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# Water Absorption, Thickness Swelling and Rheological Properties of Agro Fibers/HDPE Composites

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***Abstract:*** *In the study composites were prepared using 65wt% of corncob, rice hull, walnut shell and flax shive fibers with 32 wt% of high-density polyethylene by extrusion method. Results indicated significant differences in the water absorption, thickness swelling and rheological properties of the agro fiber composites. The corncob composites exhibited the highest water absorption values. The flax shive composites showed the lowest water absorption and thickness swelling values. The rice hull composites exhibited the highest thickness swelling values. The corncob composites showed the greatest resistance to breakage whereas the walnut shell composites exhibited the least resistance to breakage. The four agro fiber composites showed higher viscosity at low shear rates and at higher shear rates the effect of the filler decreased and the matrix contributions dominated. The corncob composites exhibited the highest complex viscosity whereas the rice hull composites showed the lowest complex viscosity. The storage and loss modulus of corncob composites were the highest and increased with increasing shear rate for all the composites, except for walnut shell composites which exhibited a decrease in storage modulus with increasing shear rate. The walnut shell composites exhibited the highest damping factor whereas the corncob composites showed the lowest damping factor values.*

***Keywords:*** *Agro fibers, High-density polyethylene, Rheological properties, Thickness swelling, Water absorption*

## I. Introduction

The use of agro fibers derived from annually renewable resources renders positive environmental benefits with respect to final disposability and raw material utilization. Natural fillers have a number of techno-ecological advantages over synthetic fillers, since they are renewable and abundant resources, being less damaging to the environment, and cause less abrasive wear to processing equipment. There is a wide variety of lignocellulosic materials that can be used to reinforce thermoplastics. These include wood fibers, as well as a variety of agro-based fibers such as wheat straw, rice husk, corn stover and shells of various dry fruits [1-5].

A problem associated with using lignocellulosic materials in natural fiber thermoplastic composites is moisture absorption [6]. A moisture buildup in the fiber cell wall can lead to thickness swelling and dimensional changes in the composite [7]. The thickness swelling can lead to reduction in the adhesion between the fiber and the polymer matrix. Thus, the water absorption can have undesirable effects on the mechanical properties of the composites [8]. Temperature may severely influence amount of water absorption, and its subsequent irreversible effects and environmental aging can have major practical consequences [9]. The water uptake of natural fiber composites can be reduced considerably by using coupling agents to assist with fiber-matrix adhesion [10]. At low fiber content, the matrix restrains expansion of the fibers while at high fiber content there is insufficient matrix to maintain this restrain and the fiber can take up more water than its weight in water [11].

Rheology is the study of how materials deform when a force is applied to them. It is an effective tool to better understand quality control of raw materials, manufacturing process/final product and predicting material performance. In particular, rheology is effective in better understanding the role that fillers have on rheological properties. The rheological properties of filled polymers are not only determined by the polymer but also by the type of filler, its size, shape and amount [12]. Understanding the rheological behavior of wood-plastic-composites (WPCs) has been extensively investigated emphasizing the importance of this field of research [13-15]. Rheology can interpret 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 [16]. Maiti et al [17] 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. To better understand the effects that fillers and additives have on rheological properties, rheometry must be employed. Rheometers are used to measure the effect of fillers on polymer systems. They can be divided into two categories: rotational and capillary types. The rheometers of interest include torque rheometer (capillary and extrusion type), parallel-plat (rotational) and melt flow indexer (capillary). Four types of rheological experiments can be performed utilizing parallel-plate or rotational rheometer: (i) strain sweep, (ii) frequency sweep, (iii) temperature sweep and (iv) steady shear sweep [18].

Fiber modification is not cost effective hence the need to search for natural fibers that have relatively low percentage water absorption and thickness swelling that could be used for low cost natural fiber composite manufacture. This work is designed to primarily investigate the effect of agro fiber type and high agro fiber loading on the water absorption, thickness swelling and rheological properties of agro fiber/high-density polyethylene extruded composites. Particle geometry and morphology was also analyzed.

