



## THERMAL, MECHANICAL AND RHEOLOGICAL PROPERTIES OF AGRO FIBER FILL HIGH DENSITY POLYETHYLENE BIOCOMPOSITES

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### ABSTRACT

The thermal, mechanical and rheological properties of corncob, rice hull, walnut shell and flax shive agro-wastes/high density polyethylene bio-composites were studied. Results indicated that the fibers showed two and three mass loss steps due to moisture evaporation and decomposition of hemicelluloses, cellulose and lignin. The flax shive was thermally more stable and showed a decrease in activation energy with increase in conversion rate while the other three fibers showed increase in activation energy with conversion rate. The apparent activation energy values of the fibers was  $161 \pm 11.06$  to  $200 \pm 4.69$  kJ/mol. Particle size distribution of 60-100 mesh size of the fibers was 0.295 mm to < 0.125 mm. The composites showed remarkable increases in flexural modulus and un-notched Izod impact strength and a decrease in flexural strength compared with the neat HDPE. The rice hull composite showed superior flexural strength of 22.5 MPa. The flax shive composite gave superior flexural modulus of 3.0 GPa and the walnut shell composite gave superior un-notched Izod impact strength of 52.5 J/m. The complex viscosities of all the composites decreased with increase in frequency. The corncob composite showed higher complex viscosity of 3,600,000 Pas. The walnut shell composite exhibited higher storage modulus of 800,000 GPa at low frequency but decreased with increase in frequency, whereas the other three fiber composites showed increased storage modulus with increase in frequency. Corncob composite showed superior loss modulus of 200,000 GPa. The damping factor of the composites decreased with increasing frequency with walnut shell composites exhibiting superior damping factor. The study has shown that the properties of the composites varied substantially based upon the type of agro fiber utilized.

**Keywords:** Agro-waste fiber, Thermal properties, Mechanical properties, Rheological properties, Thermo gravimetric analysis, Activation energy, Bio-composites.

### Contribution/ Originality

The paper's primary contribution is finding that corncob, flax shive, rice hull and walnut shell fibers are viable, eco-friendly, alternative raw materials of low cost for the production of HDPE composites. The evaluation and comparison of their thermal, mechanical and rheological properties indicate their potential as engineering materials.

### 1. INTRODUCTION

Natural fibers from agricultural residues and forest products' processing mainly consist of natural lignocelluloses polymers. As a result, they are subjected to thermal degradation during composite processing [1]. The low degradation temperatures of natural fibers are also a limitation found when considering their use as fillers for thermoplastic polymers. Natural fibers are composed of a variety of chemical substances that present different degradation profiles. The three most important are cellulose, hemicelluloses and lignin [2]. The degradation of some other components during processing may produce a detrimental effect on the mechanical properties of the

composites, both by changing the structure of the fiber by producing volatile compounds that create micro voids across the interfaces. Shih [3] developed waste water bamboo husk fibers-reinforced epoxy composites and studied their performance. Mangal, et al. [4] prepared pineapple leaf fiber-reinforced polyethylene composites and reported that these fibers were thermally stable at the processing temperature of polyethylene. The fact that natural fibers have to be mixed with molten polymers in a processing system implies that thermal stability of natural fiber plastic composites need to be evaluated in order to understand the composites behavior in processing phase and later while recycling.

Thermo gravimetric analysis (TGA) is the most common technique used for kinetic analysis of the decomposition process and it provides the possibility of evaluating the mass loss of a sample with temperature and time [5]. Solid state kinetic data from TGA can be analyzed by various methods [6] either by model-fitting or model-free methods. The model-free methods require several kinetic curves to perform the analysis without making any assumptions about the reaction function and reaction order. Using a variety of computational methods, researchers [7] observed that isoconversional and multi-heating methods can be useful in describing kinetics of complex material reactions. The advantage of this approach is its simplicity and the avoidance of risk of choosing the wrong kinetic parameters [8, 9]. Therefore, the multiple heating rate methods such as that of Kissinger, Friedman, Coats Redfern and Flynn-Wall-Ozawa are the most common methods used [10-12].

A large amount of agro waste materials are produced every year globally and consequently these crop residues can potentially serve as a feedstock for bio-based polymer composites. Agro residues include wheat husk, rice husk and their straws, corn stover and shells of various dry fruits. These agro wastes can be used to prepare fiber-reinforced polymer composites for commercial use [13, 14].

Understanding the rheological behavior of wood-plastic-composites (WPC's) have been extensively investigated [15-17] emphasizing the importance of this field of research. Rheology can interpret the degree of dispersion of wood fiber, behavior of interfacial region and polymer-wood fiber affinity and has a vital role in processing of these composites Mohanty, et al. [18]. Maiti, et al. [19] studied the effect of wood flour concentration on the rheological behavior of isotactic-polypropylene wood composite via capillary rheometry. They reported that the shear stress rate variation follows a power law equation and the composite showed a decrease in viscosity (shear thinning) with increasing filler content.

The objective of the study is to evaluate the thermal, mechanical and rheological properties of agro waste filled high density polyethylene composites derived from corncob fiber (CCF), rice hull fiber (RHF), walnut shell fiber (WSF) and flax shive fiber (FSF) for potential applications as engineering materials.

## 2. MATERIALS AND METHODS

### 2.1. Materials

The polymeric matrix used was HDPE (Ineos®HP54-60) of density 0.95g/cm<sup>3</sup>, MFI=0.35g/10min. The corncob, rice hull, flax shive and walnut shell fibers of 60-100 mesh were used as received from the manufacturers.

