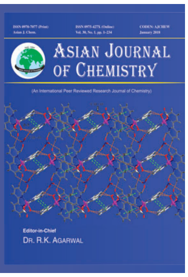
Asian Journal of Chemistry; Vol. 30, No. 8 (2018), 1902-1908

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2018.21422



Composites Based on Poly(vinyl chloride) and Organically Modified Clay

Azeh Yakubu[1,*], Elele Ugoeze Ucheoma[1], Muhammad Alhaji Muhammad[1], Yohanna Bello Paiko[1],
Fabiyi Oluwatoyin Adenike[2], Saliu Oluwaseyi Damilare[3], Muhammad Umar Badeggi[1],
Ameh Ohiga Alfa Ebune[4], Garba Babatunde[5] and Yusuf Bukhari Makunsidi[1]

[1]Department of Chemistry, Ibrahim Badamasi Babangida University, Lapai, Nigeria
[2]Department of Crop Protection, University of Ilorin, Ilorin, Nigeria
[3]Department of Industrial Chemistry, University of Ilorin, Ilorin, Nigeria
[4]Department of Pure and Industrial Chemistry, Kogi State University, Anyigba, Nigeria
[5]Department of Chemistry, Al-Hikma University, Ilorin, Nigeria

*Corresponding author: E-mail: yakubuazeh@gmail.com, azehy@ibbu.edu.ng

Received: 4 May 2018; *Accepted*: 9 June 2018; *Published online*: 30 June 2018; AJC-18994

Composites based on native and chemically modified clay have been prepared *via* stir-solution intercalation method in poly(vinyl chloride) (PVC) matrix using dimethyl sulphoxide as a solvent and ethylene glycol as a plasticizer. The composite structures based on PVC-native clay (control) and PVC-organoclay were characterized using scanning electron microscopy and FT-IR spectroscopy. The results indicated that the modified clay particles were well intercalated and homogenously dispersed in the PVC matrix. As a result, exfoliated PVC-organoclay composite were formed. The success of modification was revealed by FT-IR results, as it confirmed the formation of CO, -COO-, CH_3 and $-C-CH_3$. The formation of hydrogen bonds between the solvent molecules (dimethyl sulfoxide) and the inner surface hydroxyl groups of clay was evidenced by the appearance of hydrogen bonds. The elemental analysis of clay samples made by EDX indicated the presence of radon, a radioactive element in clay samples up to 52 % of the total concentration of elements present in the clay sample. Biodegradation studies showed that microbes were able to biodegrade composites, with high activity recorded at dump site. Absorption kinetics of composites showed that organoclay-PVC composites were resistant to water, acid and base solutions compared to control samples based on immersion time for the test. This study demonstrated that vinegar is useful for the chemical modification of clay for enhanced surface interaction with PVC and the improvement of barrier properties.

Keywords: Composite, Poly(vinyl chloride), Modified clay, Biodegradation.

INTRODUCTION

Clay is a deposit that is extensively distributed over the surface of the earth but differs greatly in its purity. It is a fine-grained soil that combines one or more clay minerals with traces of metal oxides and organic matter and differs from other fine-grained soils by differences in sizes and mineralogy [1,2]. Clay deposits are mostly composed of phyllosilicate minerals containing variable amount of water trapped in the mineral structure and depends on the origin of source rock. One of the most common clay is kaolin with the formula $Al_2Si_2O_5(OH)_4$. This simply gives the relative proportion of each element in the compound.

Various changes which takes place upon the minerals present in the earth's crust in order that clay may be formed is presented by Forchhammer formula ($Al_2O_{32}SiO_3 + 2H_2O$). The change that takes place in the original rock to produce clay is due to the action of water and carbon(VI) oxide upon feld spar as shown by eqn: 1.

$$\underset{\text{Feldspar}}{2Al_2O_3{\cdot}2K_2O{\cdot}12SiO_2} + 4H_2O + 2CO_2 \longrightarrow \underset{\text{Clay}}{2Al_2O_3{\cdot}3SiO_2} + 4H_2O + 2K_2CO_3 + 9SiO_2 \quad (1)$$