## II. Materials and methods

### 2.1 Materials

The polymeric matrix used was HDPE (Ineos®HP54-60) of density 0.95g/cm$^3$, MFI=0.35g/10min provided by the Composite Materials and Engineering Centre, Washington State University, Pullman, USA. Flax shive was supplied by Biolin Research Inc., 161 Jessop Ave. Saskatoon, Canada. Walnut shell was supplied by Composition Materials Co., Inc., 249 Pepes Farm Rd., Milford, CT, USA. Rice hull was supplied by Rice Hull Specialty Products, Stuttgart, AR, USA. Corncob was supplied by Mt. Pulaski Products, LLC. Mt. Pulaski, USA. The agro fibres were of 60-100 mesh and were used as received from the manufacturers.

### 2.2 Chemical composition of agro fibers

The basic constituents of the agro fiber samples were determined following the TAPPI Test Method T222 om-02 Standard [19], in triplicate, on dry samples kept in an oven for 24 hours at 105$^0$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 triplicate using sulfuric acid and the ash content was determined by calcinations at 500$^0$C for 2 hours. The results are presented in Table 2.

### 2.3 Particle size distribution of agro fibers

Particle size distribution analysis of the agro fibers was conducted on oven dried (OD) fibers of 100g each 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). The results are presented in Fig. 1.

### 2.4 Particle geometry of agro fibers

Particle geometry was investigated by SEM (S-570, Quanta 200F) Hitachi Scientific Instruments. Fibers were distributed to obtain clear images and the fiber geometry was measured. Figure 2 shows the light microscopic photos of the filler (80X).

### 2.5 Composites preparation

Table 1 shows the formulation of composite samples used for the study. Fibers were dried at 103$^o$C±2$^o$C in an air circulating oven for 24 h before mixing. The agro fibers at 65wt. % proportion, high density polyethylene at 32wt. % and lubricant (Lonza® WP4400) at 3wt. % 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$^o$C and screw speed of 20 rpm.

Table1. Composite formulation

| Sample code | HDPE | Rice hull | Corncob | Walnut shell | Flax shive | WP4400 |
|---|---|---|---|---|---|---|
| A | 32 | 65 | - | - | - | 3 |
| B | 32 | - | 65 | - | - | 3 |
| C | 32 | - | - | 65 | - | 3 |
| D | 32 | - | - | - | 65 | 3 |

### 2.6 Hygroscopic Tests

Hygroscopic behavior studies were conducted according to the ASTM D 570-98 method. Four specimens of each composite were dried in an oven for 24 h at 105±2$^0$C. The dried specimens were weighed with a precision of 0.001 g and their thickness was measured with a precision of 0.001 mm. Then they were placed in distilled water. At predetermined time intervals of 24 h daily the specimens were removed from the distilled water, the surface water was wiped off using blotting paper, and their wet mass and thickness were determined. Water absorption and thickness swelling were calculated using the following equations:

$M (\%) = (m_t - m_o)/ m_o \times 100$ ……………………………………………………………………………………(1)

Where $m_o$ and $m_t$ denote the oven-dry weight and weight after time t, respectively, and

$S (\%) = (T_t - T_o)/ T_o \times 100$ ……………………………………………………………………………………(2)

Where $T_o$ and $T_t$ denote the oven-dry dimension after time t, respectively.

**2.7 Rheological Tests**

Agro fibers of 65wt. %, HDPE of 32wt. % and lubricant at 3 wt. % were compounded using torque rheometer and molded into 25 mm diameter and 2 mm thick discs samples. The melt rheological properties of five replicates of the agro fiber/HDPE composites were determined using a rotational rheometer under strain-controlled conditions. The measurements were performed in the dynamic mode and 25 mm parallel plate geometry with gap setting of 2 mm. 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$^o$C and the frequency, ω, varied between 0.1 to 100 rad/s.

