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Polymer Composite Film Based on Polyethylene and Organoclay

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ABSTRACT

Clay is an inorganic material with hydrophilic surface which cannot interact well with hydrophobic polymer as a reinforcement filler phase. However, surface modification allows useful applications as fillers in composite fabrication with most hydrophobic polymers. To achieve this, native clay was activated by mineral acids, modified through acetylation using commercial vinegar to convert the hydrophilic clay surface to hydrophobic one, capable of interaction with polyethylene. The formulated composite films were biodegraded after one month of test experiment carried out at different locations. Scanning electron microscopy analysis of composite films evidently showed that surface compatible, dispersible and exfoliated type composites were formed. FT-IR spectroscopy revealed the presence of C=O, -COO-, $-CH_3$ and $-C-CH_3$ due to acetylation. Absorption studies using water, acid/base show that the composite films exhibited good resistance to these solvents. Biodegradation studies showed high microbial activities with samples buried at refuse dump sites. EDX results revealed the presence of kaolinite and montmorillonite as major minerals, whereas radioactive elements were detected in the studied clay. This study demonstrated the useful application of commercial vinegar for the modification of clay for better surface interaction with polyethylene for composite formulation.

KEYWORDS

Organo-clay, Composite, Polyethylene, Biodegradation.

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INTRODUCTION

The properties of nanocomposite materials depend not only on the properties of individual precursors, but also on their morphology and interfacial characteristics. For example, when nanomaterials are used to produce products, they need to be able to be controllably dispersed or mixed into other materials and retain their functionality in the bulk matrix. The type of polymer matrix used and the possible effects of nanofillers on its microstructure and its intrinsic properties are also essential parameters determining the composite properties. Nanocomposites of polymer and organically modified layered nanofillers (organo-clay) often exhibit improved mechanical and various other materials′ properties compared with those of virgin polymer or conventional composite. Clay is the common name for a number of fine-grained, earthy materials based on layered structures 1:1 or 2:1. Fundamentally, it is built of one tetrahedral silicate (Si-O) sheets and one octahedral metal oxide/ hydroxide (M-O- or M-OH) sheet [1,2]. Chemically, clay minerals are hydrated aluminium phylosilicates with variable amount of magnesium, iron, alkali metals and other cations found on or near some planetary surface.

The concept of nanotechnology was introduced by Richard Feynman in 1959 at a meeting of the American Physical Society [3], from which nanotechnology was coined as the science and engineering of new materials design and synthesis, devices, characterization and systems at molecular level, as phenomena associated with atomic and molecular interaction strongly influence macroscopic materials properties [4,5]. The United State is leading in nanotechnology research with over 400 research centres and companies involved with about $ 3.4 billion in funding [6]. One and leading innovation in the field of polymer technology is nanotechnology in polymer nanocomposites materials processing which hold the key to the future advances in flexible packaging, as it produces materials with enhanced properties. According to Alyssa [6], nanocomposites appear capable of approaching the elusive goal of converting plastics into a super barrier-the equivalent of glass or metal, without upsetting regulators. At this scale, physical, chemical or biological properties of materials are fundamentally different from those of the bulk material and offers new avenues in product development [4,7]. In intercalated nanocomposites, polymer chains alternate with the inorganic layers in a fixed compositional ratio with defined number(s) of polymer layers in the intra lamellar space while in exfoliated nanocomposites, the number of polymer chains between the layers are almost continuously variable and the layer agglomeration of nanoparticle may present them in large μm scale [8], though, would still perform and display the properties of nanoparticle materials. Nanocomposites have improved stiffness, strength, toughness, thermal stability, barrier properties and flame retardancy compared to their macro counterpart [9]. A few percentages of these materials are normally incorporated (1-5 %) into polymers resulting in high improvement in some mechanical properties due to their large degree of surface area [10]. Nanometric size composites have some unique outstanding properties compared to their conventional micro/macro composite counterparts [11,12]. The objective of the study was to investigate the surface chemical modification of clay *via* acetylation using commercial vinegar for enhanced surface miscibility with polymer matrix for highly dispersible and biodegradable composite material for packaging applications.

EXPERIMENTAL

Reagents and solvents: The clay used in this work was collected from a local pottery in Badeggi, Katcha Local Government Area of Niger State. All reagents used where of analytical grade.

Acid activation: Clay (30 g) was weighed separately into three different beakers and each was treated with 64 % H_2SO_4, HCl or H_3PO_4 and a magnetic stirring bar was placed and a thermometer was inserted. The mixture was mounted on a heating mantle and heated at 80 ºC while stirring for 3 h. The sample was washed with deionized water to remove negative ions until the washed water was neutral. The residue was oven dried at 105 ºC for 3 h [13,14].