### 2.2. Chemical Composition of Agro Fibers

The basic constituents of the corncob, rice hull, walnut shell and flax shive fibers were determined according to the Klason method [20] following the TAPPI Test Method T222 om-02 Standard [21] in triplicates, on dried samples kept in an oven for 24 h at 105°C. The extractives content was determined through three successive extractions (Soxhlet) with ethanol/benzene, ethanol and water. The determination of the acid-insoluble lignin was performed in triplicates using Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and the ash content was determined by calcinations at 500°C for 2 h.

### 2.3. Particle Size Analysis

Sieve analysis was conducted on oven dried (OD) fibers (100g) using a Mechanical Sieve Shaker (Model Rx-86) with standard test sieves (50, 60, 70, 80,100,120 mesh and pan) for 10 min, according to the Rotap A method (ASTM D5644-010).

### 2.4. Thermal Characterization of Agro Fibers

The thermal gravimetric analysis (TGA) was conducted by thermal gravimetric analyzer (SDT Q600), supplied by the TA Instrument. 7- 10 mg of samples were put in an aluminum pan heated at steady heating rates of 5, 10, 20 and 40°C/min from 25°C to 500°C in nitrogen medium. Analysis was performed twice for each sample.

### 2.5. Determination of Degradation Kinetics

The Flynn-Wall-Ozawa and Coats-Redfern (modified) methods were used to determine the activation energies ( $E_a$ ) of corn cob, rice hull, walnut shell and flax shive fibers. Both methods were the most 'model-free' methods in  $E_a$  determination of biomass materials.

### 2.6. Agro Fiber Preparation

Rice hull, corncob, walnut shell and flax shive fibers were oven dried at  $103^{\circ}\text{C}\pm 2^{\circ}\text{C}$  for 24 h to adjust the moisture content to 1-3% or less and then stored in sealed polyethylene bags before compounding.

### 2.7. Particle Morphology

Particle morphology of the agro fibers was investigated by SEM (S-570, Quanta 200F) Hitachi Scientific Instruments. Prior to the analyses, the specimens were mounted on stubs and imaged at low vacuum.

### 2.8. Processing of Composites

The agro fibers were dried at  $103^{\circ}\text{C}\pm 2^{\circ}\text{C}$  in an air circulating oven for 24 h before mixing. 65wt. % of each type of fiber, 32wt. % of HDPE and 3wt.% of lubricant (Lonza® WP4400) were mixed for 5 min at a rotor speed of 47 rpm using a ribbon blender (Charles Ross & Sons Co., USA). After dry mixing, the materials were extruded in a 35 mm intermeshing twin-screw extruder (Cincinnati Milacron Inc.) equipped with a 37 x 10 mm cross-section die. The extruder temperature was set to 162°C and screw speed of 20 rpm. The compounded extruded rectangular profiles were used for flexural and impact tests.

### 2.9. Mechanical Characterization of Composites

Flexural test of composites were performed at a speed of 3.8mm/min according to ASTM D790-10 on an INSTRON 4466 machine. All tests were performed at room temperature (23°C) and at a relative humidity of 50%. Un-notched Izod impact test of the composites were carried out using 7 un-notched samples according to ASTM D 256.

### 2.10. Rheological Characterization of Composites

The composites were compounded using torque rheometer and molded into 25 mm diameter and 2 mm thick discs specimens. The melt rheological properties were determined using a rotational rheometer under strain-controlled conditions. The measurements were performed in the dynamic mode and 25mm parallel plate geometry with gap setting of 2mm. The linear viscoelastic range was determined by a strain-sweep test of the composites under a frequency sweep. The strain was kept constant at 0.02% over the whole frequency range to ensure linearity. This strain was selected from a dynamic strain-sweep test, in which, within 0.001-10% strains, at a fixed frequency

of 10 rad/ s, the deviation strain from linearity was tracked; then frequency sweep test was done at constant temperature. The temperature was 170°C and the frequency,  $\omega$ , varied between 0.1 to 100 rad. /s.

### 3. RESULTS AND DISCUSSION

#### 3.1. Chemical and Physical Characterization of Fibers

From Table 1, flax shive presented greater quantities of lignin and extractives followed by walnut shell and then rice hull. Corncob fiber showed lower quantities of lignin.

Table-1. Chemical composition of the agro fibers

Composition (%)	Corncob	Rice hull	Walnut shell	Flax shive
Cellulose	50.5+0.3	35.0+0.1	47.8+0.3	47.7+0.2
Hemicellulose	31.0+0.2	25.0+0.1	22.1+0.2	17.0+0.2
Lignin	15.0+0.1	20.0+0.1	25.9+0.2	26.6+0.1
Ash	0.3+0.1	17.1+0.1	0.7+0.1	1.0+0.1
Others	3.2+0.1	2.9+0.1	2.5+0.1	7.7.+0.1