## III. Results and discussions

Table 2: Chemical composition of the agro fibers

| Fiber | Holocellulose (%) | SD | Lignin %) | SD | Extractives (%) | SD | Ash (%) | SD |
|---|---|---|---|---|---|---|---|---|
| **Flax shive** | **65.9** | **0.2** | **30.0** | **0.1** | **2.2** | **0.1** | **2.0** | **0.1** |
| **Corn cob** | **67.0** | **0.3** | **15.0** | **0.2** | **16.0** | **0.1** | **4.0** | **0.1** |
| **Rice hull** | **62.2** | **0.3** | **26.0** | **0.1** | **7.0** | **0.1** | **4.6** | **0.1** |
| **Walnut shell** | **60.0** | **0.4** | **21.0** | **0.1** | **6.5** | **0.1** | **13.2** | **0.1** |

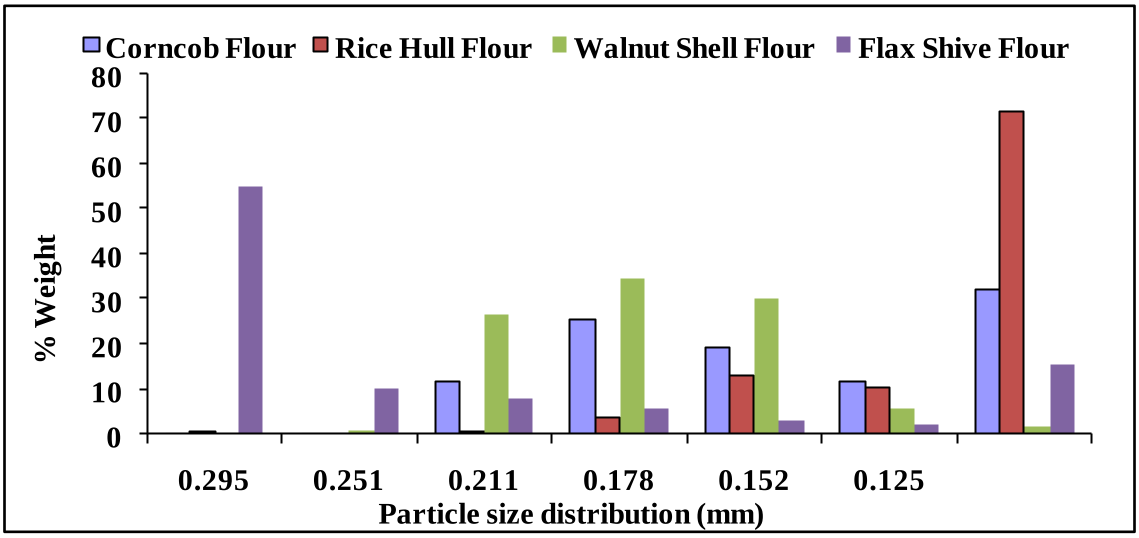

Fig. 1: particle size distribution of agro fibers

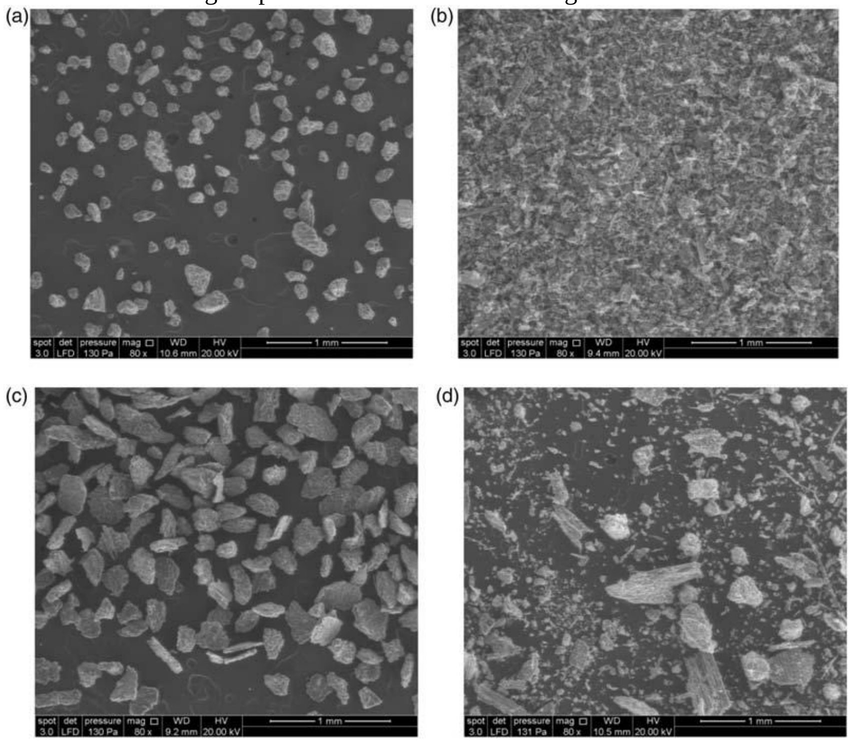


Fig. 2: Particle geometry of: (a) corncob (b) rice hull (c) walnut shell, and (d) flax shive

**3.1 Water absorption and thickness swelling**

Figs. 3 and 4 show water absorption and thickness swelling of composites after 1344 hours immersed in water. Generally the water absorption and thickness swelling increased with immersion time, reaching a certain value beyond which no more weight and thickness