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Kinetics of Isothermal Degradation studies by Thermogravimetric Data: Effect of orange peels ash on thermal properties of High density polyethylene (HDPE)

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Abstrcat

High density polyethylene (HDPE) composite reinforced with 20wt% orange peels ash particles (OPAp) was prepared by compression moulding. Thermogravimetric analysis (DTA/TGA)_(space) was conducted on the HDPE/orange peels ash particle composite to clarify the effect of OPAp on the thermal decomposition behavior of the resultant composite. The values of the activation energy for thermal decomposition reflected the improvement of the thermal stability of the HDPE/OPAp composite. This study has established that the orange peels ash particles are beneficial to act as thermal decomposition resistant and reinforcing particles in the HDPE matrix composite.

Keywords: Polymer-matrix composites (PMCs), Thermal properties, Thermal analysis and Compression moulding

1. Introduction

In recent years, natural reinforcer (rice husk, bagasse, straw, banana and maiz stalk) in form of fiber or particulate has been widely used as reinforcement in thermoplastic composite materials. The natural reinforcers are lighter and cheaper and provide much higher strength per unit mass than most inorganic reinforcers. Besides ecological considerations, several technical aspects promote the renewed interest for the natural reinforcer as supplement or replacement for traditional reinforcer (e.g., glass fibers) in polymer composites [1-3].

Natural reinforcer from agricultural residues and forest products processing consist of lignocellulosic. As a resulted, they are subjected to thermal degradation during composite processing and application [1, 4]. It is of practical significance to understand and predict the thermal decomposition process of natural reinforcers and the knowledge will help better design composite materials for thermal apllication.

Previous research of thermal decomposition of natural reinforcers was primarily motivated by applications such as renewable biomass energy/natural fuels [5-7], forest fire propagation control [8]. Due to the complexity of thermal decomposition reactions of natural reinforcers, extensive researches has been done in determining individual behaviors of the main components or pseudo- components(e.g., pure cellulose, lignin, and hemicelluloses) [5-8].

Earlier works on the thermal decomposition of polymer reinforced with natural fibers shows that it has low thermal degradation of the polymer composites as a resulted of the lignocellulosic nature of natural fibers [4], which is not satisfactory. Hence there is need, to improve the thermal properties of polymer composites reinforced with natural fillers. It is in the light of the foregoing that the research on the investigation of the effects of orange peels ash on thermal properties of High density polyethylene was motivated.

2. Materials and method

2.1 Materials and Equipment

The orange peels were obtained from orange seller in Zaria, Nigeria, High density polyethylene (HDPE) was purchased from Chemical shop in Kaduna, Nigeria (see Plate 1). Equipment used in this research were; Metal mould, hydraulic press, Scanning electron microscope (SEM) and DTA/TGA Machine.

Plate 1: Photograph of orange peels and HDPE pellets

2.2 Method

The orange peels were grinded into powder; the powder was packed in a graphite crucible and fired with electric resistance furnace at a temperature of 1200^{o}C to form orange peels ash (OPA) (see Plate 2). The particle size analysis of the orange peels ash was carried out in accordance with BS1377:1990 [9]. 100g of the OPA particles were placed unto a set of sieves arranged in descending order of fineness and shaken for 15minutes. The particle retained in the BS. 63µm was used in this study.

Plate 2: Photograph of orange peels ash particles

The HDPE and OPAp were compounded by melting in a Haake 9000 mixer (New Jersey, U.S.A). 20wt%OPAp was added to HDPE matrix. The mixture were mixed at speed progressively up to 64rpm(3min with mixing speed of 8rpm, 4min at 38rpm and finally 3min at 64rpm) at a temperature of 185^{o}C was used. The samples were produced by compression moulding. The pellets obtained after compounding were placed in the moulding frame with the desired dimensions. The compression was done at a temperature of 185^{o}C and held for ten minutes with a progressively increasing pressure from 50 to 150bar. The press was cooled using cold water flow.

The scanning electron microscope (SEM) JEOL JSM-6480LV was used to identify the surface morphology of the composite sample. The samples were washed, cleaned thoroughly, air-dried and coated with 100 Å thick platinum in JEOL sputter ion coater. The digitized images were recorded.

