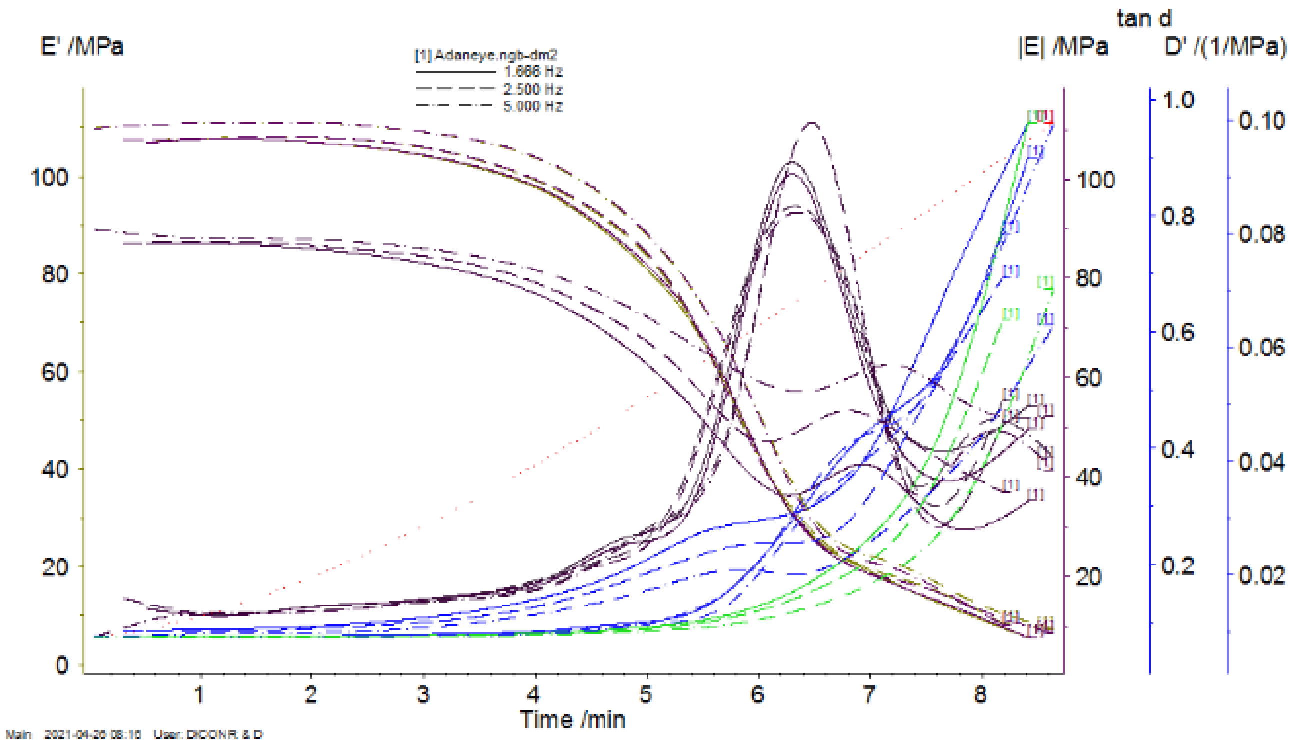

Fig. 5 DMA test curve for sample containing 100% Resin

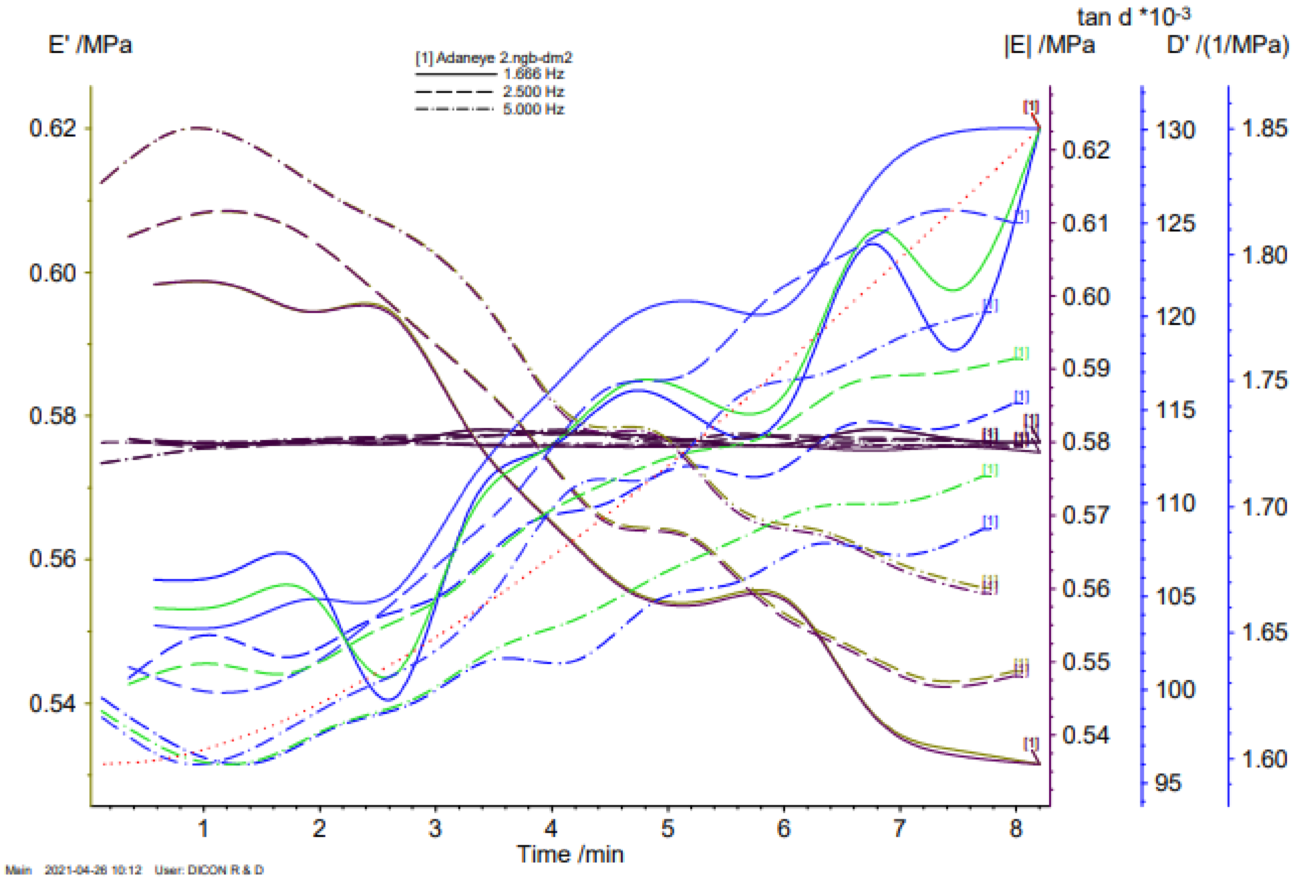

Fig. 6 DMA test curve for