Some of its properties include plasticity, shrinkage and fineness of grain, colour change after firing, hardness and cohesion. The particles are in micrometer size and conferred unique crystal structure and special properties on clay minerals including cation exchange capabilities, catalytic abilities, swelling behaviour and low permeability [1]. Various types of clay have been modified *via* chemicals and/or physical means. For example, chemicals such as maleic anhydrides have been employed to change native clay into organoclay with improved properties and performance [3]. Organic acids have been used to transform clay surface [2,4]. Poly(vinyl chloride) (PVC) is a toxic and non-biodegradable polymer used in the production of enormous range of domestic and industrial products such as raincoats, shower curtains, window frames and door plumbing. Composites consist of two or more physically distinct and mechanically separable constituents, such that when one of these constituents is dispersed in the other, the new material gains superior properties that are significantly different compared with the properties of individual components [4,5]. Polymer nanocomposites have been a subject of increasing interest in recent years, because of their enhanced properties over neat polymer or traditional polymer composites. Incorporation of mechanically robust nano/micro scale fillers, such as nanoclay, graphite and inorganic nanoparticles into polymer matrices has been reported by many authors [6]. Polymer nanocomposites are materials developed by adding reinforcing nanoscale materials with certain geometries to polymers to improve their thermal, mechanical and barrier properties [7,8]. Modification of the filler surface is done using some reagents for the purpose of enhancing surface miscibility. The degradability of polymeric materials is a function of polymer structure. The products of synthetic polymers are usually inert to microorganism etching, which contributes to long-time persistent in the environment and consequently, may cause serious environmental problems. However, the addition of biodegradable reinforcing fillers such as clay/fibres to synthetic polymers, do improve the mechanical, barrier, thermal, flame retardancy and its degradability.

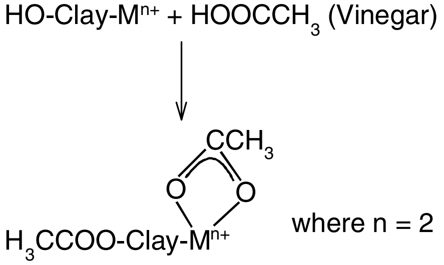
In recent years, the prospect of developing nanocomposites with improved properties has attracted much attention. In this respect, PVC/cellulose whisker, PVC/organoclay [9] and PVC/nano $CaCO_3$ [10] have been studied. Yoshihiko [11] reported that the addition of nanoclay to pure PVC, improved the flame retardancy of the composite significantly. Although, such property, reduce with increase in percentage of clay loading. Nanoclay was found to have an effect on PVC degradation after evaluation using gravimetric analysis [12]. Indeed, many studies have reported the effectiveness of nanoclay in decreasing oxygen [13] and water vapour permeability [14,15]. The aim of this study is to prepare biodegradable nanocomposites of PVC with modified nanoclay as a filler.

EXPERIMENTAL

Clay samples used in this experiment were obtained from a local pottery in Badeggi, Niger state. All chemicals and reagents used were of analytical grade.

Pre-treatment of samples (acid activation): Fine powdered native clay (30 g) was weighed and placed in a beaker followed by the addition of HCl (70 mL of 64 %). The mixture was stirred for 3 h (activation). The mixture was then allowed to settle and neutralized using 10 % NaOH and washed with deionized water repeatedly using centrifugation at 2500 rpm until the filtrate was clear and neutral to pH paper. After washing, the residue was dried for 2 h at 105 ºC and weighed. This procedure was repeated for H_3PO_4 and H_2SO_4 activation.

Acetylation: Each of H_2SO_4, H_3PO_4 and HCl activated clay (3 g) was acetylated (modification) using commercial vinegar (Heinz) by refluxing at 80 ºC for 3 h. After acetylation, the residues were thoroughly washed with distilled water until the washed water was clear and neutral, and dried for 3 h at 105 ºC (**Scheme-I**). The dried sample was weighed and used for further analysis [16-18].



Scheme-I: Model reaction for clay acetylation

Dissolution of PVC and incorporation of acetylated clay: PVC (1 g) was dissolved in 15 mL of dimethyl sulfoxide (DMSO) at 90 ºC by gradual heating until a clear solution was obtained, then 1 mL of ethylene glycol (plasticizer) was added, followed by the addition of H_2SO_4 activated acetylated clay (0.5, 1.0 and 1.5 g) into the polymer solution. The mixture was stirred vigorously for 1 min. The solution was then spread on a glass petri dish to afford a composite matrix [19].

Biodegradability test of composites: Acid activated acetylated/PVC-nanoclay and PVC-native clay composites were subjected to microbial biodegradation test. This was carried out by taking variable grams of the composites prepared, buried under favorable conditions on a dump site. The composites were taken out after four weeks and assessed for microbial attack using appearance, strength, perforation and weight loss [17].