Thermal decomposition (TA) was observed in terms of global mass loss by using a TA Instrument TGA Q50 thermogravimetric analyzer. The apparatus detects the mass loss with a resolution of 0.1 as a function of temperature. The samples were evenly and loosely distributed in an open sample pan of 6.4 mm diameter and 3.2 mm deep with an initial sample weight of 8-10 mg. The temperature change was controlled from room temperature (25±3°C) to 700°C at different heating rate of 5, 10, 15 and 20°C/min.

High purity Argon was continuously passed into the furnace at a flow rate of 60 mL/min at room temperature and atmospheric pressure. Before starting of each run, the Argon was used to purge the furnace for 30 min to establish an inert environment in order to prevent any unwanted oxidative decomposition. The TG and DTA curves were obtained from TGA runs using universal analysis 2000 software from TA Instruments.

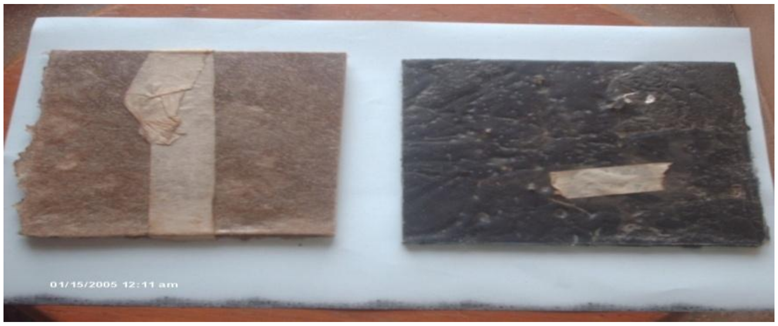
3. Results and discussion

3.1 Visual Observation

Macrostructural observation of the HDPE/OPAp composite revealed a uniform distribution of orange peels ash particles (OPA) in the HDPE matrix. The distribution of OPA particles is influenced by the compounding of the OPA particles and HDPE which results in good interfacial bonding between the OPAp and the HDPE (see Plate 3).

3.2 Surface morphology of the composite

The morphologies of the HDPE and its composite by SEM with EDS are shown in Plates 4-5. Morphological analysis using SEM clearly showed difference in morphology of the HDPE and that of HDPE/OPA composite (see Plates 4-5). The microstructure of the HDPE matrix revealed chains of lamellae and interlammeller amorphous structure with linear boundaries between adjacent spherulites (see Plate 4). The EDS spectrum of the HDPE: it can be clearly seen that the functional group of the HDPE were revealed, this is in par with earlier research of [9].



a) HDPE b) HDPE/OPAp

Plate 3: Photograph of the samples

The microstructure of the composite revealed that, when orange peels ash particles was added to HDPE, morphological change in the microstructure occurred. The microstructure revealed reasonably uniform distribution of orange peels ash particles in the HDPE matrix as a resulted of the compounding of the HDPE and the orange peels ash particles. The OPA particles phase is shown as white and the HDPE phase is dark. It can be seen that the orange peels ash particles are not detached from the HDPE surface; this support the earlier conclusion that there is good interfacial bonding between the HDPE and the OPA particles [9].

3.3 Thermal Stability

The thermal stability of the polymer composites plays a crucial role in determining the limit of their working temperature and the environmental conditions for uses, which are related to their thermal decomposition temperature and decomposition rate [10]. Figures 1-4 contains plots of the DTA/TGA decomposition data of the HDPE and HDPE/OPAp composite and their results are summarized in Table 1-2.

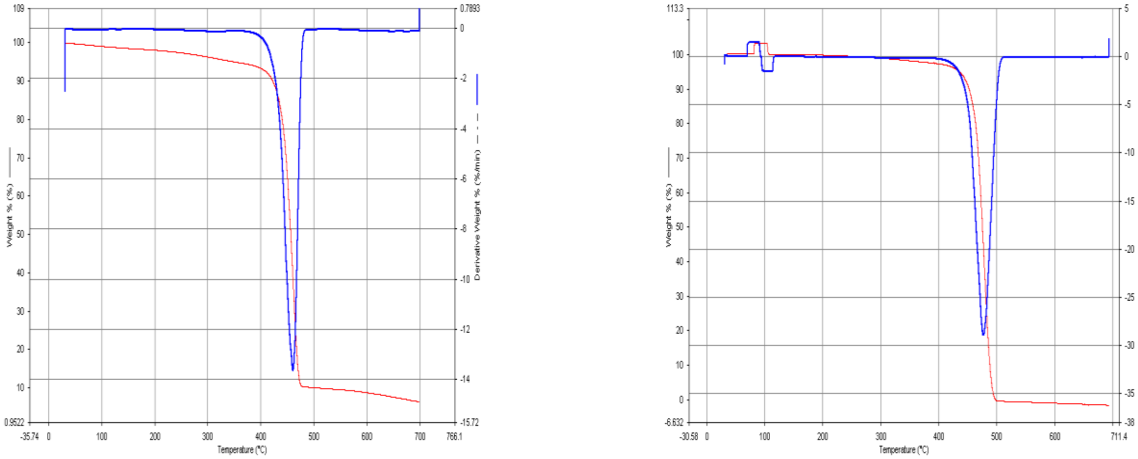
Table 1: Degradation Temperature of HDPE determined by DTA/TGA

