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Thermal and Diffusion Characterization of High Density Polyethylene/Cellulose Blend Inoculated with *Aspergillus niger* Fungus

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ABSTRACT

Wider applications of plastics in packaging and agriculture have raised serious issue of waste disposal and pollution. The synthetic plastics normally resist microbial degradation and persist in the environment for longer times. This study focused on the effect of inoculating high density polyethylene/cellulose (HDPE/CELL) blends with *Aspergillus niger* on their diffusion thermal properties with a view to enhance biodegradability. HDPE granules and cellulose powder from acacia cell-sap were used to prepare the samples by hot pressing their molten mixture. Water absorption of the blends was evaluated by their immersion in water at room temperature for six weeks. Diffusion coefficients were determined using Ficks' model. The results indicate that water uptake increases with CELL loading and further on inoculation. The thermal degradation and thermal stability of HDPE/CELL blends in oxidative environment were studied using thermo-gravimetric analysis (TGA). The non isothermal kinetics of the decomposition processes were analyzed using the Broido integral method. Thermal stability of the blends decreased with CELL intake and on inoculation. The activation energies related to the correspondent reactions decreased after inoculation.

Key words: *High density polyethylene, biodegradability, Aspergillus niger, inoculation.*

1. INTRODUCTION

Most synthetic plastics were designed to be resistant to environmental degradation. The resistance of polyethylene to microbial attack is related to its hydophobicity, water repellency, high molecular weight and lack of functional groups recognizable by enzymatic systems. These entire properties limit the applications in which biodegradation is a desirable factor[1]. However, the problem related to the rampant growing of the volume of solid wastes has stimulated interest in the development of biodegradable plastics. Depletion of petroleum resources and escalating prices of the petroleum based- polymers are added causes that has led to attempts to find a promising alternative for products that have a short life cycle or cannot be practically recycled. A more feasible option can be reached by the combined usage of the synthetic polymers and the available bio-resources. The use of biotechnological materials obtained from renewable resources offers many ecological and economic advantages such as low density, high specific strength and modulus, easy of surface modification, wide availability and much cheaper compared with the synthetic polymers, Rowell *et al*[2].

High density polyethylene is one of the most vital polymers with wider applications in packaging, agriculture and industry. It is highly inert to micro-organisms and hence cannot be easily metabolized. Nevertheless, it is possible to enhance its biodegradability by simply incorporating additives such as starch and cellulose in the HDPE matrix to form a blend. The addition of biopolymers to synthetic polymers ensures susceptibility to microbial attack, Mali *et al*[3]. This leads to physical embrittlement of the polymer, leaving a porous and mechanically weakened polymer. Biopolymers also improve the hydophilicity of HDPE due to increased internal hydrogen bonding. In this study, HDPE was blended with cellulose as a biopolymer. Cellulose is an abundant natural polymer and is renewable, inexpensive and biodegradable. It is a linear polysaccharide with high molecular weight, which provides plants with rigidity.

Thermal analysis technique provides a powerful research tool for obtaining both qualitative and quantitative information about the effects of biodegradation on thermal properties of the degraded blends[4, 5]. Thermo-gravimetric analysis has been used in this study to investigate the degradation of HDPE/CELL blend by *Aspergillus niger* and consequently give information on mass loss, decomposition temperatures and the overall thermal stability. Broido integral method provided feedback on the non isothermal kinetics and activation energies of the inoculated blends. The water absorption capacity and the biodegradability are the most important properties for biodegradable materials. Water absorption is an important parameter for any polymer particularly for cellulose and starch blends since they are hydrophilic polymers. Biopolymers such as starch and cellulose influences the water absorption of HDPE/CELL blends. Fick's model was used to monitor water uptake behavior in the samples. For this purpose, several samples were submitted to a strain *Aspergillus niger* for 60 days. Both un-inoculated and inoculated samples were analyzed with a view to give an insight on the biodegradation process. The objective of this work is the study of thermo-gravimetric analysis and sorption behavior of HDPE filled with biodegradable additive

(cellulose) in order to analyze and characterize their degradation process using *Aspergillus niger* culture.

2. EXPERIMENTAL

2.1 Materials and methods

High density polyethylene-(HD6605) with a melt index of 0.005Kg/10min (190 °C, 2.16 Kg) and a density of 948 Kg/m^3 was obtained from Afro-plastic industry in Nairobi-Kenya. Cellulose was obtained from the cell sap of acacia tree at Kenyatta University while spores of *Aspergillus niger* fungus were provided by the Plants and Microbial Science of Kenyatta University.