Chemical modification of samples: Acetylation of sample was carried out using commercial vinegar. In a typical experiment 10 g of oven dried acid activated clay was placed in a reaction flask followed by introducing 70 mL of vinegar. The mixture was placed on a heating mantle and refluxed for 3 h. After modification, the reaction mixture was washed repeatedly using deionized water and then acetylated product was oven dried at 105 ºC. This procedure was repeated for HCl and H_3PO_4 activated clay products. Weight percentage gain in acetylation was calculated using the following formula:

$$\text{WPGs}\ (\%) = \frac{W_2 - W_1}{W_1} \times 100$$

where, W_1 = Initial weight, W_2 = Final weight.

Composite preparation: The dissolution of high density polyethylene follows the method described by Azeh *et al*. [15]. In brief, 0.1 g pieces of non-printed portion were placed in a reaction flask and 20 mL of toluene was added. The content was place on a heating mantle and inserted a thermometer. The sachet was swelled at 60 ºC and then rapidly dissolved at 80 ºC to give a clear solution. Composites were prepared by introducing into a clear solution of high density polyethylene (HDPE) various amounts of acetylation products of acid activated clay 0.2, 0.5, 1.0 g while stirring for 1 min and then cast on a clean glass petri-dish to afford various composite matrix compositions [16].

Absorption of polyethylene acetylated clay composite: Acetylated polyethylene/clay composite films with dimensions (3 mm × 20 mm × 200 mm) were subjected to water, 2 M H_2SO_4, NaOH absorption kinetics by immersion method for 1, 2 and 3 h, respectively. After each immersion in water, the composite film was removed and excess water was wiped off using tissue paper and then weighed accurately. This procedure was repeated for 2 M solutions of tetraoxosulphate (VI) acid and NaOH solutions. Percent absorption was calculated using the following formula:

$$\text{Absorption}\ (\%) = \frac{S_2 - S_1}{S_1} \times 100$$

where S_1 = initial weight of composite or sample before immersion in water and S_2 = weight of sample after immersion in water.

Scanning electron microscopy: The surface morphology of the composites and acid activated clay samples were characterized using a PhenomWorld ProX Scanning Electron Microscope with integrated EDS system (Eindhoven, Netherlands) at Ahmadu Bello University, Zaria, Nigeria.

FT-IR spectroscopy: FT-IR spectra of composite samples and control were recorded at National Research Institute for Chemical Technology (NARICT) Zaria, Kaduna State, Nigeria. The samples were run as KBr pellets disk on Perkin-Elmer, FTIR-8400S Fourier Transform infrared spectrophotometer in the range of 4000–500 cm^{-1}.

Biodegradation test of composite films: Composite film and control samples were subjected to biodegradation test. This was carried out by taking out five sheet specimens weighing

0.1, 0.3, 0.4, 1.2 g, respectively. A total of five samples were used in this experiment and all of them were buried in the soil with favourable microbial conditions. The burial test was carried out in two different locations such as water logged area and at refuse dump site for one month. After which weight loss due to biodegradation was determined gravimetrically.

The percentage weight loss due to biodegradation was then calculated using the following formula:

$$\text{Weight loss (\%)} = \frac{W_1 - W_2}{W_1} \times 100$$

where W_1 = initial dry weight of the specimen and W_2 = dry weight after burial in the soil.

RESULTS AND DISCUSSION

FT-IR Study of acid activated acetylated and control clay samples: The FTIR bands for control and acid activated samples are presented in Table-1. The spectra showed the appearance of a new peak in the carbonyl area around 1633 cm^{-1}, associated with the formation of ester group. The intensity of the peaks located around 3697-3620 cm^{-1} assigned to surface and interlayer -OH stretch in Al-OH and Fe^{3+}-OH, decreased after acetylation in all acid-treated-acetylated samples while 3491-3170 cm^{-1} is assigned to Si-OH (silanol) absorption. Acid treatment led to decrease in intensity of free -OH absorption of water of hydration indicating a reduction in the amount of Al, Mg and Fe from native clay [17-22]. This band disappeared in H_2SO_4 activated clay. The important band at 1384 cm^{-1} was due to acetylation confirming the success of acetylation, which resulted from C-C bending in acetate groups. The significant band at 1176 cm^{-1} is assigned to -COO stretch in acetate due to esterification of the free -OH in clay. The peak at 900 cm^{-1} has been assigned to Si-O stretching vibrations and confirmed the silicate structure of the original clay. The most intensive band at 1040 cm^{-1} was attributed to Si-O in-plane stretching and CH_3 rocking in adsorbed acetate [18,23]. The band at 1091 cm^{-1} was due to Si-O out-of-plane stretching vibration [18]. The bands at 531, 510, 497 and 490 cm^{-1} are linked to Si-O-Al (octahedral) and Si-O-Si bending vibrations, respectively [18,21,22]. The absorptions around 524, 472 and 442 cm^{-1} are associated peak bending vibrations of Si-O-Al and Si-O-Si agreeing with Ahmed *et al.* [17]. The sulphuric acid and phosphoric acid treated-acetylated clay showed small peaks at 950, 937, 944 and 904 cm^{-1} attributed to Al-Al-OH [17,19,21,22]. The appearance of the bands at 840, 811 and 813 cm^{-1} in acid-treated sample are due to isomorphous substitution of Al-Al-OH stretching and Al-Mg-OH bending of -OH [17-19,21,22]. The peaks at 890 and 857 cm^{-1} are due to Al-Fe-OH. This indicates that most part of the layer charge resulted from trivalent (Al^{3+}, Fe^{3+}) to bivalent (Mg^{2+}) ion substitution in the octahedral sheet [20]. The FT-IR of the studied clay indicated that it was made up of montmorillonite and kaolinite minerals [20]. The -OH band disappeared completely in H_2SO_4 acetylated clay. The HCl-acetylated and the native acetylated clay spectrum showed a band at 795 and 695 cm^{-1} assigned to Si-O-Al and Si-O-Si bending vibrations attributed to the presence of cristobalite [17,18,22]. This band essentially decreased with acid treatment.