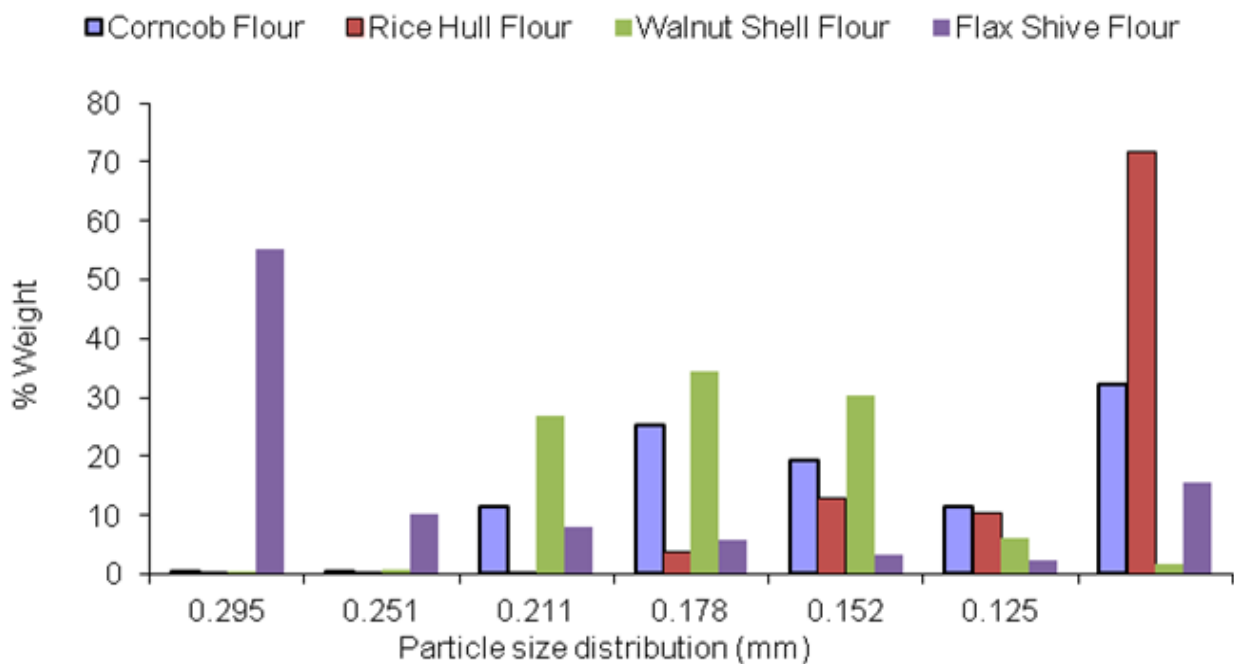


Fig-1. Particle size distribution of agro fibers

Fig. 1 shows the particle size distribution of the corncob, rice hull, walnut shell and flax shive fibers within the range of 0.295mm to < 0.125 mm. Fig. 2 presents the surface morphology of the agro fibers. Approximately 70 % of rice hull fiber was distributed in the range of < 0.125 mm (very fine particles). About 20-35 % of walnut shell fiber was distributed in the range of 0.211-0.152 mm (medium particles). About 55 % of flax shive fiber was distributed in the range of 0.295 mm (high particles). About 10-30 % of corncob fiber was distributed in the range of 0.211 to < 0.125 mm (medium to very fine particles). This inferred that the distribution frequency was not the same for the studied agro fibers.