Heating rate (min/°C)	$T_{\text{max. decomposition}}$	$T_{10\% \text{ weight loss}}$	$T_{30\% \text{ weight loss}}$	$T_{50\% \text{ weight loss}}$	$T_{70\% \text{ weight loss}}$	$T_{90\% \text{ weight los}}$
5	458.8	416.8	450.4	456.0	467.2	472.8
10	475.0	440.0	460.0	470.0	477.5	485.0
15	480.0	452.0	470.0	480.0	484.8	490.1
20	487.5	460.5	475.0	486.0	490.0	500.0

Table 2: Degradation Temperature of HDPE/OPA composite determined by DTA/TGA

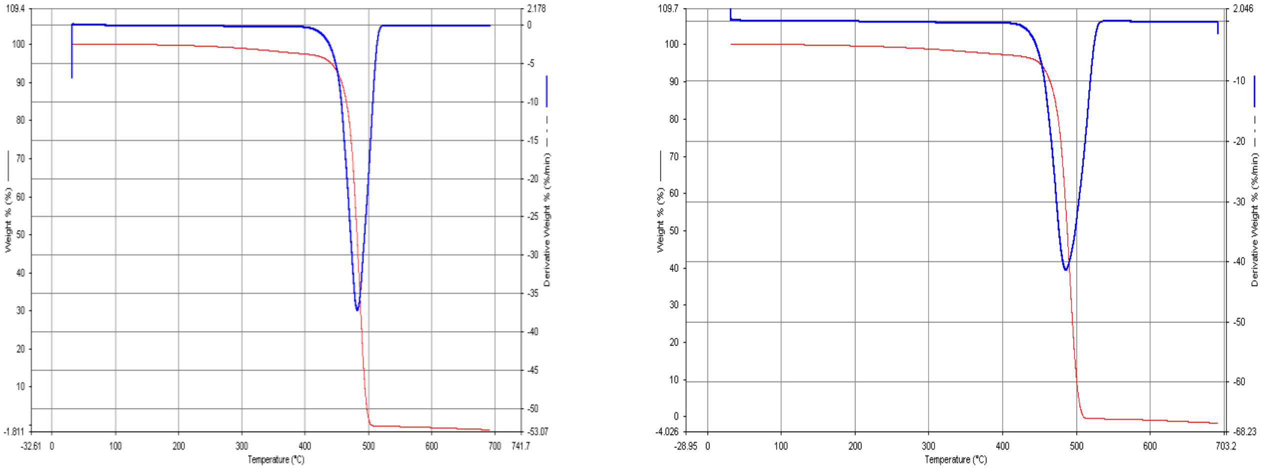
Heating rate (min/°C)	$T_{\text{max. decomposition}}$	$T_{10\% \text{ weight loss}}$	$T_{30\% \text{ weight loss}}$	$T_{50\% \text{ weight loss}}$	$T_{70\% \text{ weight los}}$	$T_{90\% \text{ weight loss}}$
5	461.0	422.4	450.4	458.8	467.2	484.0
10	475.5	445.0	464.0	470.0	480.0	490.0
15	486.8	453.0	476.0	482.2	489.0	500.0
20	490.0	465.0	480.0	485.0	495.0	514.0

TGA/DTA curves (see Figures 1-4) of the thermal decomposition for pure HDPE and the HDPE/OPAp composite exhibit only one dominant decline of the residual weight, indicating random scission of the HDPE main chains as the prevailing decomposition reaction [10-11].