TABLE-1
KEY IR BANDS OF POLYMER COMPOSITE FILMS BASED ON POLYETHYLENE AND ORGANOCLAY

Wave number (cm^{-1})	Stretching and bending vibration zone
Untreated acetylated clay	
3697-3620	Symmetric stretching vibrations due to the inner surface or inner Al-O-H and Si-OH groups
1633	-COO- stretching vibrations of the acetate groups.
1107	Partial asymmetric stretching vibrations of Si-O-Si
795 and 695	Assigned to Si-O-Al, Si-O-Si, and O-Si-O bending vibrations
1466	Characteristic band due to quaternary ammonium group
H_3PO_4 treated acetylated clay	
3673	Symmetric stretching vibrations due to the inner surface or inner Al-O-H and Si-OH groups.
3491-3170	Free hydroxyl stretching of clay in Si-OH Silanol group.
1384	C-C bending vibrations in acetyl due to acetylation.
1176	Due to –COO stretch in acetate.
1105	Might be due to partial condensation of Si-O-Si and Al-OH asymmetric stretching mode.
1091	Si-O-Si and O-Si-O stretching vibration of clay.
950-937	Al–Al–OH bending vibrations of clay.
813	Al-Mg-OH hydroxyl bending vibrations at the edges of clay.
550	Due to in-plane vibrations of octahedral ions and their adjacent oxygen.
531, 510, 497 and 490	Associated with Si-O-Al, Si–O–Si and O-Si-O deformations.
473-437	Deformation site indicates the presence of illite.
H_2SO_4 treated acetylated clay	
1384	C-CH_3 bending deformations in acetyl due to acetylation.
944-904	Assigned to Al-Al-OH bending vibrations in clay.
840-811	Al-Al-OH stretching and Al-Mg-OH bending of Hydroxyl.
890-857	Assigned to Al-Fe-OH bending vibrations of hydroxyl.
524	Si–O–Al bending vibrations associated peaks.
472-442	Si–O–Si deformation signal.
944-904	Assigned to Al-Al-OH bending vibrations in clay.
HCl treated acetylated clay	
3697-3620	Symmetric stretching vibrations due to the inner surface or inner Al-OH and Si-OH groups.
3435	Free hydroxyl stretching of clay.
1384	C-C bending of acetate group (-C-CH_3-) in acetyl due acetylation.
2909	CH_3 asymmetric stretching vibrations of aliphatic methyl in acetate due to acetylation.
1624	-COO- stretching vibrations of the surface acetate groups in a bidentate configuration.
1004	Stretching vibrations of Si-O in Si-O-Si
795 and 695	Assigned to Si-O-Al and Si-O-Si bending vibrations

Morphological study using scanning electron microscopy (SEM): Scanning electron microscopy was employed to study the particle morphology of the prepared composites. The SEM morphology revealed the presence of agglomeration of primary small size clay particles in different geometrical forms. For example, cuboidal or *d*-like geometry of varied agglomerates could be seen in treated clay samples. This was attributed to process conditions. Acid activated clay samples showed different clusters of agglomerated particles in Fig. 1.