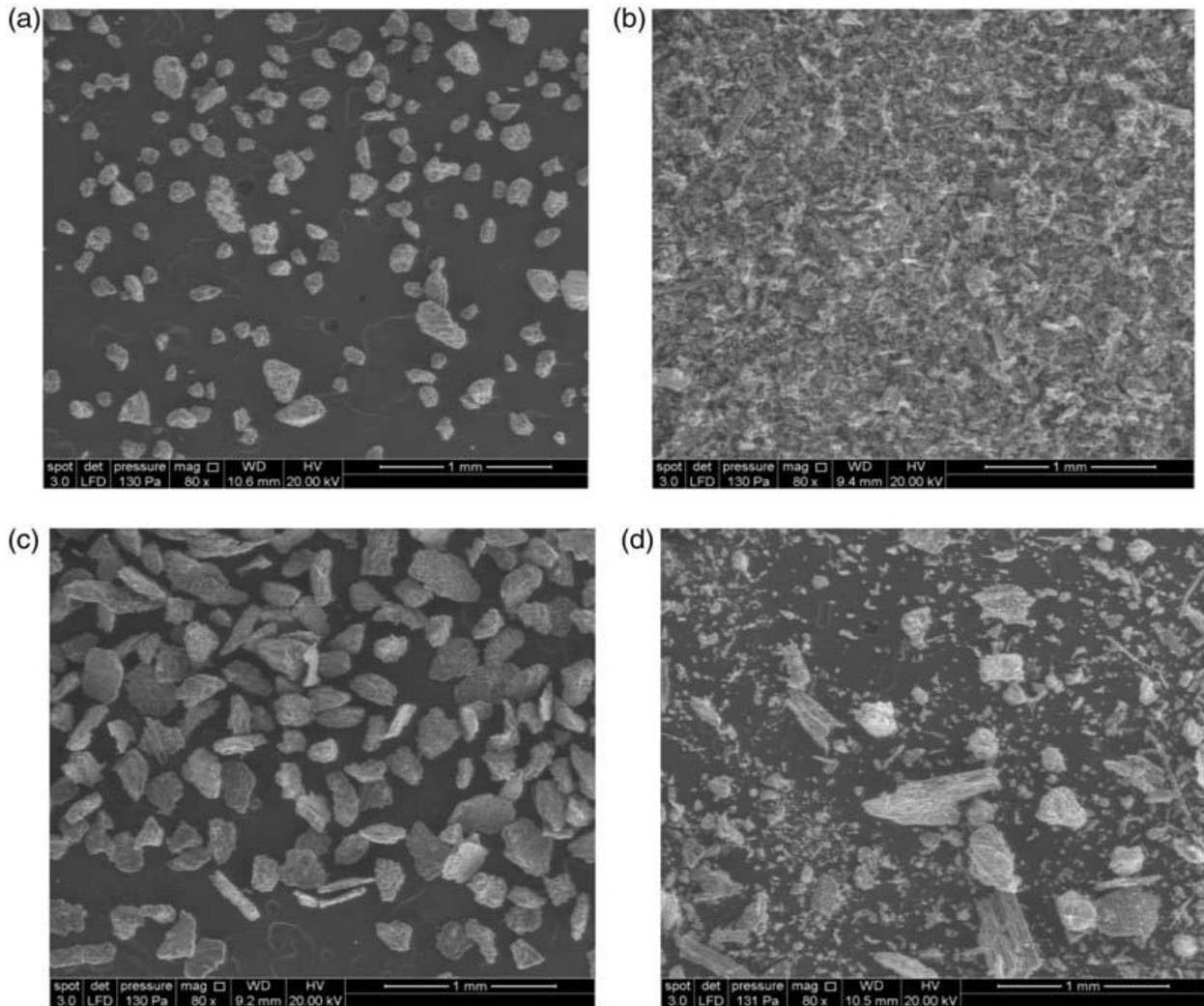


Fig-2. Particle geometry of: (a) corncob (b) rice hull (c) walnut shell, and (d) flax shive

### 3.2. Decomposition Process of Agro Fibers

Figs. 3 and 4 depict the TGA and DTG curves of corncob, flax shive, rice hull and walnut shell fibers. Thermal degradation showed two and three mass loss steps attributed to the evaporation of moisture and to the decomposition of hemicelluloses, cellulose and lignin contents of the agro fibers. The evaporation of moisture occurred below 100°C, decomposition of hemicelluloses and cellulose occurred from above 100°C to 280°C, the decomposition of lignin occurred above 300°C. The mass loss rate increased gradually up to 200°C and then a more marked mass loss occurred between 200°C and 400°C. There was a lateral shift in the TGA/DTG curves to higher temperatures with increased heating rate from 5 to 40°C/min for all the agro fibers as found in Figs. 5 and 6. The agro fibers showed differences in weight-loss and derivative weight-loss with increase in temperature from 25 to 500°C. These differences are attributable to variations in the chemical compositions of the agro fibers as shown in Table 1.

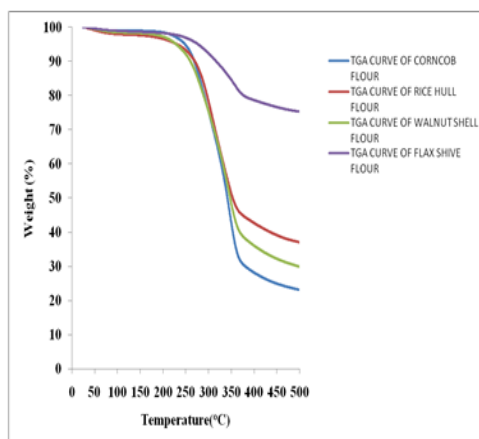


Fig-3. TGA of agro fibers

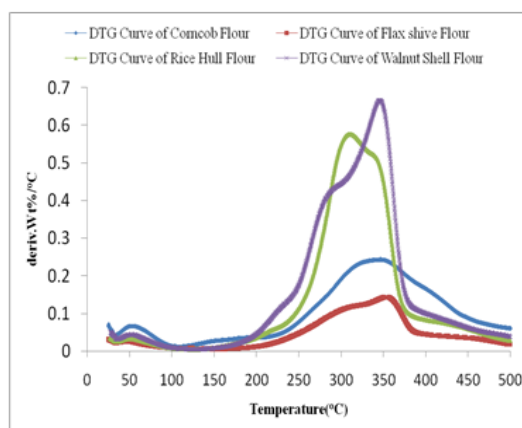


Fig-4. DTG of agro fibers

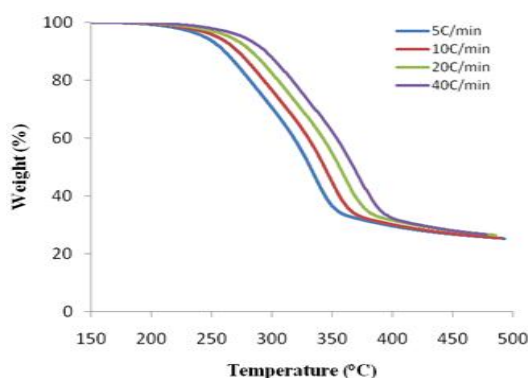


Fig-5. TGA of CCF at heating rates of 5-40°C/min.

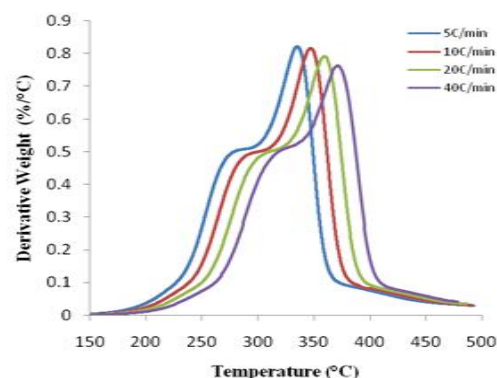


Fig-6. DTG of CCF at heating rates of 5-40°C/min

Table-2. Thermal degradation of agro fibers at 10°C/min

Fiber	Deco. beg temp (°C)	Deco. peak temp (°C)	Residue (%)
Corn cob	140	286/350	25
Rice hull	250	310	38
Walnut shell	243	287/350	29
Flax shive	270	354	65

Table 2 showed the initial decomposition, peak decomposition and residues of corncob, rice hull, walnut shell and flax shive fibers at a heating rate of 10°C/min. Reed and Williams [22] reported that a high lignin content of fibers produced higher levels of char during pyrolysis. The lignin and char content of flax shive was significantly higher compared to other fibers.

