VOL. 7, NO. 6, JUNE 2012 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences


www.arpnjournals.com

PROCESSING OF WASTE POLYETHYLENE INTO POLYMER-CERAMIC COMPOSITE THROUGH LIPID ASSISTED MELT COMPOUNDING

Yaw Delali Bensah, Benjamin Agyei-Tuffour, Lucas N. W. Damoah and Johnson K. Efavi
Department of Materials Science and Engineering, University of Ghana, Accra, Ghana
E-Mail: ydbensah@ug.edu.gh

ABSTRACT

In this work, a modified approach to melt compounding has been successfully developed to study the dispersion of kaolin particles in polyethylene and properties of polyethylene-kaolin clay composites. The process involved the use of melt compounding technique with vegetable lipid acting as a melting medium with the capability to enhance miscibility of the polyethylene with the kaolin which is necessary for strength improvement of the polyethylene-kaolin composite. Eight different compositional batches were formulated and cast at 245 ^{o}C. In all the thermal and mechanical properties as well the microstructure of the composites were studied. Comparisons of the composites with pristine polyethylene-lipid have shown an improved glass transition temperature (T_g) and the thermal decomposition temperatures as a result of changes in the chemical structure. Proportional kaolin additions did not change the crystallization temperature (T_c) of the blends as compared to the pristine polyethylene-lipid blend. Incorporation of 60% kaolin by weight in the polyethylene-lipid matrix significantly improved the mechanical properties of the composites to its peak and an increased compressive strength of 2.0 to 8.7 MPa has been measured. Scanning electron microscopic (SEM) analyses shows the formation of a web-like entanglement caused by the dispersion of the kaolin particles in the matrix.

Keywords: waste polyethylene, polymer ceramic composite, kaolin, lipid, coconut oil, melt compounding.

INTRODUCTION

Current increases in industrial and economic activities worldwide demands new, low-cost materials to meet the surging stringent conditions. In recent times, scientific and technological research has been focused on tailoring and modifying polymer properties through the assembly of inorganic layered fillers and polymers [1, 2].

Polyethylene (PE) has become one of the most widely used polyolefin polymers in the bag (grocery, piping and packaging), car (fuel tanks), toy industries etc., due to their versatility and low cost of production. Low density polyethylene (LDPE) accounts for almost 20 percent of polymer consumption, of which 40 percent is used in packaging applications. The waste from these polyethylene based materials which are by nature non-biodegradable, however, end up littering cities and towns, blocking gutters and drainage channels as a result of poor environmental management systems experienced in most developing countries such as in Ghana [3].

Recycling of these polyethylene based waste materials into composite materials for industrial applications is attractive due to the possibility of solving the environmental challenges it posses to communities. Highly and uniformly dispersed fillers in a polyethylene composite material can bring about an extensively enhanced gas barrier properties, heat distortion temperatures, enhanced flame resistance, decreases thermal expansion coefficient and improved mechanical properties as compared to that of conventional polymers [4, 5]. The most widely adopted approaches to forming polymer-clay composite materials are melt compounding of polymer and fillers, and in-situ polymerization of monomer that has been premixed with the filler materials. It has been well established that producing a high adhesion between the polymer matrix and the filler along with a good dispersion of the filler is very challenging [6, 7]. As a result of this, there is a clear demand to chemically bond the filler and the polymer materials, and disperse the filler material more homogeneously throughout the polymer matrix in order to gain the desired properties of the polymer-clay composites. Since polyethylene has no polar group in its structure, the homogeneous dispersion of the clay minerals in the polyethylene is hardly realized. In this respect, the clay is modified to enhance its interaction with the polyethylene because the modifiers make the hydrophilic clay surface organophilic. However, the organically modified clay does not disperse well in the polyethylene because it is still too hydrophobic [8-10].

In this study, lipids in the form of vegetable oil were used as a medium for melting the polyethylene. The underlying concept was in two folds. First is to reduce the viscosity of the polymer melt to enhance uniform dispersion of the filler, and second, is to utilize the alkyl, hydroxyl, carboxylic and the ester components of the triglyceride molecules in the oil to bond the polymer and the clay particles. Moreover, the triglyceride molecules through their hydrophilic functional groups favour the formation of a possible exfoliated structure. Triglycerides also offer the ability to control the number of polar groups through chemical modifications [11]. The polyethylene-kaolin composites were prepared with polyethylene and unmodified kaolin clay. The PE-kaolin composites were prepared for eight different compositional batches using this modified approach of melt compounding, and their physical and microstructural characteristics have been investigated.