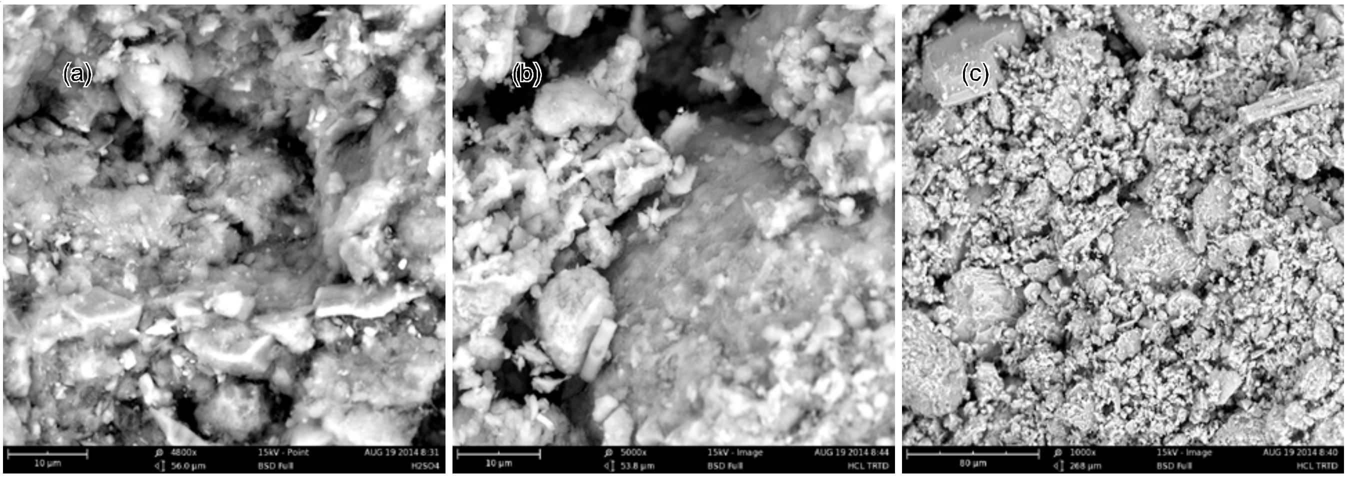

Fig. 1. SEM micrographs of (a) H_3PO_4 acid activated clay; (b) H_2SO_4 acid activated clay; (c) HCl activated clay

This has been attributed to the small sizes of the particles resulting from acid degradation of grain particles and the elimination of porous and amorphous organic components. The presence of large number of agglomerated and clustered particles may be attributed to lack of ultrasonic treatment of the samples. It has been reported that 21 agglomerated particles observed before ultrasonic treatment in one study became 245 smaller agglomerates after ultrasonication [24]. In this work, the SEM morphologies of both acid activated clay and composites of organoclay/polyethylene showed various agglomerates and clusters of particles with different morphologies ranging from cuboidal to spherical to rod-like shapes. It was observed that acid-treated clay samples had smaller particles and thus, exhibited high agglomeration tendency. Since, smaller the particles, the higher the tendency for physical interaction to form agglomerates [24]. Most of the nanomaterial usually exists as agglomerates. One major difference we found in the acid-treated and untreated clay samples was that acid activated samples had high tendency to form various sizes of agglomerates which signified that these particles have smaller scale dimensions than untreated clay samples. Even though, they both appeared microscopically. It cannot be disputed that acid activated clay sample are in nanometer scale since, an agglomerate of sample appear as one particle, the individual primary particle are in nanoscale in one of its dimensions [24,25].

Surface miscibility of composite samples: The scanning electron microscopy (SEM) images taken at different magnifications showed the crystalline pattern of acetylated clay and the interfacial interaction between polyethylene and organoclay particles. This shows the dispersibility of acetylated clay into the polyethylene matrix attributed to the presence of acetyl moieties on clay particle surface, as modified clay particles interact well with polyethylene. This behaviour was due to chemical transformation of the hydrophilic surface of clay particles through acetylation. As a result, enhanced interfacial dispersion between acetylated clay particles and polyethylene matrix was observed. The presence of voids, cavities, pores and agglomerates in the polymer-matrix composites has been attributed to poor mechanical stirring of the cast solution. It could be seen that at higher magnification of organoclay/polyethylene composite, a worm-like structure of the composite showed even dispersion of organoclay particles in polyethylene matrix (Fig. 2).

This was a clear evidence of hydrophobic interactions between polyethylene and acetyl groups on the surface of acetylated clay particles. The white spots in the composites are agglomerated clay nanoparticles.