2.2 Sample preparation

Fourteen kinds of samples were prepared by hot pressing the molten mixture of HDPE and cellulose mixture carefully mixed with a stirrer fitted on a motor with variable rotation speed to ensure blend homogeneity. Their composition is detailed in Table 1. Seven samples were un-inoculated; labeled P and the rest were inoculated; labeled PF.

Table I: Masses of HDPE and cellulose as well as their % concentrations.

MASS (g)		MASS CONCENTRATIONS (%)	
HDPE	Cellulose	HDPE	Cellulose
8	0	100	0
7.6	0.4	95	5
7.2	0.8	90	10
6.8	1.2	85	15
6.4	1.6	80	20
6.0	2	75	25
5.6	2.4	70	30

2.3 Sample inoculation

A suspension of potato dextrose agar (PDA) was prepared and equal amounts (150 ml) sub-divided into seven sterilized conical flasks. The PDA in the flasks was allowed to cool in order to solidify. A strain of *Aspergillus niger* was then dropped on top of the PDA in the sterile laminar flow safety hood. Seven samples were then inoculated with *Aspergillus niger* culture in the conical flasks and incubated at 30 ºC for 60 days.

2.4 Diffusion test

This test was carried out to study the water resistance in both inoculated and un-inoculated HDPE/CELL blends. All the samples were dried at 80 °C in a vacuum oven for 3 hours, cooled in a desiccator and immediately weighed to the nearest 0.001 g. Each sample was placed in a conical flask containing 10 ml of distilled water maintained at room temperature. The flasks were firmly covered by aluminium foil to prevent entry of moisture. The samples were then removed weekly from the water one at a time, gently blotted with tissue paper to remove the excess water on the surface, weighed to the nearest ± 0.001 g immediately and returned in the water. The weighings were repeated at the end of every week for 6 weeks and values recorded. Percentage increase in weight during immersion was calculated to the nearest 0.01 %.

2.5 Thermal degradation

Thermal-gravimetric analysis was used to determine the degradation temperature of the samples. Both un-inoculated and inoculated HDPE/CELL blend samples were scanned using Lindiberg Blue Tube Furnace (TF55035c-1) within a temperature range of 25 °C-550 °C at a heating rate of 5 °C/minute. The mass of the samples was measured using a sensitive balance and the initial mass of each blend was 10 mg. The process was carried out in an oxidative environment.

3. RESULTS AND DISCUSSION

3.1 Effect of cellulose on water uptake

The water uptake phenomenon can be observed through figure I which shows that water uptake of the HDPE/CELL blends increased with CELL content and immersion time.

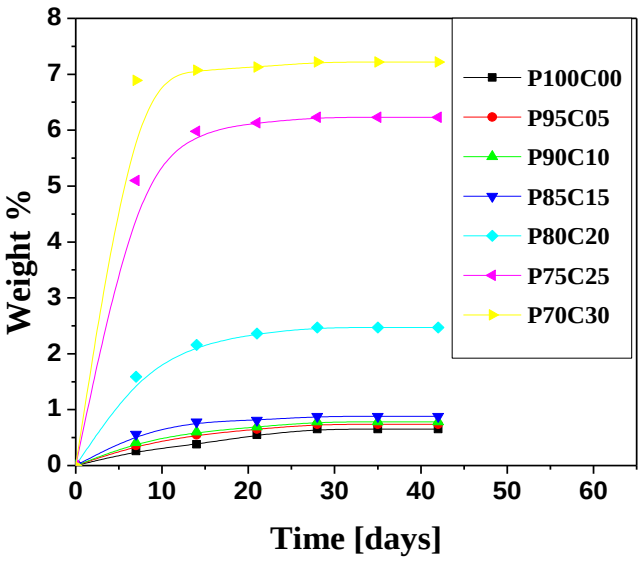


Figure I: Weight % water uptake versus immersion time in days for un-inoculated HDPE/CELL blends.