increased. The corncob composites showed higher values of water absorption, followed by walnut shell composites and rice hull composites. The flax shive composites showed the lowest value for water absorption. In fact, the higher values of water absorption for corncob composites can be related to larger particle size as shown in Fig. 3 and more hygroscopic chemical constituent as shown in Table 2.

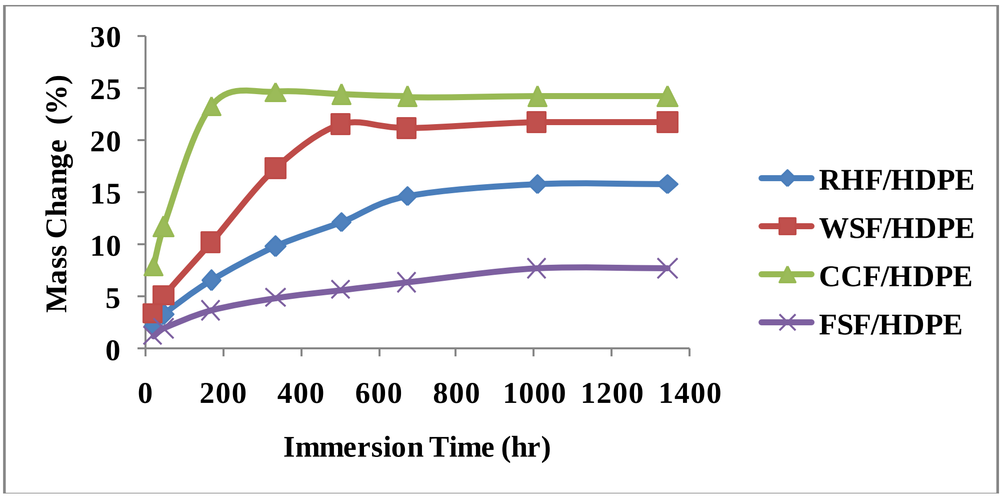


Fig 3: water absorption of composites after 1344 hours immersed in water

The rice hull composites gave higher values of thickness swelling, followed by corncob composites and walnut shell flour composites. The higher values of thickness swelling for rice hull composites can be attributed to the finer particle size and the probability of agglomeration at 65 wt % filler content which increased its ability to retain water. The flax shive composites showed the lowest value for thickness swelling. Figs. 3 and 4 show that the flax shive composites exhibited longer equilibrium time (i.e., time to reach equilibrium water absorption and thickness swelling). The flax shive composites swelled and gained weight very slowly.