### 3.3. Apparent Activation Energy

Figs. 7 and 8 represent the  $E_a$  values of corn cob, rice hull, walnut shell and flax shive calculated according to the conversion rate range from 5-50 using Flynn-Wall-Ozawa and Coats-Redfern (modified) methods. The  $E_a$  values of corn cob, rice hull, walnut shell and flax shive fibers were around 162.4-199.9KJ/mol at conversion rate from 5-50 for Flynn-Wall-Ozawa method. The similar results of Coats-Redfern (modified) method also confirmed this observation, where the  $E_a$  values were around 161.3-188.6KJ/mol. The  $E_a$  values of corn cob, rice hull and walnut shell were gradually increased with the conversion rate increase from 5 to 50; whereas the  $E_a$  values of flax shive were gradually decreased with the conversion rate increase from 5- 20. The higher  $E_a$  values indicated that thermal decomposition of flax shive was more difficult. The fitted lines were nearly parallel at conversion rate from 5-50, which indicated approximate  $E_a$  values at different conversions and consequently implied the possibility of single reaction mechanism.

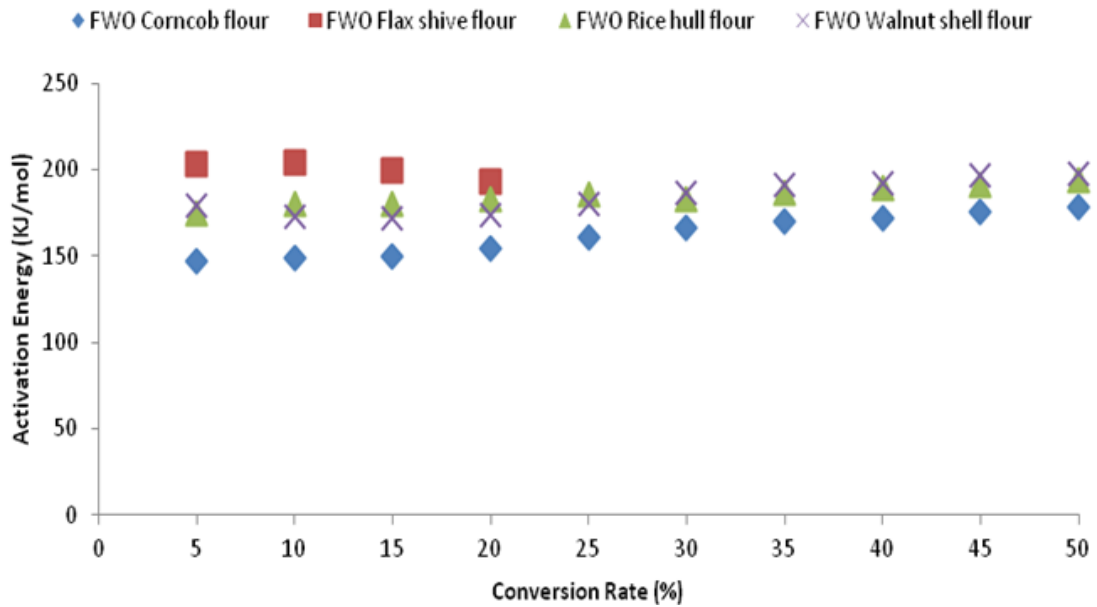


Fig-7. Activation energy vs. conversion rate (FWO)

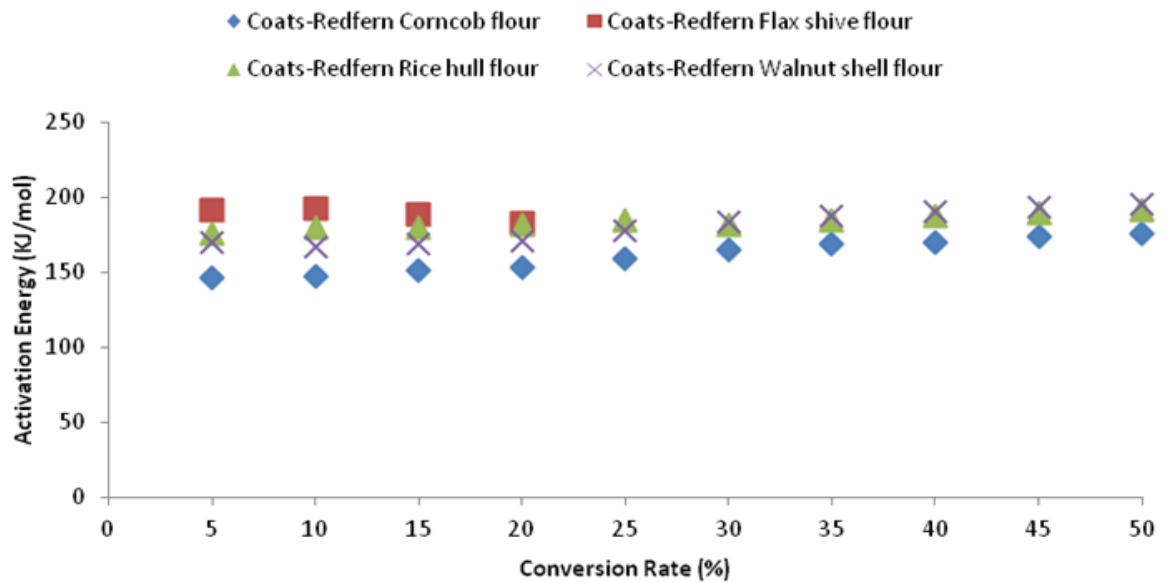


Fig-8. Activation energy vs. conversion rate (Coats Redfern)