From the graph, it is evident that there was little water uptake in the pure HDPE (P100:C00). This resistance to the water absorption capacity by the pure HDPE was contributed to by the hydrophobicity of the polymer matrix. The water diffusion was strongly influenced by cellulose content as showed by the higher weight percentage of HDPE/CELL: 70/30. Bio-based synthetic polymers tend to absorb water due the presence of hydroxyl groups in the biopolymers. Starch and cellulose do form hydrogen bonds with water due to their polar character[6]. Since cellulose is highly hydrophilic, it's a higher affinity for water molecules and thus the high content of cellulose in HDPE influenced higher water uptake. There was a sharp increase of water absorption during the first seven days which then slowed down reaching equilibrium. The progressive decrease in the rate of water uptake with duration of immersion could be due to a concentration gradient across the two materials of the blend. The blends containing 20 %, 25 % and 30 % of cellulose showed higher water uptake and those blends containing 0 %, 5 %, 10 % and 15 % of cellulose content differ slightly from each other. This was expected due to the low concentration of cellulose particles near the blend surfaces while the rest were positioned deep in the matrix. The interior cellulose particles were not available for hydrogen bonding with the water molecules since they were trapped in the HDPE matrix. Higher cellulose loading made it possible for the cellulose particles to crowd in the blend resulting into its higher concentration near the blend surface. The exposed cellulose particles readily interacted with the water molecules leading to increased moisture uptake.

3.2 Effect of inoculation by *Aspergillus niger* on water uptake

Cellulose is a biopolymer that degrades when exposed to the fungi and bacteria environment. HDPE is formed by carbon-carbon (C-C) linkages in which these linkages are not susceptible to microbial attack. The presence of alkyl groups which are non-polar also offer an increased resistance to moisture uptake. Cellulose when blended with HDPE introduces hydroliphic characteristics into the polymer matrix thereby increasing the moisture infiltration tendency as well as microbial attack. HDPE/CELL blends when exposed to a strain of *Aspergillus niger*, the fungus attacks the hydrogen bonds in the cellulose zones in the matrix which is entirely utilized as the sole provider of energy for the fungus. During inoculation of the diffusion samples, the growth of *Aspergillus niger* colony increased with cellulose loading. Inoculation thus creates holes and voids in the HDPE/CELL blends making the polymer perforated. This in turn creates room for water infiltration in the polymer.

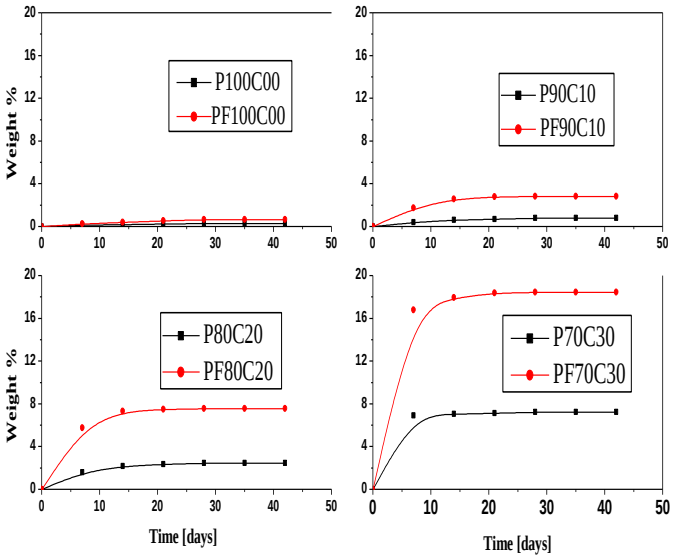
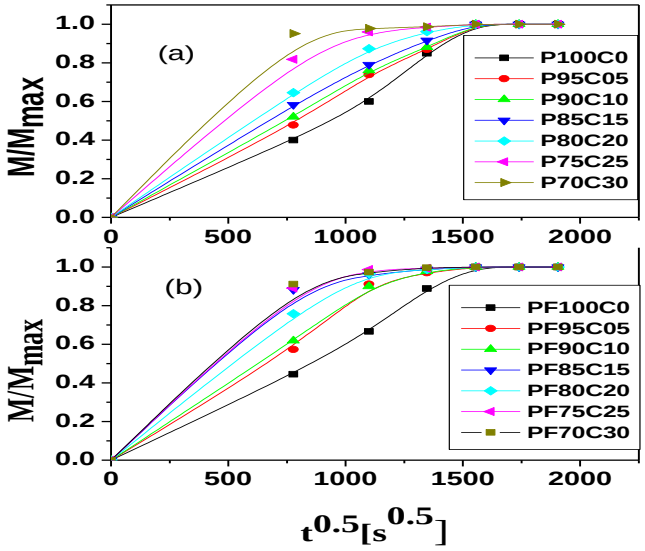


Figure II: Effect of inoculation on weight % of selected HDPE/CELL blends.