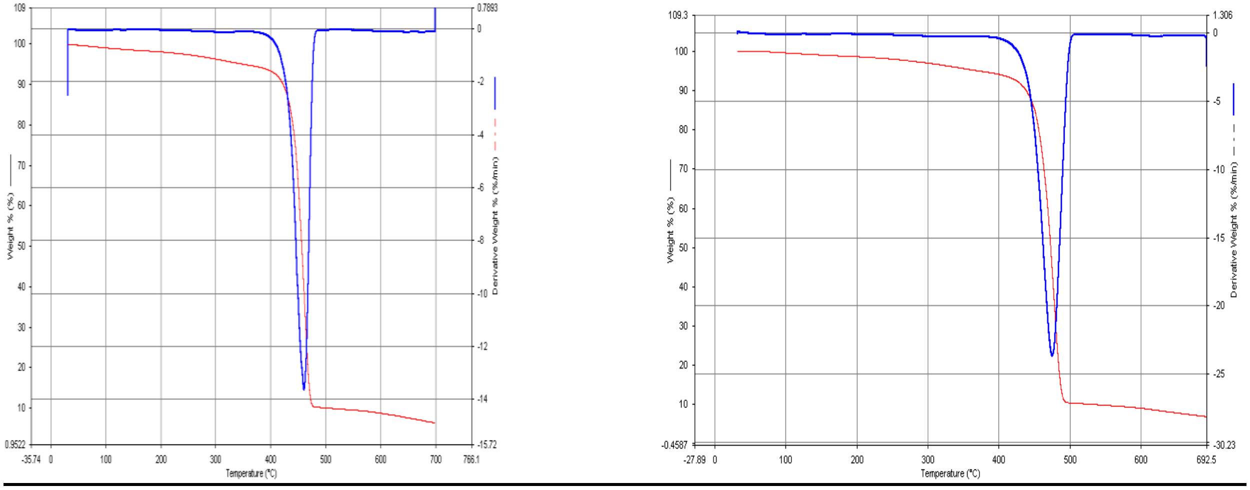
a) Heating rate of 5min/°C b) Heating rate of 10min/°C

Figure 1: DTA/TGA analysis of the HDPE at heating rate of 5 and 10min/°C



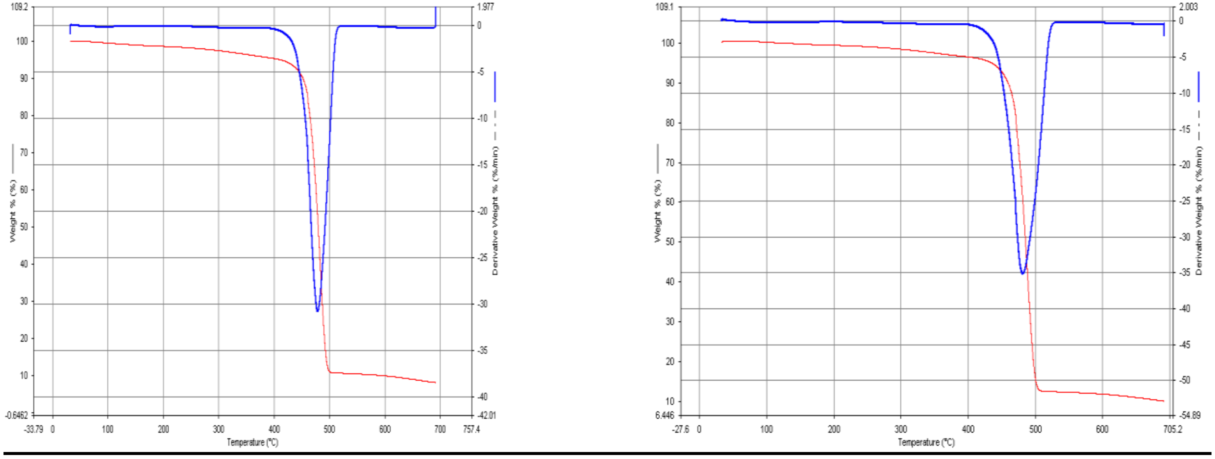
a) Heating rate of 15min/^{o}C b) Heating rate of 20min/^{o}C

Figure 2: DTA/TGA analysis of the HDPE at heating rate of 15 and 20min/^{o}C



a) Heating rate of 5 min/^{o}C b) Heating rate of 10min/^{o}C

Figure 3: DTA/TGA analysis of the HDPE/OPA composite at heating rate of 5 and 10min/^{o}C



a) Heating rate of 15 min/^{o}C b) Heating rate of 20min/^{o}C

Figure 4: DTA/TGA analysis of the HDPE/OPA composite at heating rate of 15 and 20min/^{o}C

In addition, the patterns of TGA curves for HDPE/OPAp composite is similar to that of HDPE (compare Figures 1-2 with Figures 3-4), meaning that the thermal decomposition of HDPE/OPAp composites may mostly stem from HDPE.