sample containing 75% Resin + 25% Fiber

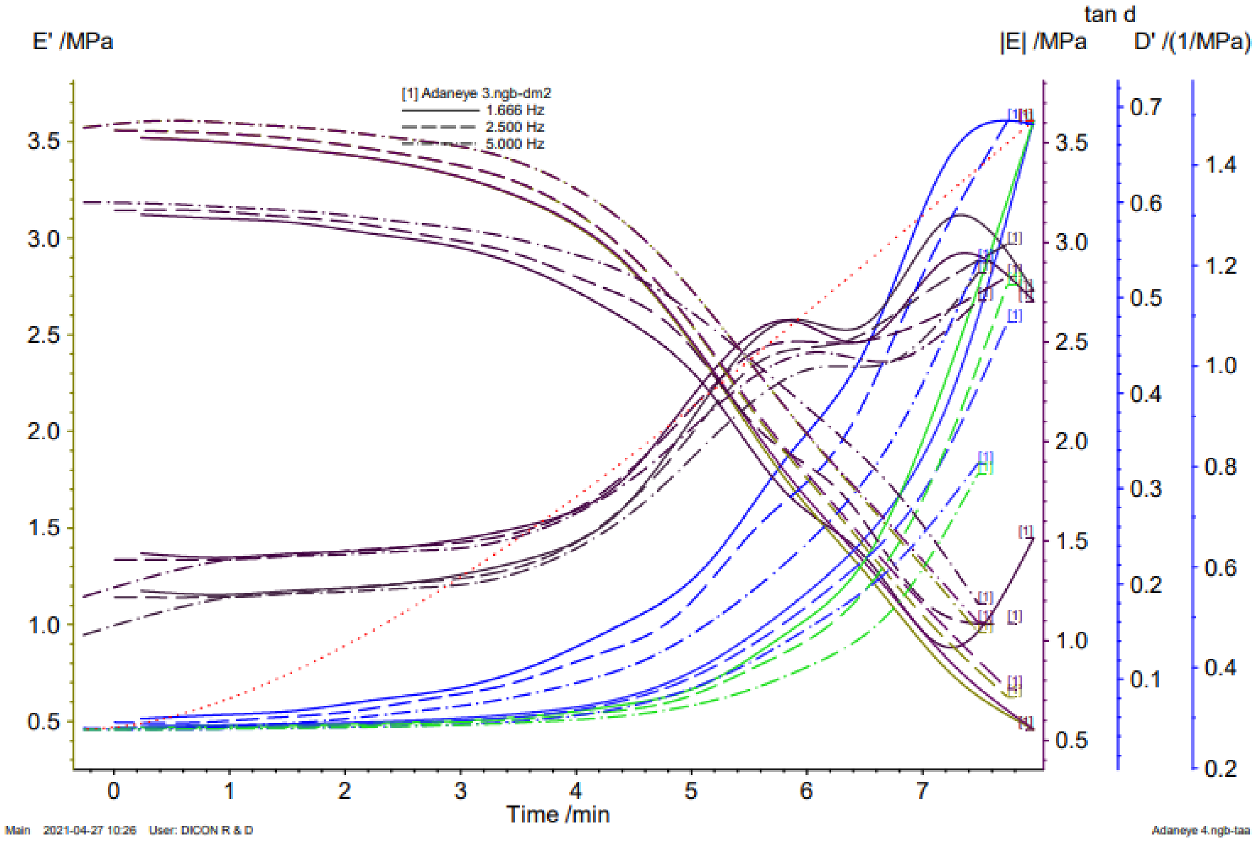

Fig. 7 DMA test curve for sample containing 75% resin + 6.25% clay + 18.75% fiber