MATERIALS AND METHODS

The kaolin clay material used for the study was obtained from deposits at Kibi in the Eastern region of

Ghana. The lipid used was from coconut vegetable obtained from industrial source as refined, bleached finished oil. The polymer materials used here were waste low density polyethylene (LDPE) used for water packaging. The polyethylene materials were collected from dustbins, households and the surroundings in the city of Accra, Ghana.

The collected polyethylene were washed and clean dried. The obtained kaolin was washed and dried in an oven at a temperature of 105°C for 3 hours. The kaolin was ball milled and sieved into particle sizes ranging between 50-125 μm.

The polyethylene-kaolin composites were formulated into eight different compositional batches (Table-1) with varying clay and lipid contents. The weighed clays were mixed with the polyethylene matrix in a solution mixing process using vegetable oil as the solvent at 245^{o}C with vigorous and continuous stirring to promote homogeneity of the melt. The polymer-ceramic melt was cast using aluminium mould at 245^{o}C and allowed to cool to room temperature.

The chemical composition of the kaolin was analyzed by X-ray fluorescence (XRF) using spectro-X Lab 2000. The bulk density (BD), apparent porosity (AP), the modulus of rupture (MOR) and the compressive strength (CS) of the formulated composite batches were determined by applying the principles of the American Society for Testing and Materials (ASTM) methods ASTM D6111-09, ASTM C830-09, ASTM C99 / C99M – 09, respectively. The surface morphology of the as synthesized composites was analyzed using Philips scanning electron microscope (SEM) model XL 30 ESEM-FEG. The thermal properties of the composites were studied by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) using SDT Q600 DSC-TGA standard instrument. The powder samples were subjected to a linear heating ramp from 20 °C to 850 °C with a heating rate of 10°C/min.

Table-1. Summary of the composite batch formulation.

Composition (Batch code)	**Polymer** (wt %)	**Ceramic** (wt %)	**Volume of added lipid** (ml)
PE-100-150	100	0	150
PE-90-138	90	10	138
PE-80-125	80	20	125
PE-70-112	70	30	112
PE-60-100	60	40	100
PE-50-88	50	50	88
PE-40-62	40	60	62
PE-30-50	30	70	50

RESULTS AND DISCUSSIONS

The kaolin used in the study has high volatile matter which is typical of Ghanaian kaolin with moderately low levels of fluxes as shown in chemical analysis data in Table-2.

Table-2. The chemical composition of the kaolin clay.

Oxides	**Composition** (wt. %)
SiO_2	34.72
Al_2O_3	23.66
Fe_2O_3	4.78
K_2O	1.18
Na_2O	0.97
Others	0.60
LOI	34.10

The first stage of the composite batch formulation is the dissolution of the polyethylene in the triglyceride which requires that the Gibb's free energy of mixing (ΔG_{mix}) must be zero or negative [12-14]. For the ΔG_{mix} to be negative as shown in equation (1) then the enthalpy of mixing (ΔH_{mix}) should be negative or weakly positive and the entropy of mixing (ΔS_{mix}) should also be positive:

$$\Delta G \text{ mix} = \Delta H_{mix} - T\,\Delta S_{mix} \quad (1)$$

The entropy of (ΔS_{mix}) because of increasing entropy will always be positive. Therefore, the only terms that influence the solubility are the absolute temperature (T) and the enthalpy of mixing (ΔH_{mix}). For solvent-polymer such as the triglyceride-polyethylene interactions the most recognizable theory that deals with these interactions is the Flory-Huggins theory [12-14]:

$$\Delta H = R\,T\,\chi\,\Phi_2 n_1\,x_1 \quad (2)$$

where χ is the Flory-Huggins interaction parameter, n_1 is the number of moles of solvent, Φ_2 is the volume fraction of the polymer, x_1 is the number of segments in the solvent molecule, and R is the molar gas constant. The value of the interaction parameter comes from the solubility parameters and the molar volume of the solvent:

$$\chi = v\,(\delta_1 - \delta_2)^2 / RT \quad (3)$$

By taking into account the non-symmetrical nature of the molecular sizes and each individual

polyethylene segment, then the lipid molecule occupy sites on the lattice. If each site is occupied by one molecule of the lipid or a monomer of the polyethylene chain, then the total number of sites is:

$$N = N_1 + \chi N_2 \quad (4)$$

Where N_1 is the number of solvent molecules and N_2 is the number of polymer molecules, each of which has χ segments. From statistical mechanics the entropy of mixing the solute and solvent is given by:

$$\Delta S = -k\,[N_1 \ln (N_1/N) + N_2 \ln (\chi N_2/N)] \quad (5)$$

By expressing $R = kN_A$, N_1 and N_2 can be converted to n_1 and n_2. Now, putting equations (2) and (5) into equation (1) gives the Gibbs free energy of mixing as:

$$\Delta G = RT\,[n_1 \ln \varnothing_1 + n_2 \ln \varnothing_2 + n_1 \varnothing_2 \chi] \quad (6)$$

From Equation (2), it becomes important that the dissolution of the polyethylene must correlate the triglyceride that is large enough to handle the macromolecule, but not to large to enlarge the value for the enthalpy of mixing so that the difference in solubility parameters must be close to zero and the molar volume must be very small. This has the overall effect of reducing the Gibb's free energy of mixing to larger negative numbers, and thereby improving the thermodynamics for the dissolution. It is therefore conclusive from Equations (2) and (5) that polyethylene solubility is strongly influenced by temperature, chemical structure, molar volume, and the value of the solubility parameter. Since the nature of the chemical structure of the polyethylene and the lipid are known but not for their solubility parameters hence matching the solubility parameters of the triglyceride and the polyethylene, the conditions for solubility can be advantageously increased by increasing the temperature. Thus, knowing that polyethylene is hydrophobic and the triglyceride molecules in the lipids have both polar and non-polar components, and without a fore-knowledge of the solubility parameters of the lipid and the polyethylene the dissolution of the polyethylene was capitalized on temperature increment. The dissolution of the polyethylene was monitored with increasing temperature until the minimum temperature that gave complete dissolution was attained. However, further increase in temperature above the casting temperature will cause excessive burning and charring of the triglyceride to carbon residue which may negatively affect the properties of the composite. Hence different temperature ranges were tried till an optimum temperature of 245°C to facilitate complete dissolution of the polyethylene in the lipid.

The effect of the triglyceride volume on the bulk density (BD), apparent porosity (AP), modulus of rupture (MOR) and compressive strength (CS) is seen in Figures 1 and 2. The porosity levels and the MOR generally decrease with an increase in volume of the lipid. This may be as a result of the breakdown of the polyethylene into its monomers, dimers or trimer than their continuous chain of monomers. Though this is thought to enhance the homogeneous dispersion of the kaolin in the matrix its deleterious effect of other materials properties must be curtailed. The authors' next line of research is to develop a synthetic pathway of networking the triglyceride molecules of the lipid and the polyethylene molecules by cationic polymerization. This is possible because the triglycerides have active sides such as double bonds and ester groups which are responsive to chemical reactions when the polyethylene are added as reactive diluents.

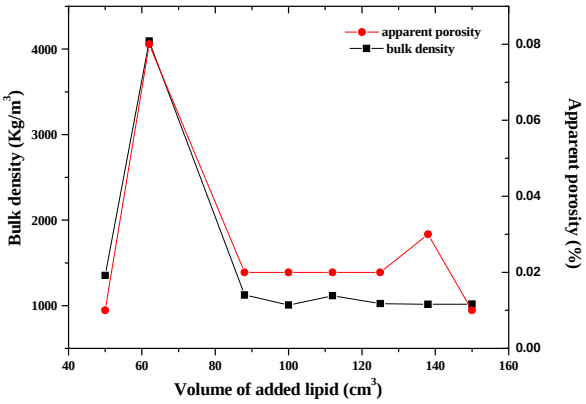


Figure-1. Bulk density and apparent porosity of the composite batches formed at different lipid content.