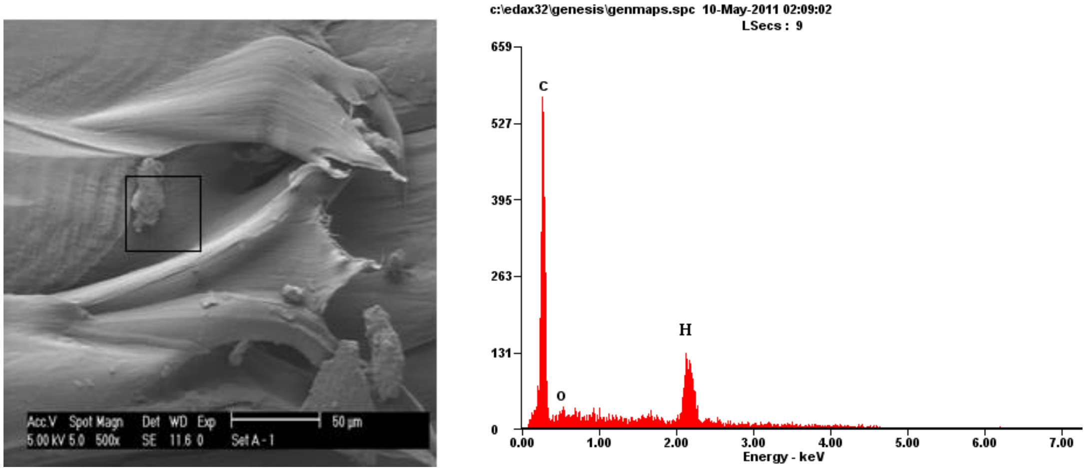


Plate 4: SEM/EDS of the HDPE matrix

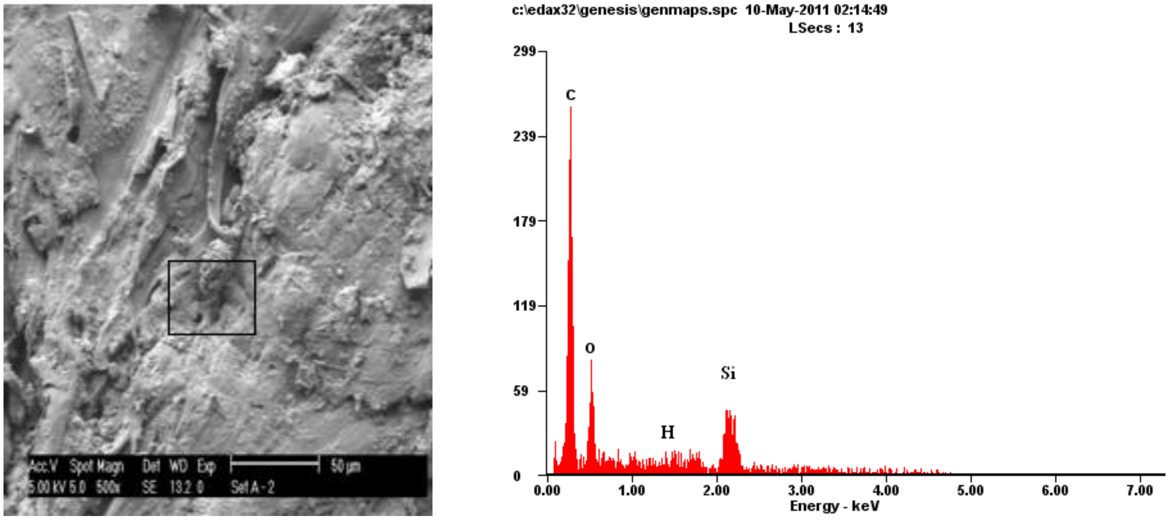


Plate 5: SEM/EDS of the HDPE/OPA composite

The pronounced single endothermic effects observed in the DTA curves correspond to the oxidative degradation process and the release of volatile matters. From the DTA curves, the temperature of maximal decomposition and destruction of the HDPE matrix and HDPE/OPAp composite fall in between 400 to 500^{o}C (see Tables 1-2). The presences of endothermic effects in the samples as a results of three processes: intermolecular dehydrogenation, vaporization and solid state decomposition of some additives [9]. The total burning and degradation of the residual polymer backbone (dehydrogenation HDPE) took place at temperatures interval of 300-500^{0}C. In the last temperature interval the mass loss was minimal; this last step is due to the degradation of the OPAp material in the composite [12]. The result indicated that the HDPE/OPAp composite biomass show less percentage of decomposition. At temperature above 500^{o}C, the residual weight stabilized agrees with the silica and carbon content earlier reported in literature [13]. Also the TGA/DTA curves shifted toward higher temperature regions with increasing heating rate, which was explained by the fact that polymer molecules does not have enough time to exhaust the heat with increasing heating rate, leading to slower decomposition rate and higher decomposition temperature due to slow diffusion of heat [10].

Incorporation of the OPA particles into HDPE matrix increased the thermal decomposition temperatures and the residual yields of HDPE/OPAp composite; this enhancing effect was more pronounced at higher heating rate. This result indicated that the presence of orange peels ash particles (OPAp) lead to the stabilization of HDPE and resulted in the enhancement of the thermal stability of HDPE/OPAp composite. In the HDPE/OPAp composite, the OPA particles act as physical barriers to prevent the transport of