Acid, base and water absorption tests of acid activated-acetylated/PVC and PVC/native clay nanocomposites: Four set of acid activated acetylated/PVC/clay nanocomposites and control samples were subjected to acid, base and water absorption tests. The samples were immersed in each for 1, 2 and 3 h, respectively. After each immersion time, samples were removed and the excess acid, base or water was wiped off using tissue paper. It was then weighed using the following formula:

$$\frac{W_2 - W_1}{W_1} \times 100$$

where W_1 = initial weight of specimen sample before immersion in water/acid/base and W_2 = weight of specimen sample after immersion.

Infrared spectroscopy: The IR spectra of acid activated acetylated PVC-nanoclay, acid activated clay control samples were recorded at National Research Institute for Chemical Technology (NARICT) Zaria, Nigeria. Samples were run as KBr pellets, FT-IR - 8400S Fourier Transform infrared spectrophotometer in the range of 4000-400 cm^{-1}.

Scanning electron microscopy: The morphology of acid activated clay and composite samples were carried out using a PhenomWorld ProX Scanning Electron Microscope with an integrated EDS System (Eindhoven, Netherlands) at Ahmadu Bello University, Samaru, Zaria, Nigeria.

RESULTS AND DISCUSSION

Three sets of experiments were carried out on the barrier properties of acid activated PVC/acetylated clay nanocomposites and control samples as shown in Table-1. The absorption kinetics for 1 h and 2 h was quite interesting in the sense that no absorption was recorded in acid activated acetylated PVC-nanoclay composites samples. The per cent values for the absor-

TABLE-1
DATA OF ACID, BASE AND WATER ABSORPTION TESTS OF ORGANOCLAY AND UNACETYLATED CLAY COMPOSITE SAMPLES

Composite sample	Sample composition	Dry weight (g)	Weight after immersion			Water absorption after immersion (%)		
			1 h	2 h	3 h	1 h	2 h	3 h
		Water absorption						
PVC-Acetylated clay composite	1.0 g PVC + 0.5 g organoclay + 1 mL EG	2.7	2.7	2.7	2.8	0.0	0.0	3.7
PVC-Acetylated clay composite	1.0 g PVC + 1.0 g organoclay + 1 mL EG	1.3	1.3	1.3	1.4	0.0	0.0	7.7
PVC-Acetylated clay composite	1.0 g PVC + 1.5 g organoclay + 1 mL EG	3.1	3.1	3.1	3.2	0.0	0.0	3.2
PVC-non-acetylated clay composite (Control)	1.0 g PVC + 1.5 g native clay + 1 mL EG	3.1	3.2	3.4	3.4	3.2	9.7	9.7
		HCl (2 M)						
PVC-Acetylated clay composite	1.0 g PVC + 0.5 g organoclay + 1 mL EG	2.7	2.7	2.7	2.8	0.0	0.0	3.7
PVC-Acetylated clay composite	1.0 g PVC + 1.0 g organoclay + 1 mL EG	1.3	1.3	1.3	1.4	0.0	0.0	7.6
PVC-Acetylated clay composite	1.0 g PVC + 1.5 g organoclay + 1 mL EG	3.1	3.1	3.1	3.4	0.0	0.0	9.7
PVC-non-acetylated clay composite (Control)	1.0 g PVC + 1.5 g native clay + 1 mL EG	3.1	3.2	3.5	3.7	3.2	12.9	19.4
		NaOH (2 M)						
PVC-Acetylated clay composite	1.0 g PVC + 0.5 g organoclay + 1 mL EG	2.7	2.7	2.7	2.8	0.0	3.7	3.7
PVC-Acetylated clay composite	1.0 g PVC + 1.0 g organoclay + 1 mL EG	1.3	1.3	1.3	1.4	0.0	0.0	7.6
PVC-Acetylated clay composite	1.0 g PVC + 1.5 g organoclay + 1 mL EG	3.1	3.1	3.1	3.3	0.0	0.0	6.5
PVC-non-acetylated clay composite (Control)	1.0 g PVC + 1.5 g native clay + 1 mL EG	3.1	3.2	3.4	3.5	3.2	9.7	12.9

EG = ethylene glycol

ption kinetics for 1.0 g + 1.5 g organoclay composite samples immersed for 3 h in 2M HCl, 2M NaOH and water are 6.5, 9.7 and 3.2, respectively. This was not observed on the control, as the samples absorbed acid, base and water for the 1, 2 and 3 h interval times as shown in Table-1. The results are indications that the formulation composition 1.0 g PVC + 1.5 g organoclay was good for the production of composite films and blends that will be resistant to acid, base and water. The results of the kinetic study were in agreement with the findings of Alyssa [20], where he reported that the resistance of nanocomposites to water and gas permeation was due to the multiple parallel layers which force water and gases to flow through the polymer structure in a torturous path, forming complex barriers to gases and water vapour/molecules. In addition, PVC is resistant to concentrated acids and bases. Thus, the presence of PVC molecules contributed to poor absorption of solvent molecules by composites.