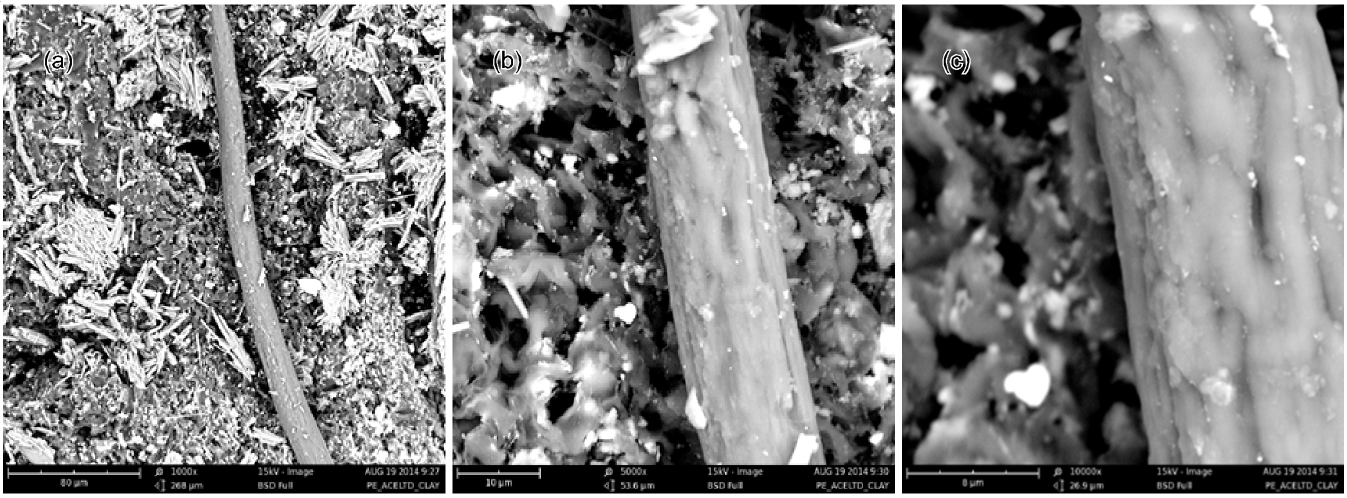

Fig. 2. SEM micrographs of PE/acetylated clay composite at different magnification

Activation of clay using inorganic acids: The results of acid activation of clay (Table-2) showed that percent weight due to activation using H_2SO_4, H_3PO_4 and HCl increased in the order; 58 < 60 < 72 %, respectively. However, the results indicated that HCl activation of clay was mild compared to H_2SO_4 (58 %) which had better activation of clay particles followed by H_3PO_4 (60 %) acid [13,14]. This evidence was further shown by the SEM micrographs of the activated clay samples due to small size of clay particles observed with H_2SO_4 and H_3PO_4 acids treated samples. In addition, these results showed that better degradation of organic/amorphous materials in native clay was best achieved with H_2SO_4 and H_3PO_4. The hydroxyl (-OH) groups and positively particles on clay surface may be converted to hydrophobic surface by the formation of acetate groups on the metal surface through chelation, which can effectively improve interlocking within the polymer matrix. This transformation may improve the adhesion at the matrix/ clay interface and thus, reduced water, acid/base absorption ability of composites films and resulted in enhanced properties of clay reinforced composites [26].

TABLE-2
ACID ACTIVATION OF CLAY USING H_2SO_4, HCl AND H_3PO_4

Acid	Initial weight of clay (g)	Weight after activation of clay (g)	Weight of activated clay (%)
H_2SO_4	30	17.4	58
HCl	30	21.9	72
H_3PO_4	30	17.9	60

The results for acetylation of acid activated and control clay samples are shown in Table-3. The percent weight gains in acetyls for 3 h acetylation for each of the acid-treated samples showed high values of acetyl gains with exception of HCl activated clay. Control sample had 60 % acetyl, which was indicative of the presence of amorphous regions/organic matter capable of acetyl consumption and subsequent acetylation led to high weight percent acetyl gain for the control sample.

TABLE-3
WEIGHT PERCENT GAIN IN ACETYLATION OF ACID ACTIVATED AND CONTROL CLAY SAMPLE

Acid	Initial weight of clay (g)	Final weight of acetylated clay (g)	Weight gain (%)
H_2SO_4	3	4.5	50
HCl	3	3.1	03
H_3PO_4	3	4.5	50
Control	3	4.8	60

Results of water, acid or base absorption of organoclay polymer composite: As expected, the presence of clay material in the formulated composites films increased the water absorbency of the composite films (Table-4). Since, polyethylene (HDPE) is hydrophobic and clay being hydrophilic the absorption of water was therefore, a function of clay alone. It was observed that as acid activated-acetylated clay loading increased, the increase in absorption of water by composite film was also observed. This analysis has shown that the hydrophilicity of clay was drastically reduced due to acetylation (Table-4). However, the highest percent absorption was found with composite film reinforced with non-acid treated acetylated clay which was attributed to its hydrophilicity, porosity and presence of amorphous organics all contributed to its ability to form hydrogen bonding with water molecules and resulted in high water uptake. Acid activated-acetylated clay composite film showed low degree of water absorption when compared with non-acid treated-acetylated clay composite film (Table-4). Absorption kinetics of acetylated clay/polyethylene composites of different formulation compositions carried out for 1, 2 and 3 h showed good evidences of better water repellence which has been attributed to factors like better composite formulation ratio, surface compatibility, exfoliation and intercalation of filler material, stirring/mixing and particle size diameter of filler material and the presence of acetyl groups. However, it was noted that composite compositions with 0.20 g acid activated-acetylated clay/1.0 g polyethylene, better film formability was achieved and this was evidenced by the absorption studies involving water, acid and base, as this formulation practically showed no absorption of water, acid or base for the test experiments involving 1 h of composite film immersion in water, acid or base compared to those with composite formulation compositions of 0.5/0.5 g or 1.0/0.5 g clay/polyethylene composite film.