### 3.4. Flexural Properties

Figs. 9 and 10 represent the flexural strength and modulus of the composites. It was observed that the flexural properties of the four different types of agro fiber/HDPE composites varied substantially depending upon the type of agro fiber utilized. It was found that the flexural strength of the agro fiber/HDPE composites were not better than that of the neat HDPE. The flexural moduli of the agro fiber/HDPE composites were superior to that of the neat HDPE. The HDPE/WSF composites exhibited inferior flexural properties compared to the other agro fiber/HDPE composites. This variation in flexural properties is due to differences in the particle size distribution of the agro fibers.

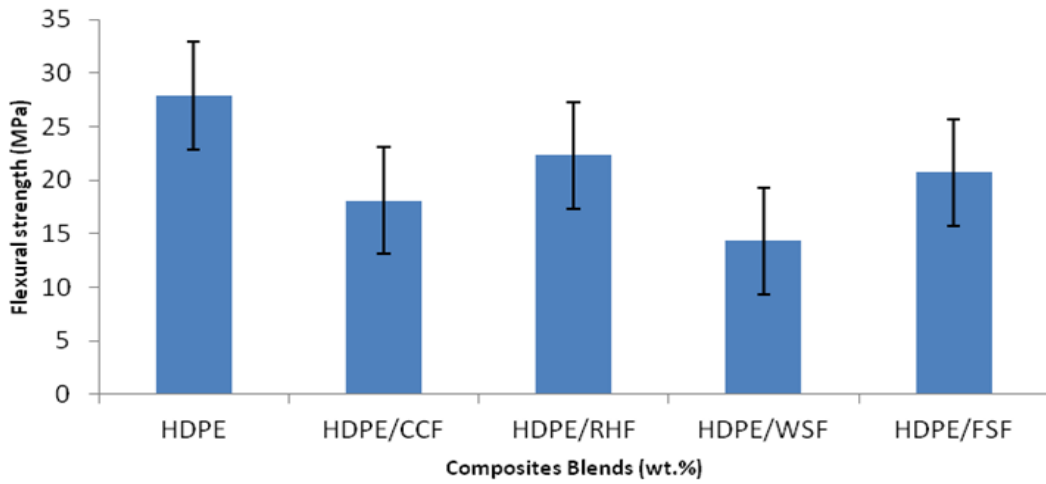


Fig-9. Flexural strength of agro fiber composites

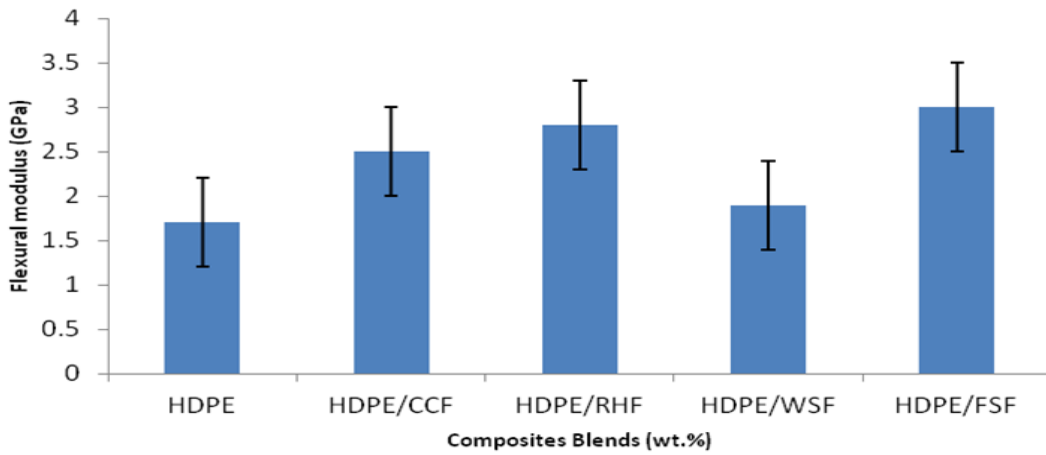


Fig-10. Flexural modulus of agro fiber composites

### 3.5. Un-Notched Izod Impact Strength

In Fig. 11 the impact strength of the agro fiber/HDPE composites improved with 65wt% load for all agro fibers. The WSF/HDPE composites showed superior impact strength compared to the other three agro fiber/HDPE composites which was better than that of the neat HDPE. This is due to fiber type and to the differences in the particle size distribution of the agro fibers.