From figure II, it can be deduced that percentage water uptake depends on both cellulose concentration and inoculation. *Aspergillus niger* assimilated the cellulose making the blends perforated and thus enhancing diffusion of water in the HDPE/CELL blends. Compared to the un-inoculated blends, the increase in the moisture uptake is higher during the initial days of immersion which then consecutively and progressively decreases reaching a plateau on saturation. Therefore, the inoculated HDPE/CEL blends allow a higher moisture uptake than the un-inoculated HDPE/CELL blends and that is probably due the impact caused by the fungus.

3.3 Determination of diffusion coefficients

The weight gain resulting from moisture absorption can be expressed in terms of two parameters, the diffusion coefficient or diffusivity, D , and the maximum moisture content, M_{max} as given by equation 1[7]. Figure III displays representative Fickian diffusion plots of M/M_{max} versus $t^{1/2}$ for both un-inoculated and inoculated HDPE/CELL blends in distilled water. The initial linear curve indicates that diffusion followed a Fickian process. Diffusivity is determined from the initial slope of the plot (slope is $D^{\frac{1}{2}}$). The results are summarized in Table II.



$$\frac{M_t}{M_{max}} = \frac{4}{h\sqrt{\pi}}\sqrt{Dt} \qquad (1)$$

Table II: Fickian diffusion coefficients for un-inoculated and inoculated HDPE/CELL blends.

%HDPE: %cellulose	Diffusivity,×10^{-8}(cm^2/s)	
	Un-inoculated	Inoculated
100 : 0	0.59±0.40	0.66±0.98
95 : 5	0.76±0.62	1.16±0.43
90 : 10	0.81±0.60	1.19±0.87
85 : 15	0.91±0.38	1.24±0.78
80 : 20	1.25±0.29	2.02±0.69
75 : 25	1.97±0.70	2.44±0.99
70 : 30	4.76±0.57	5.56±0.88

Higher M_{max} and D values are seen in blends having higher concentration of cellulose as well as those blends that have been inoculated. These results can be attributed to the increased hydrophilic nature of the HDPE/CELL by virtue of the presence of an abundance of hydroxyl groups which are available for interaction with the water molecules.

3.3 Thermal stability of the blends

3.4.1 Effect of cellulose on thermal stability of the blends

All the HDPE/CELL samples both inoculated and un-inoculated were analyzed to study their thermal stability and to obtain their kinetic parameters which give information about the thermal decomposition process of these blends. The parameters may be used to reveal the changes that occur in the molecular chains as a result of the thermal degradation process.

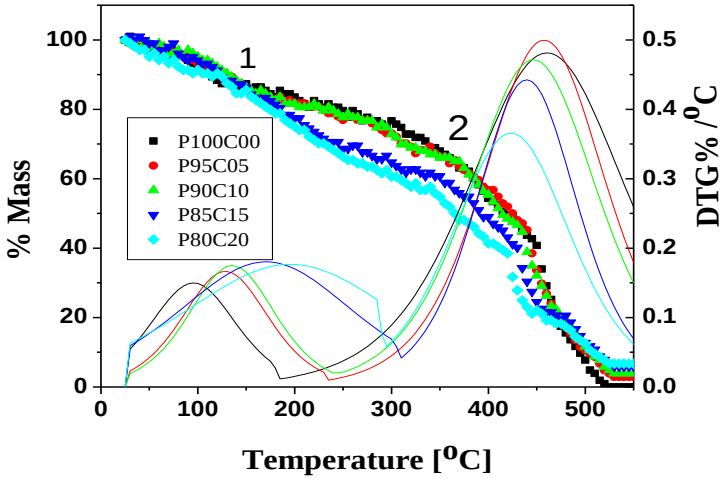


Figure IV: TG and DTG curves of HDPE and its CELL blends.

SAMPLE	T_C (^OC)	
	2nd stage	1st stage
P100C0	461.2 ±2.31E-13	93.1±4.43E-14
P95C5	457.4±8.23E-14	133.4±6.23E-13
P90C10	448.4± 7.25E-14	141.5±8.07E-13
P85C15	438.6± 9.19E-14	172.0±7.21E-14
P80C20	424.3± 8.29E-14	200.1±5.37E-14

TGA of un-inoculated HDPE/CELL blends are shown in figure IV.