volatile decomposed products out of HDPE/OPAp composite during thermal decomposition [13]. Also the OPA particles induce protective barriers against thermal decomposition for organic species and retard the thermal decomposition. The phenomenon is attributed to the physical barrier effect of the incorporated particles which act as the mass and heat transfer barriers [12].

3.4 Thermal Decomposition Kinetics

The TGA/DTA curves of HDPE and that of the composite measured with several heating rates were used to evaluated the activation energy by differential isoconversional method. The activation energy of the thermal decomposition were obtained using two models: Flynn-Wall-Ozawa (FWO) and Kissinger's .

The Flynn-Wall-Ozawa model [8] has been used to determined the activation energy from dynamic tests by plotting the logarithm of heating rate as a function of the inverse of the temperature. The Flynn-Wall-Ozawa equations are shown in equation 1-2 [8]:

$$F(\alpha) = \left(\frac{A}{\beta}\right) \int_0^T \exp\left(\frac{E_a}{RT}\right) dT$$

--(1)

Using Doyle's approximation [8], Equation 1 can be simplified as follows:

$$\log \beta = \log\left(\frac{AE_a}{F(\alpha)R}\right) - 2.315 - 0.4567\left(\frac{E_a}{RT}\right)$$

-------------------------------------(2)

Where β is the heating rate, (a) is the weight loss, A is the pre-exponential factor, R is the universal gas constant, T is the absolute temperature and Ea is the activation energy of the thermal decomposition reaction. The values of the activation energy (Ea) for a specific weight loss was calculated from the slope of log β versus 1/T at different heating rates (see Figure 5).

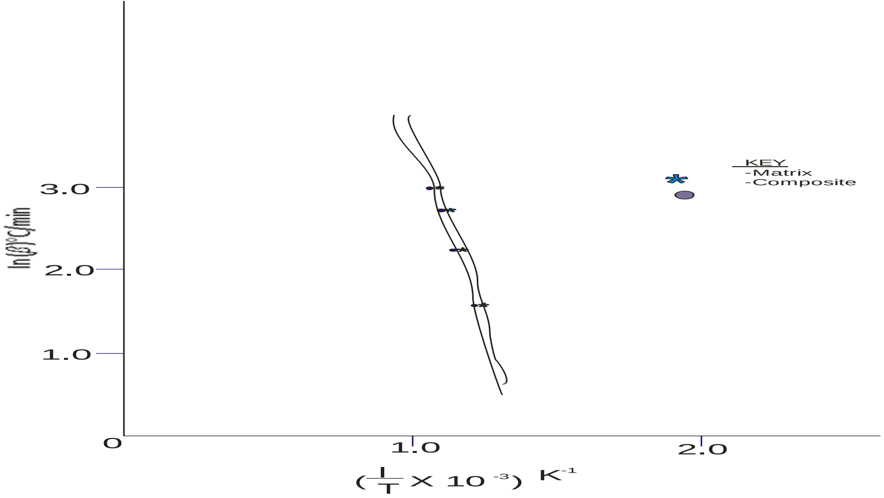


Figure 5: Plot According to Flynn-Wall-Ozawa method

The Kissinger's model [8] has been used to estimate the activation energy of the thermal decomposition involving the maximum temperature (Tdm) of the first derivative weight loss curves in TGA measurements at different heating rate. The resulting equation can be expressed as follows [8].