FT-IR Analysis of acetylation of acid activated clays: FT-IR results are represented in Table-2. The spectra showed the appearance of a new peak in carbonyl area around 1651 cm^{-1}, associated with the formation of the ester group. The intensity of the peaks located around 3697-3620 cm^{-1} assigned to surface and interlayer -OH stretching, 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 the intensity of free -OH absorption for water of hydration, which indicated a reduction in the amount of Al, Mg and Fe in native clay [21-26]. 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 1176-900 cm^{-1} has been assigned to Si-O stretching vibrations and confirmed the silicate structure of 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 [22,27]. The band at 1091 cm^{-1} was due to Si-O out-of-plane stretching vibration [22]. The bands at 531, 510, 497 and 490 cm^{-1} are linked to Si-O-Al (octahedral) and Si-O-Si bending vibrations, respectively [22,25,26]. The absorptions around 524, 472 and 442 cm^{-1} are associated peak bending vibrations of Si-O-Al and Si-O-Si agreeing with [21]. H_2SO_4 and H_3PO_4 acid treated acetylated clay showed small peak bands at 950, 937, 944 and 904 cm^{-1} attributed to Al-Al-OH [21,24-26]. 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 [21,22,24-26]. 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 [23]. The FT-IR of the studied clay indicated that it was made up of kaolinite and montmorillonite minerals [23]. 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 [21,22,25]. This band essentially decreased with acid treatment.

Morphological study of composites using scanning electron microscopy: Scanning electron microscopy (SEM) image of native clay (Fig. 1) showed clusters of clay particles measuring several micrometers, which could cause phase separation between filler material and matrix. This could results in reduced surface interactions of the native clay filler with polymer matrix. The SEM image in Fig. 2, clearly showed that H_3PO_4 activated clay has more smaller agglomerates of clay particles than the native clay (Fig. 1). The presence of large agglomerated particles is attributable to the small size of particles and high tendency for nanoscale particles to exist as clusters of agglomerated particles [28]. Consequently, different levels of dispersion can be expected in the polymer matrix by virtue of their inherent geometries, which may bring about better mechanical and barrier properties. PVC-organoclay composites SEM micrograph results indicated that PVC molecules interacted well with the galleries of organoclay particles and thus, formed exfoliated nanocomposites due to surface miscibility [20]. This could be supported by the formation of very tough composites, which resulted from strong hydrogen bonding network between SiO−OH interactions. SEM image of PVC-organoclay sample in Fig. 3 showed that silicate layers

TABLE-2
KEY IR (cm^{-1}) BANDS OF ORGANOCLAY AND UNACETYLATED CLAY COMPOSITE SAMPLES

Wavenumber (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 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 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