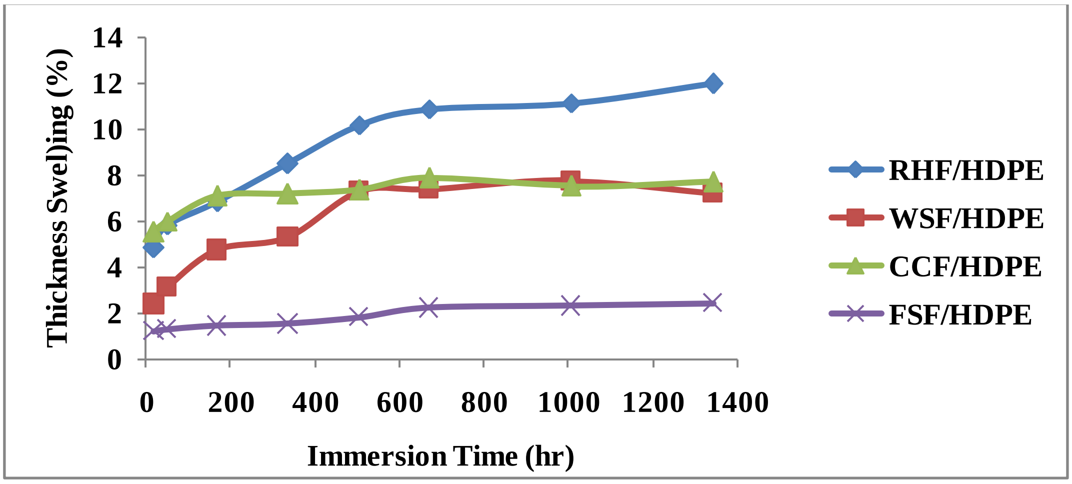


Fig. 4: thickness swelling of composites after 1344 hour immersed in water

The analysis of the water diffusion mechanism in composites was performed based on Fick's Theory. Diffusion can be distinguished theoretically by the shape of sorption curve represented by Equation (3):

$$M_t/M_s = K.t^n \quad \ldots(3)$$

Where $M_t$ is the moisture content at time t, $M_s$ is the moisture content at the equilibrium, and k and n are constants. If the value of coefficient n becomes smaller than 0.5, then water absorption behavior follows the Fickian diffusion process [6]. To understand the mechanism of the water absorption in composite materials, the experimental data were fitted to the Eq. 4 which is derived from Equation (3) [6].

$$\log (M_t/M_s) = \log k + n \log t \quad \ldots(4)$$

The diffusion coefficient is the most significant parameter in the Fickian model. The water diffusion coefficient was calculated using the Equation (5):

$$Mt/Ms = 4/L \, (D/\pi)^{0.5} \, t^{0.5} \quad \ldots(5)$$

In the equation Mt is the moisture content at time t, Ms is the moisture content at equilibrium, L is the thickness of samples, and D is the water diffusion coefficient [6].

Table 3 showed the diffusion parameters for the studied composites. The values of n indicate that the water absorption in lignocellulosic filler/HDPE composites followed a Fickian process. It can be seen that the diffusion coefficient of composites of corncob flour was the highest. This result can be related to big size of corncob flour particles (Figure 1). The lowest value diffusion coefficient in flax shive flour composites as filler can be due to chemical constituents (Table 1).

Table 3: Diffusion Coefficient for Studied Composites

| Composites Code | n | log k | k ($h^2$) | D ($m^2s^{-1}$) |
|---|---|---|---|---|
| CCF/HDPE | 0.408 | -1.296 | 0.050 | 8.57 E-12 |
| RHF/HDPE | 0.168 | -0.544 | 0.286 | 7.64 E-12 |
| WSF/HDPE | 0.478 | -1.485 | 0.033 | 7.97 E-12 |
| FSF/HDPE | 0.479 | -1.523 | 0.030 | 5.14 E-12 |

### 3.2 Rheological properties

#### 3.2.1 Strain sweep

Fig. 5 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 corncob composites gave superior storage modulus with increase in strain. This showed that the corncob composites composite exhibited greater resistance to breakage compared to the other agro fiber/HDPE composites.