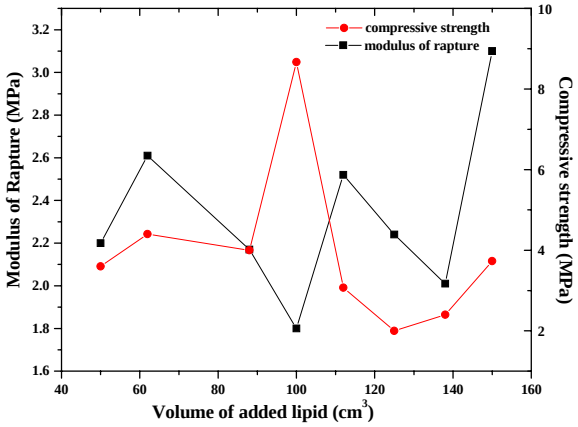


Figure-2. Modulus of rupture and compressive strength of the composite batches formed at different lipid content.

The bulk density obviously increased with an increase in the kaolin content as shown in Figure-3. The apparent porosity on the other hand decreased with lower content of the kaolin as a result of the decreased closed and blind pores in the kaolin particles. Sample composition PE-40-62 (Table-1) showed the highest in both the bulk density and the apparent porosity. Depending on the application of the composite there shall always be a trade-off between the bulk density and the apparent porosity. Thus a lower apparent porosity favours a higher tensile property whereas a higher bulk density favours a higher compressive property. This was evident in the modulus of rupture (MOR) and the compressive

strength (CS) results shown in Figure-4, as the MOR was highest for composition batch PE-100-150. This could be explained by the potential of a complete transesterification of the triglyceride molecules of the lipid by the ethylene monomers of the polyethylene. Furthermore, the absence of the kaolin particles intercalating between the continuous transesterified triglyceride chains enhanced the MOR value. Also, composition batch PE-40-62 and PE-70-112 also showed appreciable MOR values in spite of the high kaolin content of 60 wt% and 30 wt%, respectively. The compressive strength was recorded for composition batch PE-60-100 which has the highest lipid/polyethylene ratio. This gives the clue that a high lipid/polyethylene ratio coupled with optimum kaolin content will deliver an appreciable increase in both CS and MOR as it is in the case of composition batch PE-40-62 in Figure-4. From Figures 3 and 4 the optimum batch formulation can be achieved by toggling around composition batch PE-40-62.

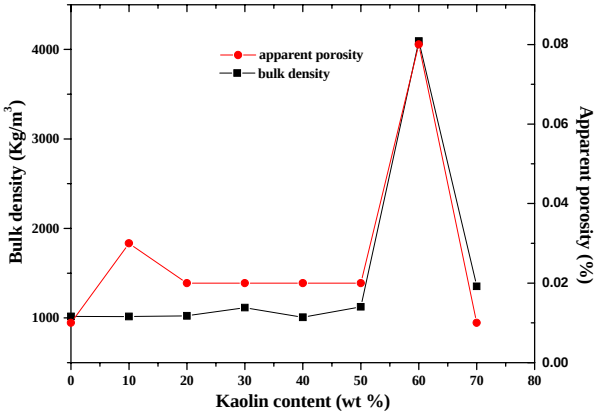


Figure-3. Bulk density and apparent porosity of the composite batches formed as a function of the loading amount of kaolin.

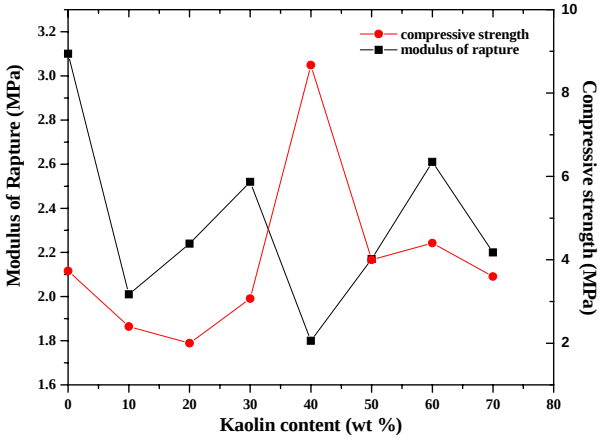


Figure-4. Modulus of rupture and compressive strength of the composite batches formed as a function lipid content.