Biodegradation of composite films in water-logged and refuse dump sites: The biodegradation experiment of comp-

TABLE-4
ABSORPTION RESULTS OF ORGANOCLAY POLYMER COMPOSITE IN WATER, ACID AND BASE

Composite composition (g)	Composite film sample	Dry weight (g)	Weight after immersion			% of Water absorption		
			1 h	2 h	3 h	1 h	2 h	3 h
Water absorption								
0.2 g AcetClay + 1.0 g PE	Acetylated clay/PE	0.40	0.40	0.40	0.40	0.00	0.00	0.00
0.5 g AcetClay + 0.5 g PE	Acetylated clay/PE	1.00	1.30	1.30	1.30	30.0	30.0	30.0
1.0 g AcetClay + 0.5 g PE	Acetylated clay/PE	1.00	1.30	1.40	1.50	30.0	40.0	50.0
Acid (H_2SO_4) absorption								
0.2 g AcetClay + 1.0 g PE	Acetylated clay/PE	0.40	0.40	0.40	0.40	0.00	0.00	0.00
0.5 g AcetClay + 0.5 g PE	Acetylated clay/PE	1.00	1.30	1.30	1.30	30.0	30.0	30.0
1.0 g AcetClay + 0.5 g PE	Acetylated clay/PE	1.00	1.30	1.40	1.50	30.0	40.0	50.0
Base (NaOH) absorption								
0.2 g AcetClay + 1.0 g PE	Acetylated clay/PE	0.40	0.40	0.40	0.40	0.00	0.00	0.00
0.5 g AcetClay + 0.5 g PE	Acetylated clay/PE	1.00	1.30	1.20	1.20	30.0	20.0	20.0
1.0 g AcetClay + 0.5 g PE	Acetylated clay/PE	1.00	1.40	1.40	1.50	40.0	40.0	50.0

Key: AcetClay = Acid activated-Acetylated clay; PE = Polyethylene

TABLE-5
BIODEGRADATION OF COMPOSITE FILMS AT DIFFERENT SITES

Composite composition (g)	Water logged site			Refuse dump site		
	Initial dry weight before burial (g)	Final dry weight after burial (g)	Degradation after one month (%)	Initial dry weight before burial (g)	Final dry weight after burial (g)	Degradation after one month (%)
1.0 + 0.5 PE/Acetylated clay	0.10	0.10	0.00	0.10	0.10	0.00
0.5 + 0.5 PE/Acetylated clay	0.30	0.30	0.00	0.30	0.20	33.0
0.2 + 0.1 PE/Acetylated clay	1.20	1.10	8.33	1.10	0.40	64.0
0.5 + 0.5 PE/Acetylated clay	0.40	0.40	0.00	0.40	0.30	25.0
1.0 + 0.5 PE/Acetylated clay (control)	1.20	0.00	100	1.20	0.00	100

osite films buried at water logged location lasted one month after which burial samples were removed and assessed for biodegradation using weight loss parameter due to microbial activities (Table-5). It was observed that only the sample of acetylated clay/polyethylene composite film with the initial formulation weight, 1.20 g (0.2/1.0 g) acetylated clay/polyethylene decreased to 1.10 g after one month burial while control composite film sample with initial weight of 1.20 g completely disappeared due to biodegradation. The low microbial activities observed with composite film buried at water logged location could be attributed to the presence of few degrading microbes in the burial location.

The biodegradation burial experiment carried out at refuse dump location lasted one month after which samples were removed and assessed for biodegradation activities using weight loss parameter. The results showed that the composite film sample with 1.10 g as initial weight and 0.2/1.0 g composite formulation by mass decreased to 0.40 g after one month burial, with 64 % weight loss by mass. Others with initial mass of 0.30 g and 0.40 g degraded to 0.20 g and 0.30 g, respectively. Composite film with composition of 0.5/0.5 g by mass had 33.0 and 25.0 % mass loss due to biodegradation. Thus, sheet specimens buried at two different locations were biodegraded. However, samples buried at the refuse dump location exhibited high microbial susceptibility compared to samples buried at the water logged location. This has been attributed to the recognition of tiny clay particles as food and good habitat by microbes/nematodes present in the soils of burial location.