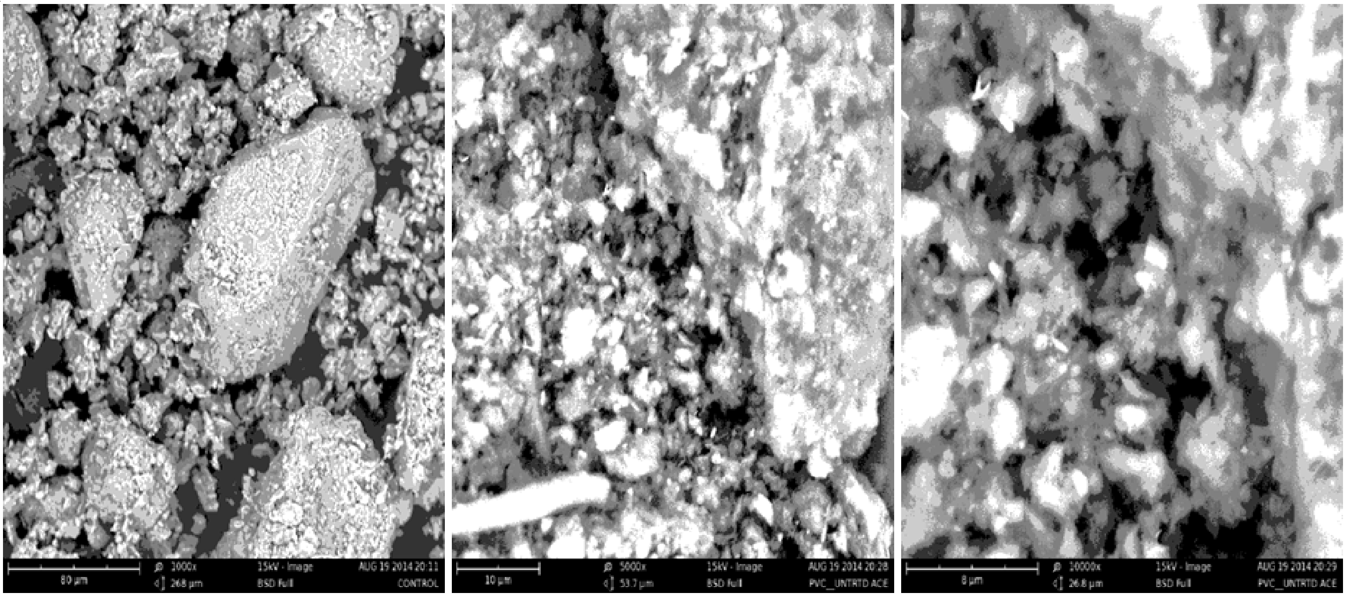


Fig. 1. SEM images of native clay

were dispersed evenly in the PVC matrix, which gave composites there smooth surfaces. This was attributed to effective mixing of the clay filler into the polymer matrix and the stir-solution method used for composites preparation. At low magnification (5000×), SEM image clearly showed that organically modified clay particles were homogeneously distributed into the PVC