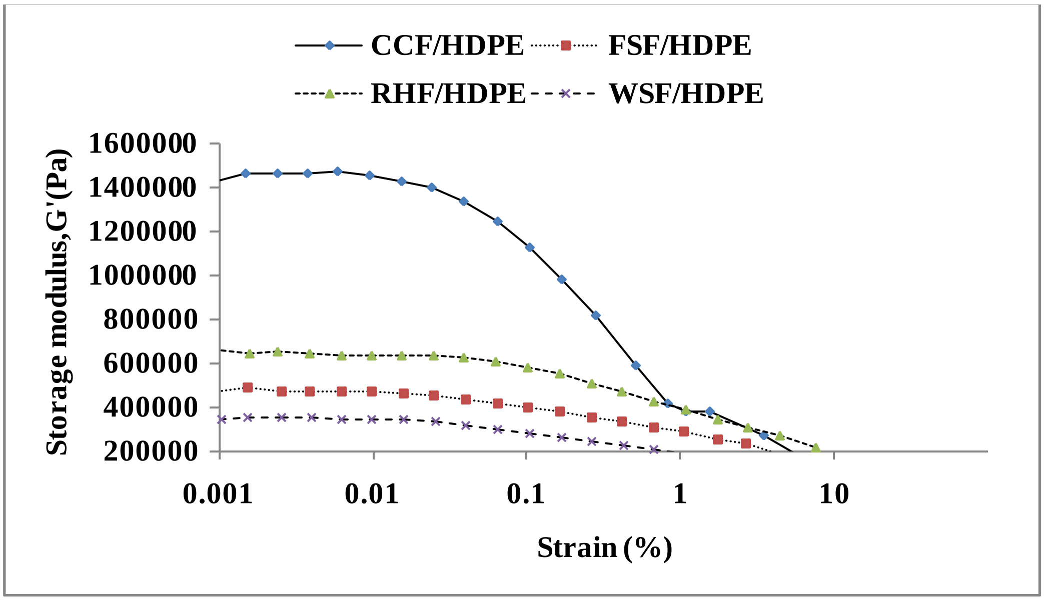


Fig.5: storage modulus as a function of strain

### 3.2.2 Complex viscosity

Fig. 6 shows that 65wt% agro fiber resulted to increased viscosity of the agro fiber/HDPE composites, which varied among the composites. The corncob 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.