Elemental analysis of polyethylene-clay composites: Elemental analysis of polyethylene-organically modified clay composites revealed the presence of the following elements in clay at various percent concentrations; yttrium, strontium, fluorine, nitrogen, oxygen, carbon, rubidium, niobium, gadolinium, samarium, selenium, magnesium, calcium and sodium (Table-6). This confirmed the presence of radioactive elements in the studied clay. This research has provided some evidence and knowledge on the cause of lung cancer on local potters in Tako-ndajiya area of Badeggi in Katcha Local Government area, Niger state, Nigeria, based on undocumented reports from the indigenous citizens of the area. The deaths of many local potters before this study had been linked to lung cancer, which may be due to long-time exposure to radiations from these elements.

TABLE-6
EDX-ELEMENTAL COMPOSITION

Element	Confidence (%)	Conc. (Wt %)	Error (%)
Yttrium (Y)	100.0	19.7	0.7
Strontium (Sr)	100.0	14.1	0.8
Fluorine (F)	100.0	30.1	1.1
Nitrogen (N)	100.0	14.5	1.1
Oxygen (O)	100.0	16.0	1.6
Carbon (C)	100.0	1.9	1.9
Rubidium (Rb)	100.0	1.5	2.9
Niobium (Nb)	100.0	2.2	4.7
Sodium (Na)	100.0	5.9	1.9
Magnesium (Mg)	100.0	7.3	1.2
Selenium (Se)	100.0	1.7	3.9
Calcium (Ca)	100.0	1.1	5.0
Gadolinium (Gd)	100.0	21.5	2.5
Samarium (Sm)	100.0	12.1	3.4
Vanadium (V)	100.0	0.8	4.0

Conclusion

This study has demonstrated that vinegar is a useful and commercially low-cost chemical with possible practical application for surface functionalization of clay for enhance surface miscibility with polyethylene in composite formulation. Water, acid/base resistance composite films have been formulated. The identity of the major clay type minerals; kaolinite and montmorillonite was determined. The presence of radioactive elements was detected in the sample studied. It has also provided evidence why the deaths of some local potters were attributable to lung cancer.

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REFERENCES

1. S. Guggenheim, Definition of Clay and Clay Mineral: Joint Report of the AIPEA Nomenclature and CMS Nomenclature Committees, *Clays Clay Miner.*, **43**, 255 (1995); https://doi.org/10.1346/CCMN.1995.0430213.
2. A. Aishat, S. Olalekan, A. Arinkoola and J. Omolola, Effect of Activation on Clays and Carbonaceous Materials in Vegetable Oil Bleaching: State of Art Review, *Br. J. Appl. Sci. Technol.*, **5**, 130 (2015); https://doi.org/10.9734/BJAST/2015/11942.
3. M.M. Subedi, Ceramics and its Importance, *The Himalayan Phys.*, **4**, 80 (2013).
4. L. Goran, R. Hubert, R. Gert, S.K. Birgit, G. Neil, P. Jean-Philippe and S. Hermann, (2010). Considerations on a definition of nanomaterial for regulatory purposes. EUR 24403 EN – Joint Research Centre – Institute for Health and Consumer Protection, Institute for Reference Materials and Measurements, Institute for Environment and Sustainability; European Commission.
5. Z. You, J. Mills-Beale, J.M. Foley, S. Roy, G. M. Odegard, Q. Dai and S.W. Goh, Nanoclay-Modified Asphalt Materials: Preparation and

Characterization, *Constr. Build. Mater.*, **25**, 1072 (2011); https://doi.org/10.1016/j.conbuildmat.2010.06.070.