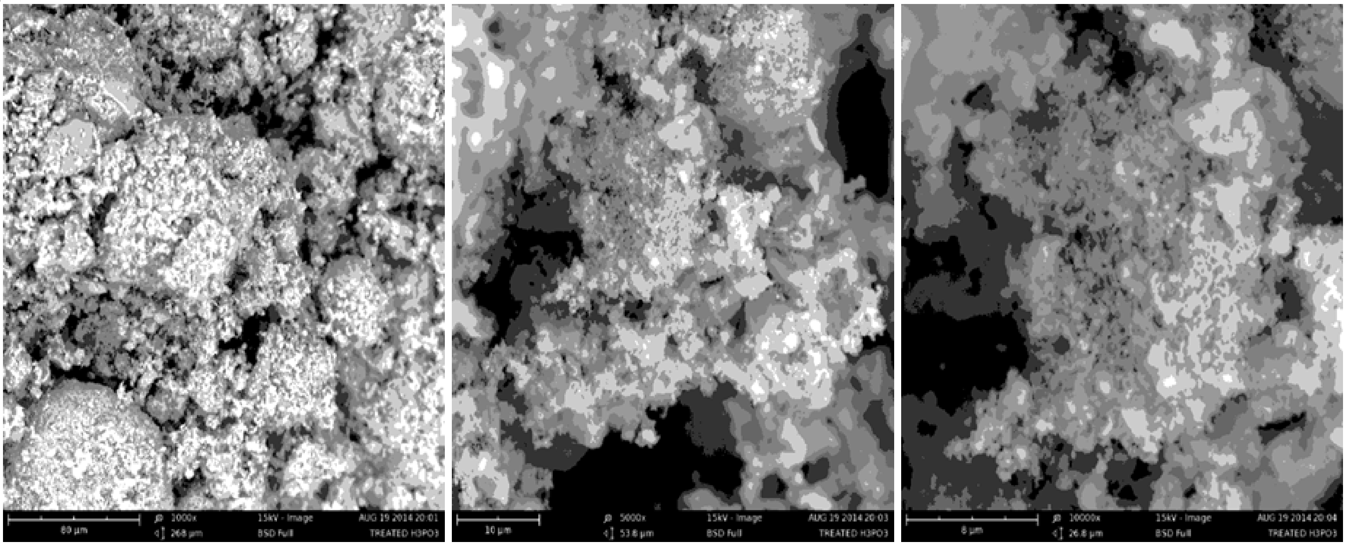


Fig. 2. SEM images of H_3PO_4 activated clay

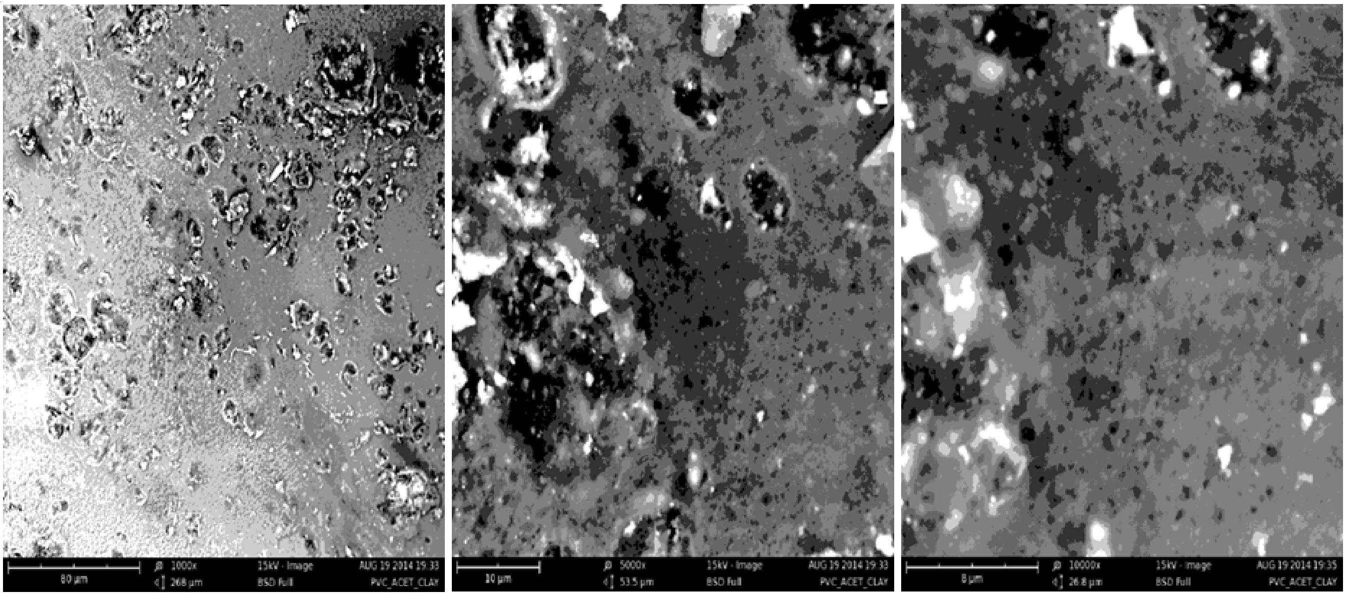


Fig. 3. SEM images of acid activated acetylated clay/PVC composite

matrix (Fig. 3). At higher magnification (10000×), it could be seen that some single and exfoliated particles in the PVC matrix formed upon shearing. The uniformity in clay distribution in between the polymer chains was due to the presence of polar groups on the clay surface, formation of electrostatic attractions between PVC molecules bearing $^{\delta+}C–^{\delta-}Cl$ partial polar bonds, the interaction of carbon chains of PVC molecules and hydrophobic acetyl groups that substituted the active hydrogen atom of the hydroxyl groups in clay due to acetylation.

PVC-native clay composites showed very poor surface intercalation of silicate layers into PVC matrix, because of the hydrophilic nature of clay. The polar surface of silicate and high silicate-silicate interaction force, made it difficult for native clay to disperse in the PVC matrix, due to differences in surface energies between filler particles and PVC matrix. SEM images of PVC-native clay composites (Fig. 4) showed agglomerates of silicate particles having different shapes and sizes were determined. This evidently showed poor interaction of clay-PVC matrix, which produced rough morphological surface. While acid activated acetylated clay particles had smaller particles (58 nm), which enhanced their dispersion into the PVC matrix.

Elemental analysis of nanocomposites: The elemental analysis of PVC-organoclay composites revealed the presence of Sr, Si, Al, Ru Na, Ca, Te and Rn. Table-3 is an expression of the elemental composition determined in clay sample. The results showed that the native clay sample had more appreciable amount of radioactive element-radon, with mass concentration of 52.4 %, than the concentration of other elements determined in the sample. This study has provided the evidence of the cause of lung cancer on local potters in Takondajiya area of Badeggi, Katcha Local Government area, Niger State, Nigeria.

Biodegradation of composites: Biodegradation of acid activated acetylated clay/PVC composites showed that there was microbial adherence to PVC/organoclay composite films. The biodegradation of composites was investigated using physi-cal changes such as appearance, perforation, strength and weight loss [29]. After one month burial, composites lost their strength and appreciable colour change from white-brown