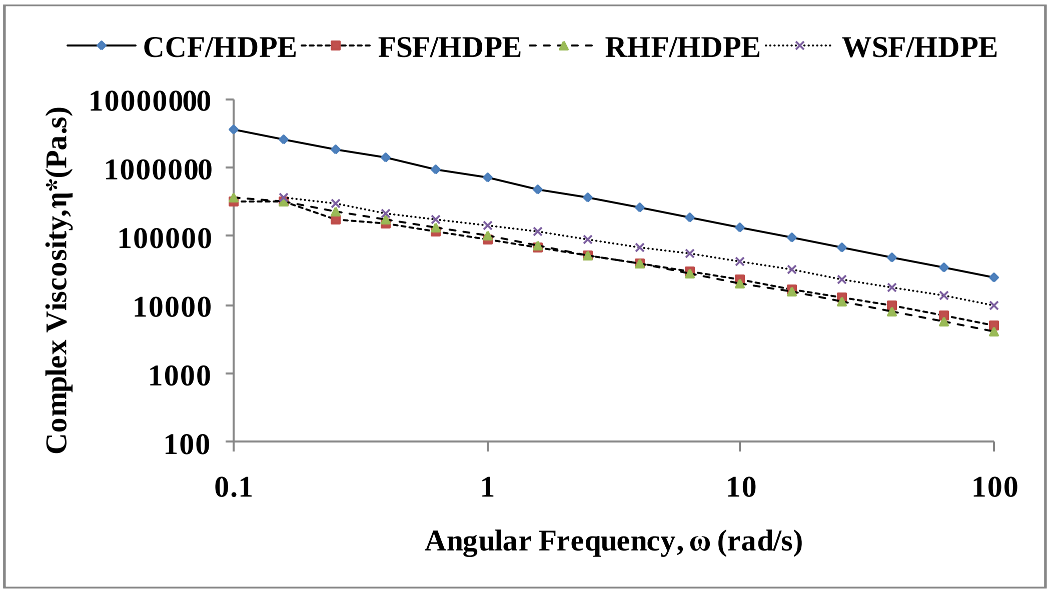


Fig. 6: complex viscosity as function of frequency

### 3.2.3 Storage modulus

In Fig. 7 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 walnut shell composites was due to higher number of smaller particles resulting in more particle-particle interactions and an increased resistance to flow.

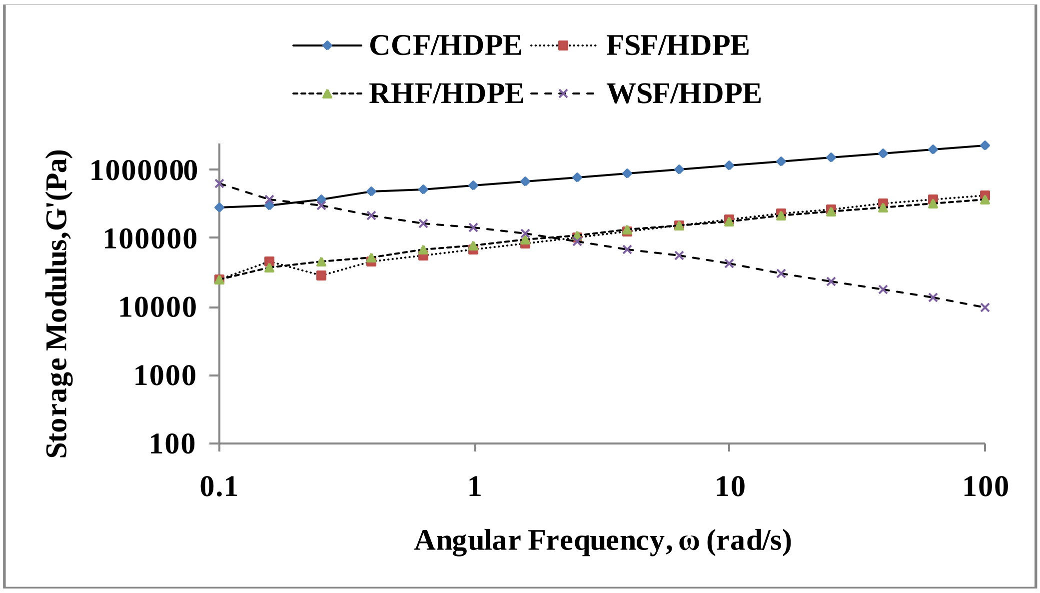


Fig. 7: storage modulus as function of frequency

### 3.2.4 Loss modulus

Fig. 8 shows the variation of the dynamic loss (G") modulus with frequency (ω), for agro fiber filled HDPE composites at $170^0$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 corncob composites, 63000 GPa for walnut shell composites and 29000 GPa for rice hull composites and flax shive composites at 0.1 rad/s. The corncob composites showed greater ability for impact absorption, followed with walnut shell composites, in comparison with rice hull and flax shive composites respectively.