6. D. Alyssam; http://www.packworld.com/cds_print.html?rec_id=1788 http://www.iopp.org/ files/nanostructures.pdf?pageid= pageid>. Access in: 20 Nov. 2001) (2005).
7. S. Kamel, Nanotechnology and its Applications in Lignocellulosic Composites, A Mini Review, *Polym. Lett.*, **1**, 546 (2007); https://doi.org/10.3144/expresspolymlett.2007.78.
8. J. Kurt, Ph.D. Thesis, Hybrid Inorganic–Organic Materials: Novel Poly (Propylene Oxide) Based Ceramers, Abrasion Resistant Sol–Gel Coatings for Metals, and Epoxy–Clay Nanocomposites with an Additional Chapter On: Metallocene Catalyzed Linear Polyethylene, Virginia Polytechnic Institute and State University: Blacksburg, VA, USA (1999).
9. M. Alexandre and P. Dubois, Polymer-Layered Silicate Nanocomposites: Preparation, Properties and Uses of a New Class of Materials, *Mater. Sci. Eng. R Rep.*, **28**, 1 (2000); https://doi.org/10.1016/S0927-796X(00)00012-7.
10. S. Roberta, Ph.D. Thesis, Synthesis and Characterization of New Polymeric Materials for Advanced Applications, Università Degli Studi di Sassari Dipartimento di Dhimica and Farmacia Dottorato di Ricerca in Scienze and Tecnologie Chimiche indirizzo in Scienze Chimiche (2013).
11. P.H.C. Camargo, K.G. Satyanarayana and F. Wypych, *Mater. Res.*, **12**, 1 (2009); https://doi.org/10.1590/S1516-14392009000100002.
12. Y. Lei, Q. Wu, C.M. Clemons, F. Yao and Y. Xu, Influence of Nanoclay on Properties of HDPE/Wood Composites, *J. Appl. Polym. Sci.*, **106**, 3958 (2007); https://doi.org/10.1002/app.27048.
13. P. Pushpaletha and M. Lalithambika, Modified Attapulgite: An Efficient Solid Acid Catalyst for Acetylation of Alcohols using Acetic Acid, *Appl. Clay Sci.*, **51**, 424 (2011); https://doi.org/10.1016/j.clay.2010.12.033.
14. L. Bieseki, H. Treichel, A.S. Araujo and S.B.C. Pergher, Porous Materials Obtained by Acid Treatment Processing Followed by Pillaring of Montmorillonite Clays, *Appl. Clay Sci.*, **85**, 46 (2013); https://doi.org/10.1016/j.clay.2013.08.044.
15. Y. Azeh, G.A Olatunji and P.A. Mamza, Scanning Electron Microscopy and Kinetic Studies of Ketene-Acetylated Wood/Cellulose High-Density Polyethylene Blends, *Int. J. Carbohydr. Chem.,* **2012**, 456491 (2012); https://doi.org/10.1155/2012/456491.
16. Y. Azeh, G.A. Olatunji, C. Mohammed and P.A. Mamza, Acetylation of Wood Flour from Four Wood Species Grown in Nigeria Using Vinegar and Acetic Anhydride, *Int. J. Carbohydr. Chem.,* **2013**, 141034 (2013); https://doi.org/10.1155/2013/141034.
17. A. Yahiaoui, M. Belbachir and A. Hachemaoui, An Acid Exchanged Montmorillonite Clay-Catalyzed Synthesis of Polyepichlorhydrin, *Int. J. Mol. Sci.*, **4**, 548 (2003); https://doi.org/10.3390/i4100548.
18. M.M.M. Kashani, A.A. Youzbashi and R.Z. Amiri, Effect Ofacid Activation on Structural and Bleaching Properties of a Bentonite, *Iran. J. Mater. Sci. Eng.*, **8**, 50 (2011).
19. M.L.S. Suedina, R.C.B. Carla, V.L.F. Marcus, M.O.R. Claudia, H.C. Laura and L.C. Eduardo, Applications of Infrared Spectroscopy to Analysis of Chitosan/Clay Nanocomposites, Infrared SpectroscopyMaterial Science Engineering and Technology, Theophanides Theophile, ISBN: 978-953-51-0537-4, InTech (2012).
20. M. Djebbar, F. Djafri, M. Bouchekara and A. Djafri, Adsorption of Phenol on Natural Clay, *Afr. J. Pur. Appl. Chem.*, **6**, 15 (2012).
21. P. Djomgoue and D. Njopwouo, FT-IR Spectroscopy Applied for Surface Clays Characterization, *J. Surf. Eng. Mater. Adv. Technol.*, **3**, 275 (2013); https://doi.org/10.4236/jsemat.2013.34037.
22. O.M. Sadek, S.M. Reda and R.K. Al-Bilali, Preparation and Characterization of Silica and Clay-Silica Core-Shell Nanoparticles Using Sol-Gel Method, *Adv. Nanopart.*, **2**, 165 (2013); https://doi.org/10.4236/anp.2013.22025.
23. L.-F. Liao, C.-F. Lien and J.-L. Lin, FTIR Study of Adsorption and Photoreactions of Acetic Acid on TiO_2, *Phys. Chem. Chem. Phys.*, **3**, 3831 (2001); https://doi.org/10.1039/b103419g.
24. K. Rodelsperger, S. Podhorsky, B. Brückel, D. Dahmann, G.D. Hartfiel and H.J. Woitowitz, Characterization of Ultrafine Particle Aerosols for Occupational Safety, Final Report of Project F 1804, Dortmund-Berlin-Dresden (2003) (in German).
25. D. Walter, Characterization of Synthetic Hydrous Hematite Pigments, *Thermochim. Acta*, **445**, 195 (2006); https://doi.org/10.1016/j.tca.2005.08.011.
26. J.M. Park, S.T. Quang, B.S. Hwang and K.L. DeVries, Interfacial Evaluation Of Modified Jute and Hemp Fibers/Polypropylene (PP)-Maleic Anhydride Polypropylene Copolymers (PP-MAPP) Composites Using Micromechanical Technique and Nondestructive Acoustic Emission, *Comp., Sci., Technol.*, **66**, 2686 (2006); https://doi.org/10.1016/j.compscitech.2006.03.014.