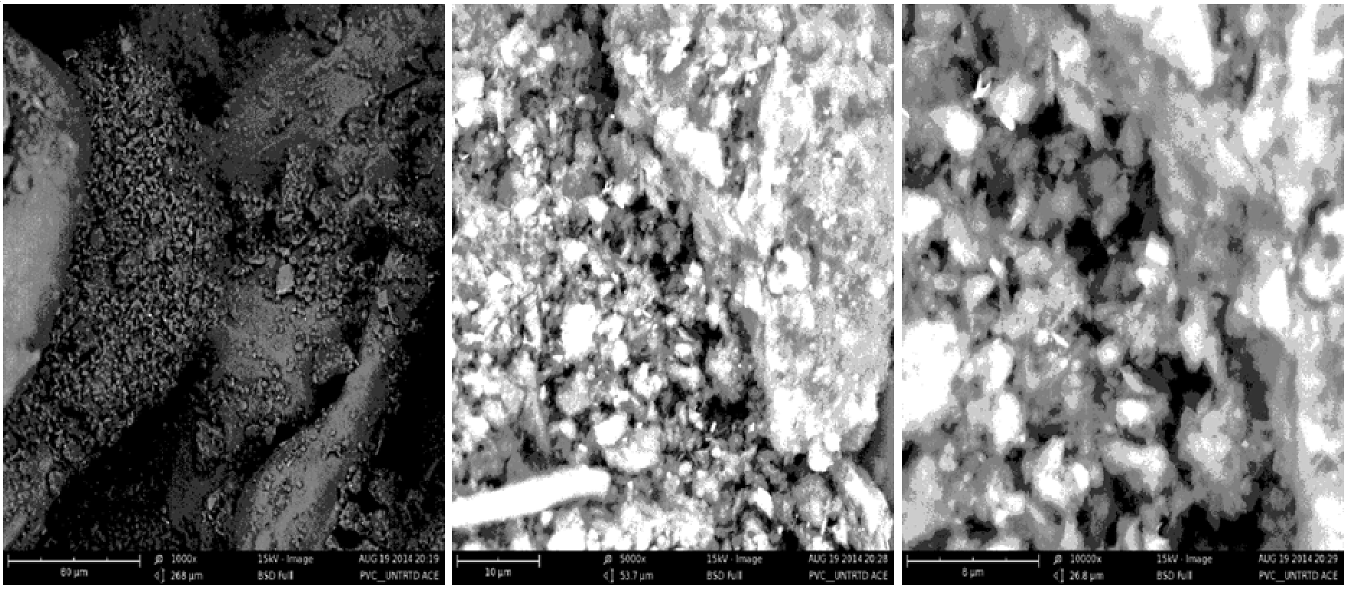


Fig. 4. SEM images of non-acetylated clay/PVC composite

TABLE-3
EDX-ELEMENTAL COMPOSITION

Elements	Confidence (%)	Concentration (wt. %)	Error
Strontium	100.0	24.9	0.5
Silicon	100.0	8.6	0.7
Radon	100.0	52.4	0.5
Aluminium	100.0	5.9	0.8
Ruthenium	100.0	1.7	3.1
Sodium	100.0	3.2	2.0
Calcium	100.0	0.7	3.4
Tellurium	100.0	2.6	3.1

to dark-brown was observed, which indicated the presence of microorganisms and nematodes. Weight loss was also determined in the first 4 weeks of burial. In another experiment, 0.5 g of composite was completely biodegraded after 7 weeks of burial at a refuse dump site. This was attributable to changes in climatic conditions such as temperature and relative humidity, as these influence microbial activities in the burial site. In addition, clay is rich in both major and trace nutrients, biologically important for the physiological function of microbe. It was observed that composites buried at a refuse dump site biodegraded faster than the composites buried at areas tagged less microbial sites, this could results from high microbial activities at the refuse dump sites.

Conclusion

This research work has demonstrated the use of commercial vinegar to modify clay. SEM results of composite films showed that interfacial interactions and dispersibility of acetylated clay in the PVC matrix were improved. Fibre metric image measurement of both composite films and acid activated samples showed the appearance of particles in the nanometer scale. EDX results indicated the presence of radioactive element radon, in clay samples upto 52 %. Kinetics for both acid activated acetylated clay/PVC and control composites samples showed that acid activated acetylated clay/PVC composite was resistant to water and 2 M acid/base uptake.