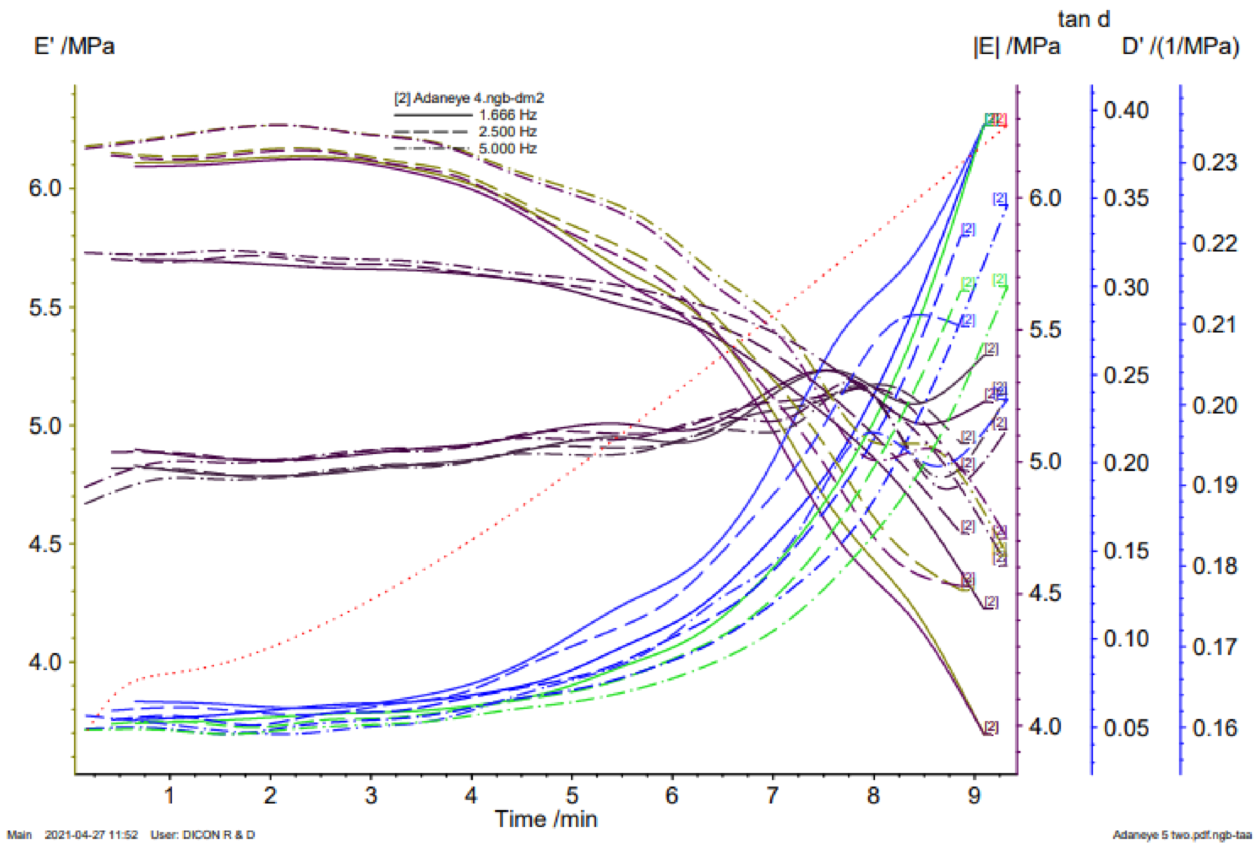

Fig. 8 DMA test curve for sample containing 75% resin + 12.5% clay + 12.5% fiber

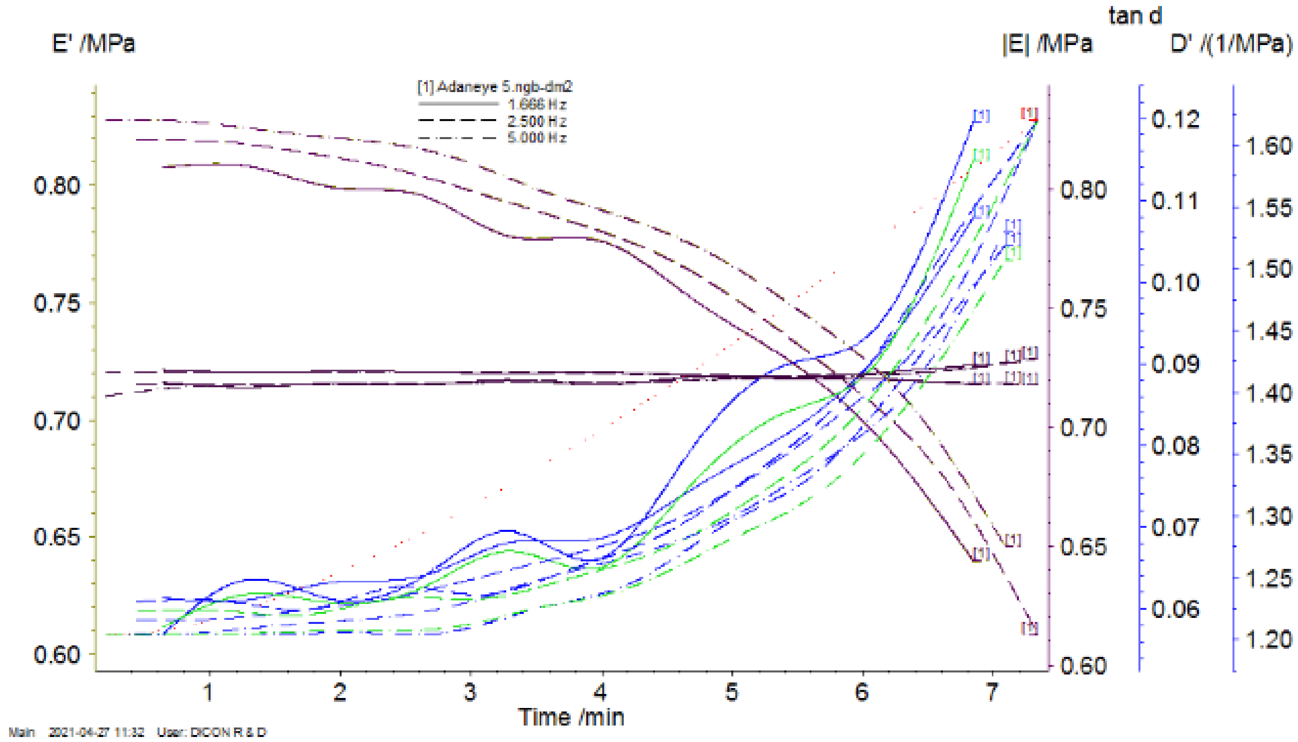

Fig. 9 DMA test curve for sample containing 75% resin+18.75% clay+6.25% fiber

IV. Conclusions

A composite was successfully produced from this study from akerebiata clay, plantain fiber and polystyrene resin. The morphological and dynamic mechanical analyses of the produced composite were carried out. Good adhesion and interaction of the fiber, clay and the polystyrene resins are observed via the SEM analysis. The result demonstrates that the composition of clay in the composite matrix enhances the mechanical property of hybrid composites. It was observed from the DMA result that as time increases, the storage modulus reduces generally for all the samples with more decrease at higher frequency. The result clearly confirms an increase in the stiffness of the material and diminishing values of *tan d* as the clay and fiber filler are added to the matrix. The storage modulus values clearly prove an enhancement in the rubbery plateau as the fillers are being added.

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