The images in Figure-5 are SEM images of the surface morphologies of the composite batch compositions. The images in Figures 5(a) and 5(b) representing sample PE-100-150 free of kaolin at 20µm and 5µm resolution, respectively. The presence of nodules (solid) as observed in the micrograph indicate the development of phases due to differences in molecular weights formed at different portions in the bulk during the dissolution of the polyethylene in the lipid. The nodules are also thought to be formed as a result differences in surface tension between the two media. The Figures 5(c) and 5(d) of composition PE-30-50 forms a dispersion of web-like entanglement thought to be caused by the high kaolin content of 70 wt% as this nature of morphology becomes less visible with a decrease in kaolin content. The formed composite has the kaolin dominating as the matrix resulting in a lower property values as in Figures 1-4. The Figures 5(e) and 5(f) for composition PE-40-62 shows the dominant dispersion of the kaolin which accounts for the high BD and AP with a simultaneous appreciation in MOR and CS. This composition also shows the promise of being close to the optimum composition desired.

The observed trend shows that lower kaolin-lipid ratio does not favour nodule formation which is evident in sample PE-70-112 in Figures 5(g) and 5(h).

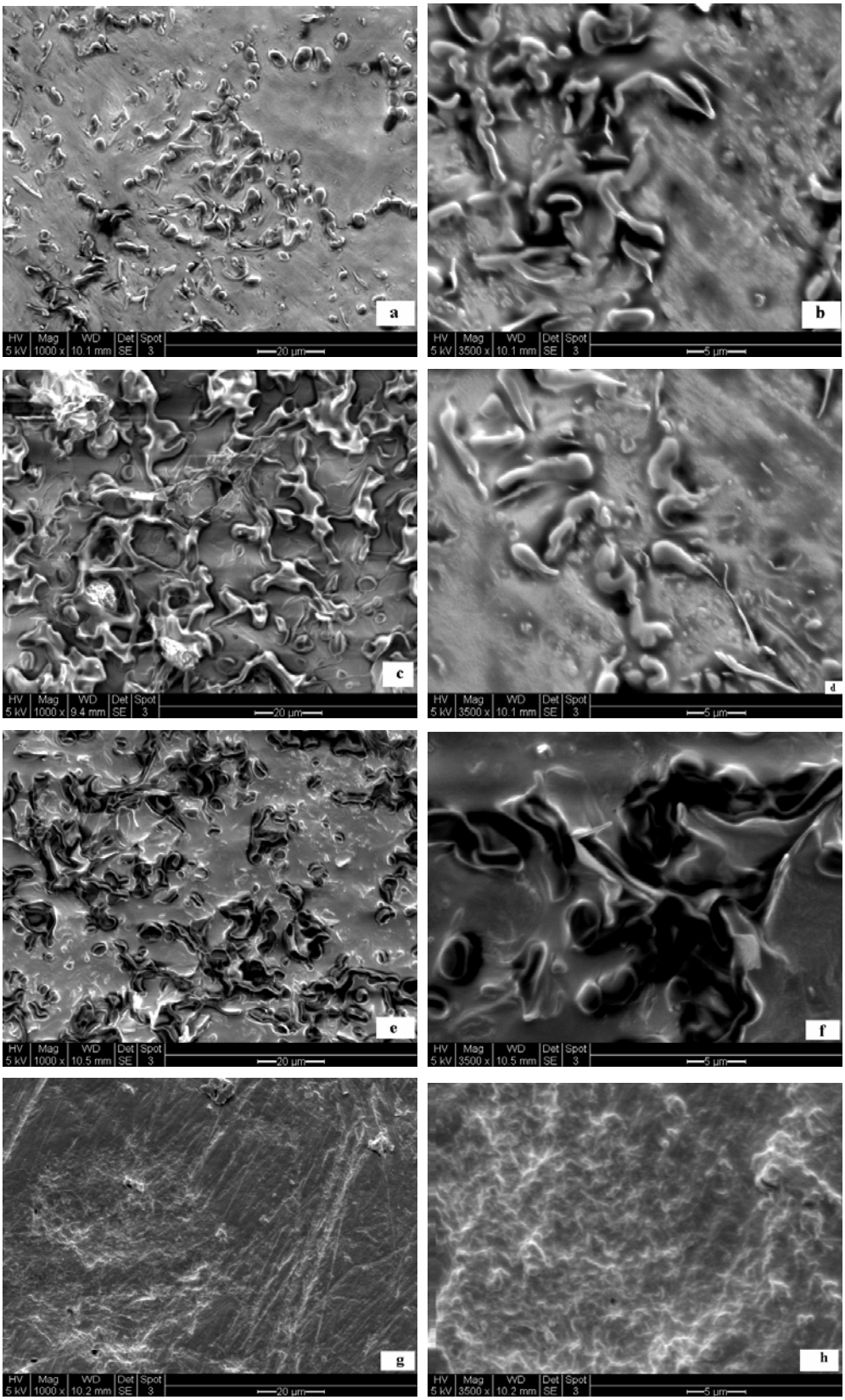
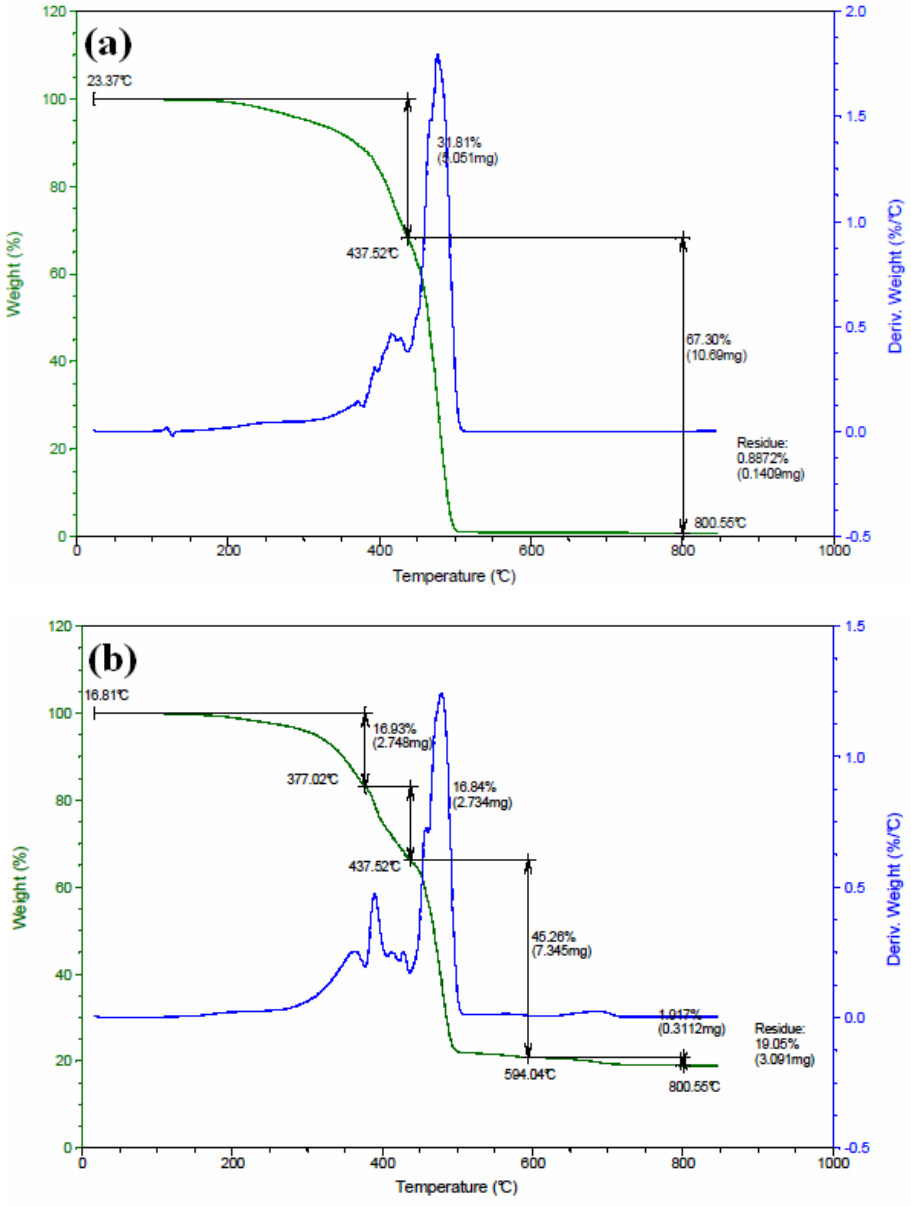


Figure-5. SEM images showing the surface morphologies of the composite batch compositions: (a-b) PE-100-150 (c-d) PE-30-50 (e-f) PE-40-62 (g-h) PE-70-112.