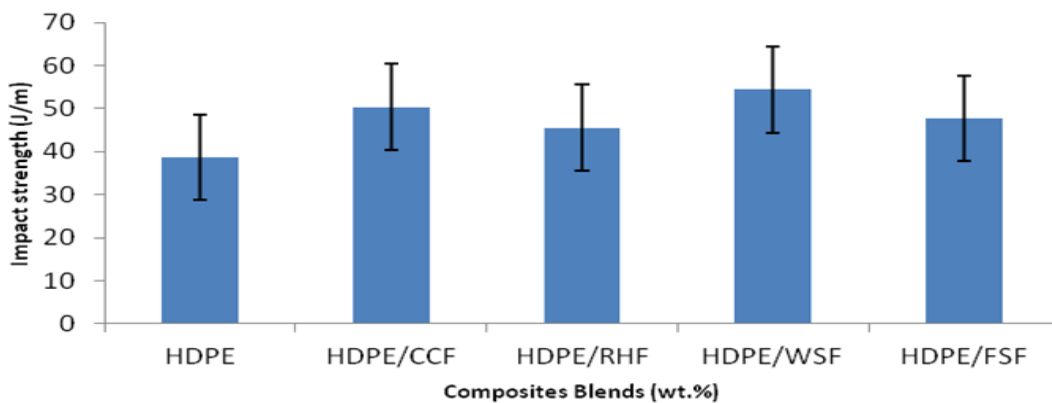


Fig-11. Un-notched Izod impact strength of agro fiber composites



### 3.6. Rheological Properties

#### 3.6.1 Storage Modulus vs. Strain

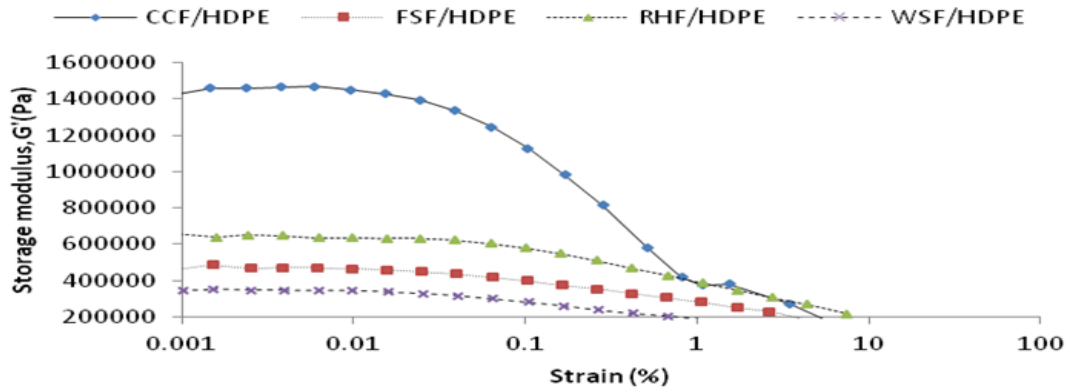


Fig-12. Storage modulus as a function of strain

Fig. 12 shows that storage modulus of the agro fiber/HDPE composites decreased with increase in strain with 65wt% agro fiber load. This trend varied according to the type of agro fiber. The CCF/DHPE gave superior storage modulus with increase in strain. This showed that CCF/HDPE composite exhibited greater resistance to breakage compared to the other agro fiber/HDPE composites.

#### 3.6.2. Complex Viscosity

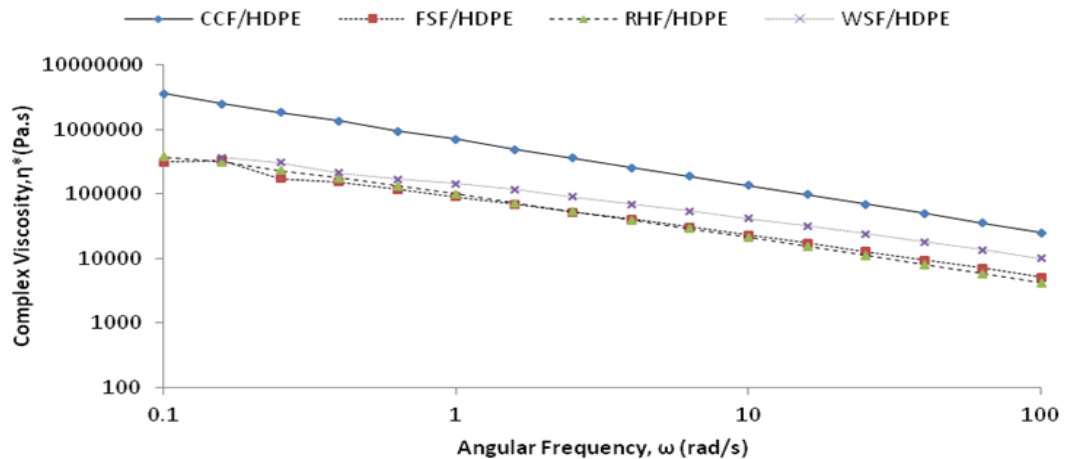


Fig-13. Complex viscosity as function of frequency

Fig. 13 shows that 65wt% agro fiber resulted to increased viscosity of the agro fiber/HDPE composites, which varied among the composites. The CCF/HDPE composites exhibited superior complex viscosity compared to the other agro fiber/HDPE composites. This is attributable to differences in the particle size distribution and agro fiber type utilized.

#### 3.6.3. Storage Modulus

In Fig. 14 the agro fiber/HDPE composites exhibited varying storage modulus values with increase in frequency. The storage modulus behavior indicated that the ability to store the energy of external forces in the corncob, rice hull and flax shive composites was increased while that for walnut shell composites decreased with increasing frequency. The anomalous behavior of the WSF/HDPE composites was due to higher number of smaller particles resulting in more particle-particle interactions and an increased resistance to flow.