It is apparent from figure IV that weight loss occurred in a two-step process. Specifically, two well-defined stages can be observed in the TG and DTG thermo-grams of all the samples. **Stage 1** is characterized by random chain scission, branching and breakage of glucosidic linkage in cellulose. This is a secondary thermo-degradation process occurring between 50 ^oC and 200 ^oC during which slight mass loss was registered. This is attributed to the initial moisture trapped in HDPE matrix, Lomakin *et al*[8]. **Stage 2** is due to pyrolysis of HDPE backbone. This stage represents the main weight loss occurring at a temperature range of (350 ^oC-480 ^oC) and is assigned to the complete degradation of the carbon chains of the HDPE matrix, which constitute the main component of the samples. For both stages, the rate of mass loss and ash content increases with cellulose loading. The phenomena leading to mass loss due to thermal degradation can be better studied using the derivative mass loss curves which show the rate at which materials decompose[9]. The highest weight loss occurred at 461.2 ^oC for the pure HDPE.

This explains the presence of a maximum peak in the derivative weight loss curve (DTG) at 461.2 ^oC as shown in figure IV. The results also show that the peak decomposition temperatures (T_c) of stage 2 are higher than those of stage 1 since the former stage is assigned to main decomposition of HDPE whose strong covalent bonds require greater heat energy to dissociate. This degradation is due to the fact that HDPE is composed of C-C bonds in the main chain, thereby allowing a temperature increase promotes random chain scission, with associated thermal degradation and de-polymerization occurring at the weak sites of the HDPE main chain, Kim *et al*[10]. T_c for stage 1 increases with CELL intake due to increase in the glucosidic linkages in cellulose while T_c for stage 2 decreases with increasing CELL intake due to the decrease of the HDPE backbone. This in turn leads to decreased thermal stability of the blends. Peak thickness for stage 1 increases with cellulose loading with the blend with 20 % cellulose being broader.

This effect is as a result of increased fraction of cellulose and its heterogeneity in the matrix. Conversely, the trend in stage 2 is such that peak thickness narrows with cellulose intake due decreased fraction of HDPE in the blend matrix. Above 500 ^oC, the quantity of HDPE residue was very small due to its breakdown into gaseous products at higher temperature. The thermal degradation of all the blends was retarded above 500 ^oC because of the increased ash content. Table III gives a summary of the peak decomposition temperatures of HDPE/CELL blends obtained from the DTG curves.

Table III: Peak decomposition temperatures of un-inoculated HDPE/CELL blends.

The peak decomposition temperature for pure un-inoculated HDPE was found to be 461.2 ^oC. The peak decomposition temperature reduced with cellulose content hence subsequent decrease in thermal stability.

3.4.2 Effect of inoculation on thermal stability of the blends

The HDPE/CELL samples both inoculated and un- inoculated have been analyzed by TGA to establish the effect of *Aspergillus niger* fungus on the thermal degradation and more so the peak decomposition temperature of the blends. The effect of cellulose and inoculation on the peak decomposition temperature is summarized in figure V.

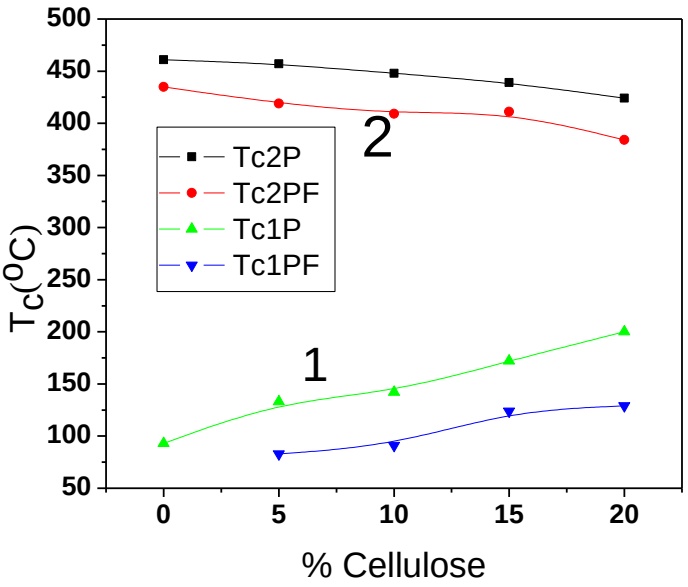


Figure V: Effect of inoculation on the T_c of the HDPE/CELL blend.