The results of differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) for four compositions whose thermal properties were promising are presented in Figure-6. The sample PE-40-62 showed a high glass transition temperature (T_g) of 390°C whereas the other samples showed their T_g between 280 - 300°C. This may be due to an appropriate blend between the lipid and the polyethylene evolving into an improved chemical structure making it able to withstand a higher thermal stress. All the samples showed no significant difference in the crystallization temperature (T_c) and melting temperature (T_m). Samples PE-30-50 and PE-40-62 improved retardation to combustion compared to sample PE-100-150 is mainly due to the high kaolin content which acts as suppressant. Two major weight losses were detected by the TGA for all the batch compositions. The pristine batch compositions PE-100-150 was completely burnt out at 500°C due to the organic nature of compositions leaving behind a residue of 0.89% of the starting material. Batch compositions (c) PE-70-112 (a) PE-40-62 (f) PE-30-50 left a residue of 20.97%, 44.22% and 70.45%, respectively at 500°C which approaches the T_m of the compositions. The presence of the exothermic peaks in all the batches shows that the losses are mainly due to the removal of organic compounds by combustion and gaseous materials than a decomposition reaction.



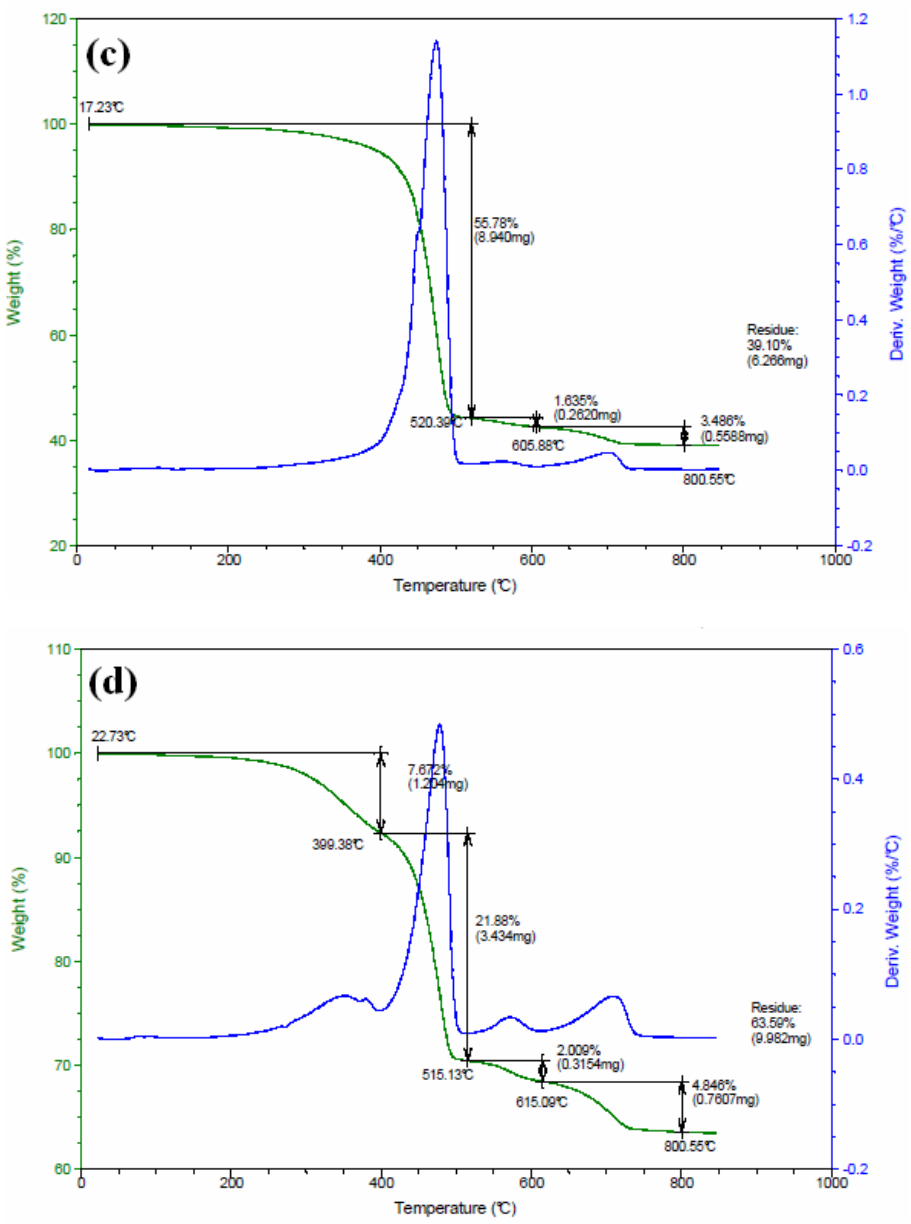


Figure-6. DSC-TGA thermographs for (a) PE-100-150 (b) PE-70-112 (c) PE-40-62 (d) PE-30-50

CONCLUSIONS AND FUTURE WORK

Chemical modification of polyethylene structure with the aid of a lipid to form composites has been successfully investigated and reported for the first time. The lipid was important to generate polyethylene-kaolin composites by melt compounding and the ability of the polyethylene to dissolve in the lipid facilitated the dispersion of the kaolin in the matrix. Preliminary results indicate that the resulting bulk density, apparent porosity, modulus of rupture and the compressive strength are sensitive