REFERENCES

1. S. Gugeinheim and R.T. Martin, *Clays Clay Miner.*, **43**, 255 (1995); https://doi.org/10.1346/CCMN.1995.0430213.
2. A. Aishat, S. Olalekan, A. Arinkoola and J. Omolola, *Br. J. Appl. Sci. Technol.*, **5**, 130 (2015); https://doi.org/10.9734/BJAST/2015/11942.
3. H.M.C. Azeredo, *Food Res. Int.*, **42**, 1240 (2009); https://doi.org/10.1016/j.foodres.2009.03.019.
4. J.-J. Lin, Y.-N. Chan and Y.-F. Lan, *Materials*, **3**, 2588 (2010); https://doi.org/10.3390/ma3042588.
5. D. Hull and T.W. Clyne, An Introduction to Composite Materials, Cambridge University Press, U.K., edn 2, p. 1 (1996).
6. F. Hussain, M. Hojjati, M. Okamoto and R.E. Gorga, *J. Compos. Mater.*, **40**, 1511 (2006); https://doi.org/10.1177/0021998306067321.
7. M. Alexandre and P. Dubois, *Mater. Sci. Eng.*, **28**, 1 (2000); https://doi.org/10.1016/S0927-796X(00)00012-7.
8. L.N. Ludueña, V.A. Alvarez and A. Vazquez, *Mater. Sci. Eng. A*, **460-461**, 121 (2007); https://doi.org/10.1016/j.msea.2007.01.104.
9. W.H. Awad, G. Beyer, D. Benderly, W.L. Ijdo, P. Songtipya, M.M. Jimenez-Gasco, E. Manias and C.A. Wilkie, *Polymer*, **50**, 1857 (2009); https://doi.org/10.1016/j.polymer.2009.02.007.
10. N. Chen, C. Wan, Y. Zhang and Y. Zhang, *Polym. Test.*, **23**, 169 (2004); https://doi.org/10.1016/S0142-9418(03)00076-X.
11. A. Yoshihiko, Flame Retardants, Engineering Materials, Springer International Publishing, Switzerland, pp. 1-44 (2015).
12. D.Y. Wang and C.A. Wilkie, *J. Vinyl Addit. Technol.*, **8**, 238 (2002); https://doi.org/10.1002/vnl.10369.
13. L. Cabedo, E. Gimenez, J.M. Lagaron, R. Gavara and J.J. Saura, *Polymer*, **45**, 5233 (2004); https://doi.org/10.1016/j.polymer.2004.05.018.
14. R.K. Bharadwaj, *Macromolecules*, **34**, 9189 (2001); https://doi.org/10.1021/ma010780b.
15. C. Lotti, C.S. Isaac, M.C. Branciforti, R.M.V. Alves, S. Liberman and R.E.S. Bretas, *Eur. Polym. J.*, **44**, 1346 (2008); https://doi.org/10.1016/j.eurpolymj.2008.02.014.
16. Y. Habibi, L.A. Lucia and O.J. Rojas, *Chem. Rev.*, **110**, 3479 (2010); https://doi.org/10.1021/cr900339w.
17. Y. Azeh, G.A. Olatunji, C. Mohammed and P.A. Mamza, *Int. J. Carbohydr. Chem.*, **2013**, 1 (2013); https://doi.org/10.1155/2013/141034.
18. C. Breen, R. Watson, J. Madejová, P. Komadel and Z. Klapyta, *Langmuir*, **13**, 6473 (1997); https://doi.org/10.1021/la970507w.
19. S. Carlos, I. Gemma, Polymers and Composite Group, ACCIONA Technology Centre: Spain (2014).

20. D. Alyssam Polymer Nanocomposites are the Future (2005). Available from: <http://www.iopp.org/ files/nanostructures.pdf?pageid= pageid>.
21. A. Yahiaoui, M. Belbachir and A. Hachemaoui, *Int. J. Mol. Sci.*, **4**, 548 (2003); https://doi.org/10.3390/i4100548.
22. M.M. Kashani Motlagh, A.A. Youzbashi and Z.A. Ragi, *Iran. J. Mater. Sci. Eng.*, **8**, 50 (2011).
23. M. Djebbar, F. Djafri, M. Bouchekara and A. Djafri, *African J. Pure Appl. Chem.*, **6**, 15 (2012).
24. M.L.S. Suedina, R.C.B. Carla, V.L.F. Marcus, M.O.R. Claudia, H.C. Laura and L.C. Eduardo, Infrared Spectroscopy-Matetrials Science Engeering and Technology, ISBN: 978-953-51-0537-4, InTech (2012).
25. O.M. Sadek, S.M. Reda and R.K. Al-Bilali, *Adv. Nanopart.*, **2**, 165 (2013); https://doi.org/10.4236/anp.2013.22025.
26. P. Djomgoue and D. Njopwou, *J. Surf. Eng. Mater. Adv. Technol.*, **3**, 275 (2013); https://doi.org/10.4236/jsemat.2013.34037.
27. L.-F. Liao, C.-F. Lien and J.-L. Lin, *Phys. Chem. Chem. Phys.*, **3**, 3831 (2001); https://doi.org/10.1039/b103419g.
28. L. Goran, R. Hubert, R. Gert, S.K. Birgit, G. Neil, P. Jean-Philippe and S. Hermann, EUR 24403 EN, European Commission, pp. 1-36 (2010).
29. M.U. Cheku. B.Sc. Project, Department of Chemistry, Ibrahim Badamasi Babangida University, Lapai, Nigeria (2012).