The effect of inoculation on the peak decomposition temperature for both stages is clearly seen from figures V whereby the peak decomposition temperature of un-inoculated blends are higher than the inoculated ones due to continuous polymer chains in the un-inoculated ones. Certainly, inoculation by *Aspergillus niger* perforated the HDPE matrix which required less heat energy to thermo-degrade. This in turn lowered the decomposition temperature. $T_{c\ p100}$= 461.2 ^oC, $T_{c\ pf\ 100}$=434.7 ^oC, $T_{c\ p80}$=424.3 ^oC, $T_{c\ pf80}$= 383.7 ^oC. The effect of inoculation improved with increase in the cellulose loading due to the presence of hydroxyl groups in cellulose that provided comfortable zones for attack by *Aspergillus niger*.

3.4.3 Activation energy

The Broido method has been used to evaluate the kinetic analysis of the main thermal decomposition process for both inoculated and un-inoculated blends. Figure VI shows the activation energy plots for the un-inoculated HDPE/CELL blends.

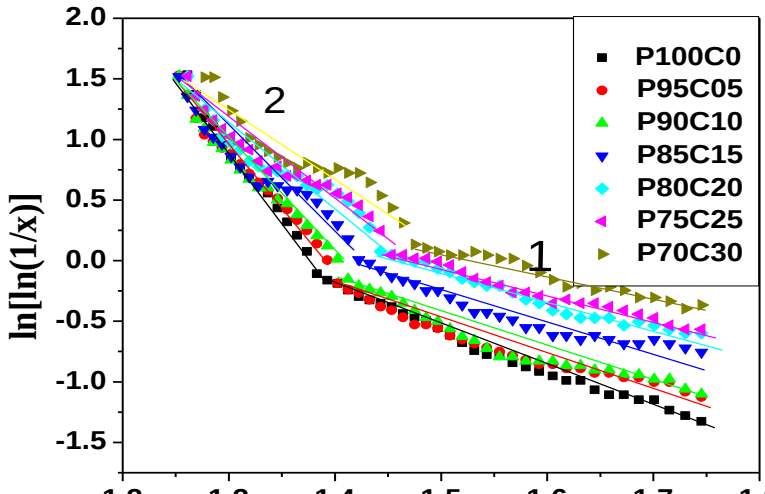


Figure VI: Master curves fitted with the Broido equation for un-inoculated HDPE/CELL blends

SAMPLE	E_a1 (kJ/mol)	E_a2 (kJ/mol
P100C0	27.4±0.38	100.6±0.53
P95C05	20.5±0.46	81.4±0.53
P90C10	22.0±0.82	74.0± 0.77
P85C15	20.8±0.33	57.3±0.75
P80C20	19.9±0.75	49.9±0.57
P75C25	18.3±0.48	49.0±0.66
P70C30	16.6±0.74	45.7±0.82

The activation energy was determined to describe the energy consumption of the initiation of the thermal degradation process. The analysis of the activation energy of the blends was carried out based on the Broido equation[11] and adjusting experimental values to the following equation;

$$\ln\ln\left(\frac{1}{x}\right) \cong -\frac{E_a}{RT} + \ln\left(\frac{RZ}{\beta T^2{}_{Max}}\right) \quad (2)$$

The graphs in figure VI are linear for both stages hence in total consonance with the Broido equation. The activation energy of each blend was obtained from the slopes of the plots lnln(1/x) versus 1000/T by multiplying the slope of each graph with the gas constant R. The E_a values are shown in Table IV.

Table IV: Activation energies for HDPE/CELL blends

There is a significant change in activation energy values between the 1st stage and 2nd stage for HDPE/CELL samples. From figure VI, it's evident that the activation energy of 1st stage is less than 2nd stage. This is because the former process is assigned to decomposition of cellulose which decomposes at a lower temperature than HDPE. It can be seen from Table IV that the activation energy of neat HDPE is higher than that of the blends for both stages. The activation energy is also seen to reduce with cellulose content. The blends containing 30 % loading exhibit lower activation energy indicating lesser thermal stability, whereas those with 0 % and 5 % loading show greater activation energy indicating that these samples have higher thermal stability.