$$\ln\left(\frac{\beta}{T_{\mathrm{dm}}^{2}}\right) = \left[\ln\left(\frac{ZR}{E_{\mathrm{a}}}\right) - \ln F(\alpha)\right] - \left(\frac{E_{\mathrm{a}}}{RT_{\mathrm{dm}}}\right)$$

---(3)

Where β is the heating rate, Tdm is the absolute temperature at the maximum rate of the thermal decomposition, Z is the frequency factor and R is the universal gas constant. The value of the activation energy (Ea) was calculated from the slope of $\ln(\beta/T^2)$ versus 1/Tdm(see Figure 6).

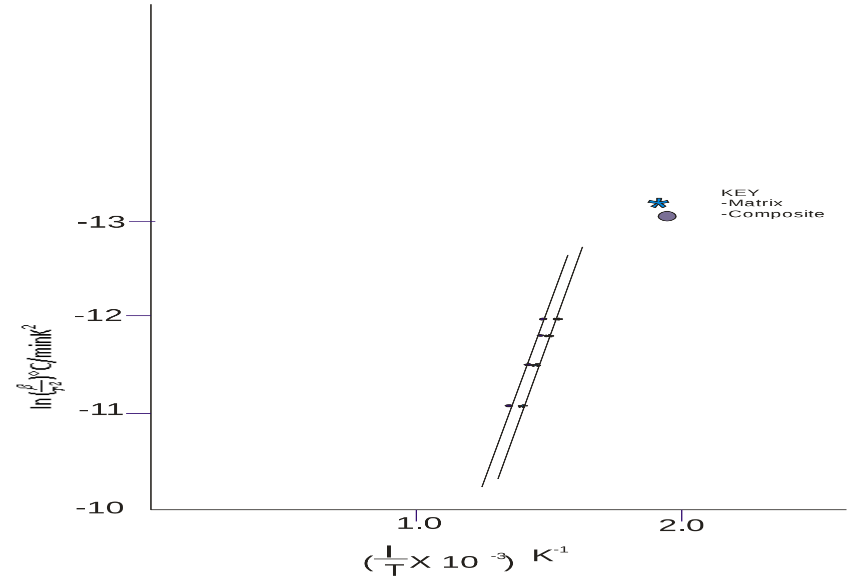


Figure 6: Plot According to Kissinger's method

The Flynn-Wall- Ozawa plot of HDPE and HDPE/OPAp composite (see Figure 5) exhibited a good linear relationship indicating that Flynn-Wall-Ozawa analysis was effective in describing the thermal decomposition kinetics of HDPE/OPAp composite. The Ea values of HDPE and HDPE/OPAp composite estimated from the Flynn-Wall- Ozawa analysis are shown in Table 3 and Figure 7.

Table 3 : The Values of Activation Energy obtained

Samples	Activation Energy(KJ/mol)	
	Flynn-Wall- Ozawa model	Kissinger model
HDPE	178.90	180.20
HDPE/20wt%OPAp	185.89	187.50

The Ea values of HDPE/OPAp composite were higher than that of HDPE matrix. The higher activation energy for thermal decomposition reflected higher thermal stability of the polymers [10]. The higher Ea values of HDPE/OPAp composite indicated that the thermal decomposition of HDPE/OPAp composite was more difficult because of the OPAp content. As previously described, the improvement in the thermal stability of HDPE/OPAp composite with the introduction of OPA particles was explained by the effective function of OPA particles as physical barriers both to retard the thermal decomposition of volatile components and to prevent the transport of volatile decomposed products in the polymer composites[5].

The Kissinger's plots of HDPE and HDPE/OPAp composite are shown in Figure 6. The Kissinger's plot of HDPE/OPAp composite exhibited a good linear relationship indicating that the Kissinger's was effective in describing the thermal decomposition kinetics of HDPE/OPAp composite. The Ea values of HDPE/OPAp composite calculated from the slopes of the plots of ln (β /T^{2}dm) versus 1/Tdm for HDPE/OPAp composite are summarized in Table 3 and Figure 7. The Ea values of HDPE/OPAp composite are higher than that of HDPE.