to the polyethylene structure, lipid and clay content. The addition of kaolin to the polyethylene matrix enhanced the thermo-mechanical properties of the polyethylene matrix. A compressive strength and modulus of rupture values of up to 8.7 MPa and 2.61 MPa respectively were measured for the composite. Scanning electron microscopy analysis showed improved dispersion of the kaolin particles which is dependent on high kaolin/lipid ratio.

Further work would be to optimize the polyethylene-kaolin-lipid blends and to polymerize the lipid to the polyethylene to enhance the material properties. The effects of stirring on the blend and the use of nanosized kaolin would also be investigated.

ACKNOWLEDGEMENTS

This work was supported financially by the Organization of Research, Innovation and Development (ORID) of the University of Ghana. The authors would like to thank Mr. Emmanuel Frimpong-Brenya for his technical suggestions.

REFERENCES

[1] Leroux F. and Taviot-Guého C. 2005. J. Mater. Chem. 15: 3628.

[2] Evans D. G. and Duan, X. 2006. Chem. Commun. pp. 485-496.

[3] Wienaah M. M. 2007. Sustainable Plastic Waste Management-A case of Accra, Ghana, TRITA-LWR Master Thesis LWR-EX-07-10.

[4] Giannelis E.P. 1996. Adv. Mater. 8: 29.

[5] Wang Z. and Piannavaia T.J. 1998. Chem. Mater. 10: 3769.

[6] Mai Y. W. and Yu Z.Z. 2006. Polymer Nanocomposites. 1st Edn. Woodhead Publishing Limited.

[7] Ray S.S. and Okamoto M. 2003. Polymer/layered silicate nanocomposites: Progress in Polymer Science. 28(11): 1539-1641.

[8] Jeon H. G., Jung H. T., Lee S. W. and Hudson S. 1998. D: Polym Bull. 41: 107.

[9] Furuichi N., Kurokawa Y., Fujita K., Oya A., Yasuda H. and Kiso M. 1996. J. Mater. Sci. 31: 4307.

[10] Heinemann J., Reichert R., Thomann R. and Mulhaupt R. 1999. Macromol Rapid Commun. 20: 423.

[11] Lu J., Hong C. K. and Wool R. P. 2004. J. Polymer Sci: Part B: Polymer Physics. 42: 1441-1450.

[12] Flory P.J. 1942. J. Chem. Phys. 10: 51-61.

[13] Huggins M. L. 1941. J. Chem. Phys. 9: 440.

[14] Huggins M.L. N.Y. 1942. Acad. Sci. 43. pp. 1-32.