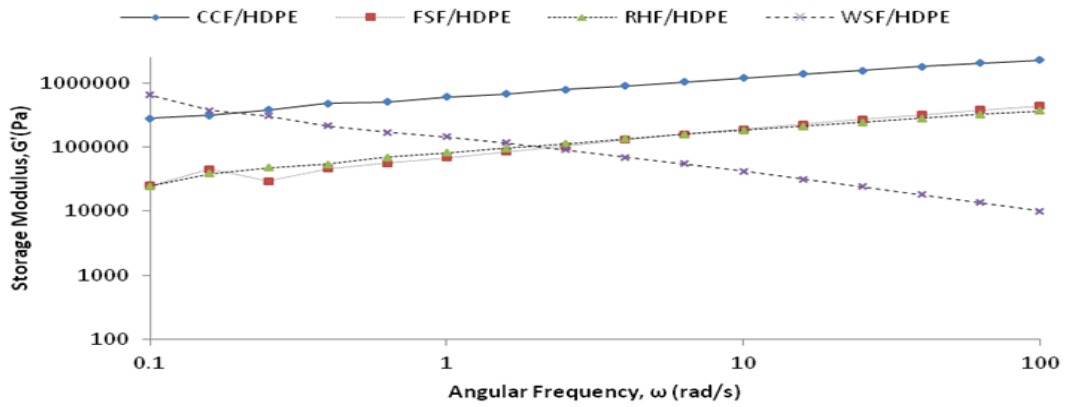


Fig-14. Storage modulus as a function of frequency

### 3.6.4. Loss Modulus

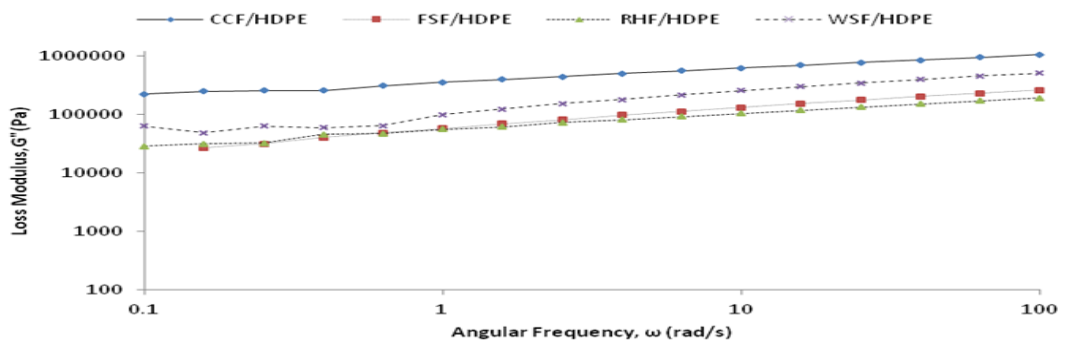


Fig-15. Loss modulus as a function of frequency

Fig 15 shows the variation of the dynamic loss ( $G''$ ) modulus with frequency ( $\omega$ ), for agro fiber filled HDPE composites at  $170^{\circ}\text{C}$ . The loss modulus increased with increased in frequency and at a filler load of 65% for all the samples. The loss modulus was 200000 GPa for CCF/HDPE, 63000 GPa for WSF/HDPE and 29000 GPa for RHF/HDPE and FSF/HDPE at 0.1 rad/s respectively. Corncob composites showed greater ability for impact absorption, followed with walnut shell composites, in comparison with rice hull and flax shive composites respectively.

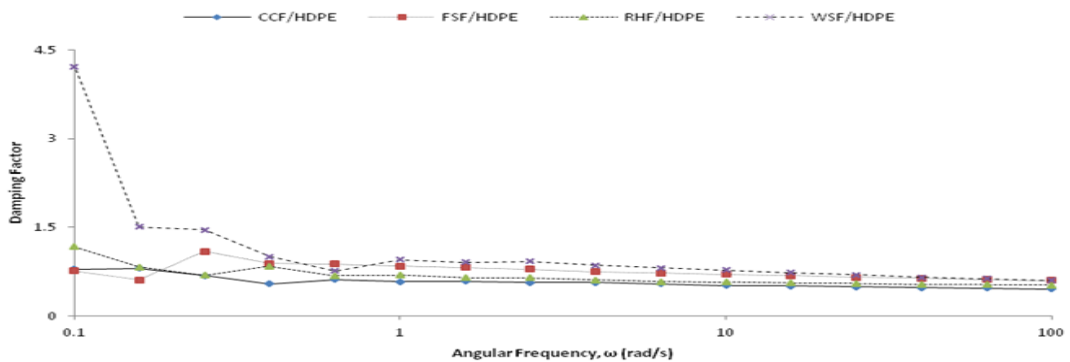


Fig-16. Damping factor as function of frequency

### 3.6.5. Damping Factor ( $\tan \delta$ )

In Fig. 16 the  $\tan \delta$  of the agro fiber/HDPE composites decreased monotonically to varying degrees in the whole frequencies range and a flattened section at  $\omega$  above 1 rad/s. The WSF/HDPE composite exhibited superior damping factor among the agro fiber/HDPE composites.

#### 4. CONCLUSIONS

From these investigations, the following conclusions were drawn:

- (i) The flax shive fiber was the most thermally stable, followed with rice hull, walnut shell and corncob. This might be related to the higher lignin content of flax shive.
- (ii) The activation energy of corn cob, rice hull, walnut shell and flax shive fibers was 162, 185, 184 and 200kJ/mol using the Flynn-Wall-Ozawa method. For the Coats Redfern method the activation energy was lower than these values.
- (iii) The properties of the agro fiber composites varied substantially based on the type of fiber utilized.
- (iv) Agro fiber sample load of 65wt% could be used in composite formulation with good results.

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