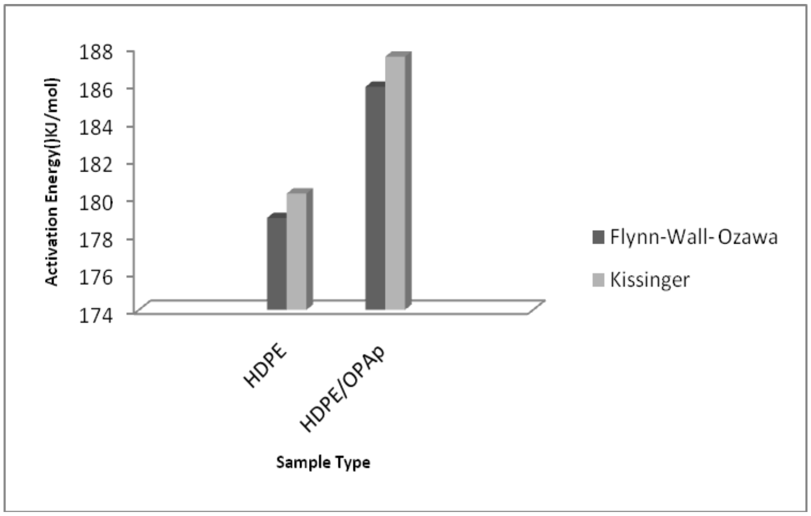


Figure 7: Variation of Activation Energy with sample type

These results revealed that the presence of OPA particles improved the thermal stability of HDPE/OPAp composite, which was attributed to the physical barrier effect to prevent the transport of volatile decomposed products in the polymer composite as well as the good thermal stability of the OPA particles. Comparing two models, the Ea values obtained from the Kissinger's model were slightly larger than that of the Flynn-Wall-Ozawa analysis, whereas two models revealed similar trend of the Ea values with the introduction of OPA particles.

In this study, the thermal stability and the thermal decomposition kinetics of HDPE/OPAp composite revealed that the activation energy of the thermal decomposition of the HDPE main chains in the polymer composite was increased with the introduction of OPA particles. Although the actual values of the activation energy for thermal decomposition should be influenced by various factors such as the estimation method of kinetic parameters, the mass and size of the specimens and their flow rate, and the operating conditions [11], two kinetic analyses used in this study exhibited their good applicability to the thermal decomposition kinetics for HDPE/OPAp composite. Varhegyi et al[12] found out that the thermal stability of polymer composites depended on the temperature of the melt, the size of the particles and the volume fraction of the reinforcers.

In the case of HDPE/OPAp composite, TGA kinetic analysis demonstrates that the introduction of orange peels ash particles into the HDPE matrix could increase the Ea values of HDPE/OPAp composite, which was related to the improvement in the thermal stability of HDPE/OPAp composite. From the morphology of the HDPE/OPAp composite (Plate 5), the HDPE/OPAp composite exhibited the dispersed structure of OPA particles in the HDPE matrix. This feature contributed to the improvement in thermal stability of HDPE/OPAp composite. This enhancing effect of OPA particles may be explained by means of high thermal resistance of OPA particles to increase the energy required for the thermal decomposition as well as good physical barrier effect against thermal decomposition [12].

Conclusion

The research is centered on the Kinetics of Isothermal Degradation studies by Thermogravimetric Data of orange peels ash particles on thermal properties of High density polyethylene (HDPE) composite. From the above results and discussion the following conclusions are made:

1. The HDPE/OPAp composite exhibited better thermal properties than that of HDPE with the introduction of 20wt%OPA particles.
2. The fairly uniform distribution of the orange peels ash particles in the microstructure of HDPE/OPAp composites is the major factor responsible for the improvement in the thermal properties.

3. The incorporated orange peels ash particles play a crucial role in improving the thermal stability by acting as effective physical barriers against the thermal decomposition in the polymer composite
4. The endothermic peaks shift to higher temperature with incorporating orange peels ash particle (OPA) in HDPE which reflects improvement in thermal stability.
5. The activation energy values of HDPE/OPAp composite calculated from the Kissinger’s and the Flynn-Wall-Ozawa models exhibited good reliance on describing the thermal decomposition of HDPE/OPAp composite.
6. This study has established that orange peels ash particles are beneficial to act as thermal decomposition resistant and reinforcing particles in the HDPE matrix composite.

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