3.4.4 Effect of inoculation on the activation energy of HDPE/CELL blends

	E_a (kJ/mol)			
	Un-inoculated		Inoculated	
SAMPLE	1st	2nd	1st	2nd
P100 C0	100.6±1.38	27.4±0.54	76.3±2.98	16.4±0.77
P95 C5	81.4 ±1.11	20.5±4.76	72.6±0.75	18.0±1.76
P90C10	74.0 ±4.32	22.0±3.87	69.2±0.75	16.2±0.87
P85 C15	57.3± 3.86	18.6±5.85	65.8±1.18	18.7±2.00
P80C20	49.9±7.03	19.9±2.64	46.3±0.99	21.2±2.51
P75C25	49.0±2.93	18.3±1.98	43.0±2.11	17.8±1.03
P70C30	45.7±3.53	16.6±2.42	42.3±2.34	16.0±0.95

Figure VII shows the impact of inoculation on activation energy of the HDPE/CELL blends.

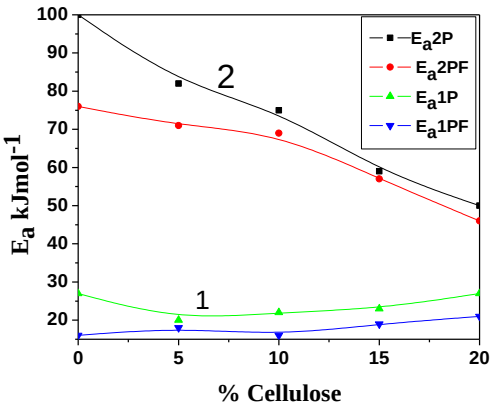


Figure VII: Effect of inoculation on the activation energy of HDPE/CELL blends.

Evidently from figure VII activation energy decreases with inoculation since microbial attack causes chain scission, breaking the polymer blends into smaller fragments. The oligomeric chains formed are less temperature resistant. Certainly, when the samples were put in the microbial consortium, the fungus *Aspergillus niger* anaerobically ruptured the chemical morphology of the HDPE matrix thereby lowering the energy required to initiate thermal degradation. The impact of the fungus on the E_a was more felt in blends with higher cellulose concentration as shown in Table V. This may be due to the fact that cellulose introduced the hydrophilic sites for better attachment of the fungus which in turn bore the holes in the polymer matrix hence weakening the structure. The inconsistency in the E_a values especially for process 1 can be attributed to the method used and experimental errors especially in-homogeneity during mixing of cellulose and the polymer.

Table V: E_a values for HDPE and its blends showing both processes before and after inoculation.

4.CONCLUSION

Blends of HDPE/CELL inoculated with *aspergillus niger* have been studied. The results obtained in this work showed that incorporation of CELL in HDPE increased moisture uptake significantly. Diffusivity values obtained after inoculation were higher. Moisture absorption of pure HDPE was almost 0 %, whereas for HDPE/CELL blends, their moisture uptake increased as cellulose content increased. This ensures that the presence of CELL in the HDPE matrix creates a polar environment which enhances hydrogen bonding. Inoculation by *A.niger* creates micro-cracks, gaps and flaws in the polymer matrix which are key zones for water infiltration. It's important to note that microbial activities increased with cellulose loading since CELL provided comfortable zones for attachment of *A.niger*. Thermal degradation of HDPE and its blends has been investigated. The TGA and DTG curves showed a two-step thermo-degradation process for all the samples. The main stage has been attributed to the complete decomposition of the carbon backbones of HDPE. The secondary stage which takes place at temperatures below 200 ^oC has been assigned to the thermal degradation of the corresponding cellulose in the blends. In general, the TGA and DTG results have proved that CELL significantly lowers the thermal stability of HDPE as seen from the decreasing thermal decomposition temperatures with CELL loading. Inoculated blends registered faster mass loss and low decomposition temperatures compared to un-inoculated ones. This is attributed to the effect of *A. niger* which assimilated the CELL particles in the blends leaving a perforated HDPE matrix with weak bonds of polymer chains.

Thus higher molar mass of HDPE is lowered subsequently leaving less material available to thermo-degrade. The activation energy greatly reduced with cellulose as seen from the Broido fits due to reduced thermal stability. Inoculated blends had the least activation energies since *A.niger* fragmented the polymer backbone forming short chain oligomers which are less temperature resistant.

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