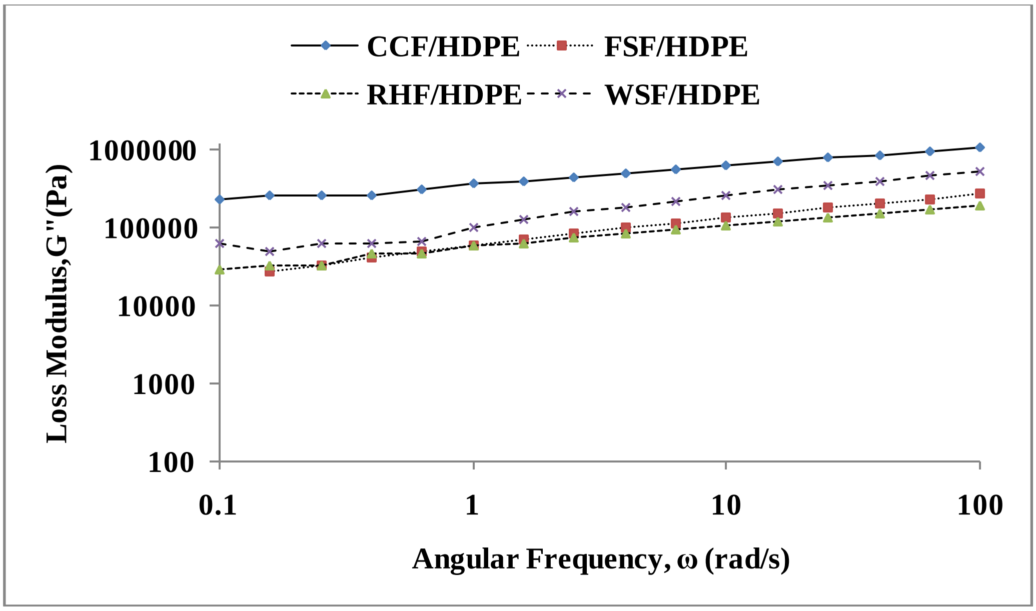


Fig. 8: loss modulus as a function of frequency

### 3.2.5 Damping factor (tan ∂)

In Fig. 9 the damping factor (tan ∂) of the agro fiber/HDPE composites decreased monotonically to varying degrees in the whole frequencies range and a flattened section at ω above 1 rad/s. The walnut shell composite exhibited superior damping factor among the agro fiber/HDPE composites.

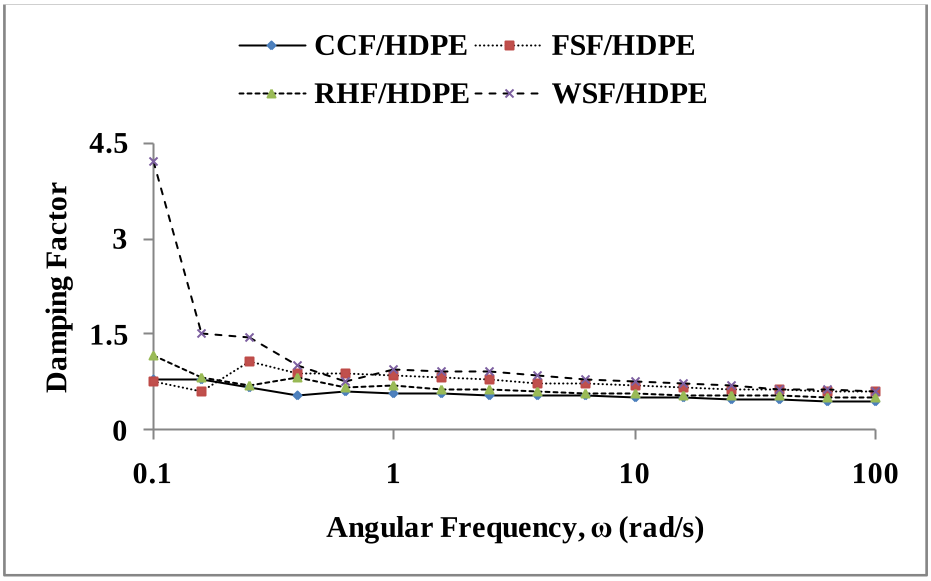


Fig. 9: damping factor as function of frequency

## IV. Conclusions

1. Agro residues such as flour of rice hull, corncob, walnut shell and flax shive could in the future be good reinforcements for HDPE. The use of these materials can be a resource for manufacturing of wood-plastic composites. Flax shive fiber seems to have the potential for creating a suitable plastic-based composite material for consumption in wet environments.
2. Agro fiber samples loading of 65 wt% could be used in composite fabrication with good results.
3. The differences in the water absorption, thickness swelling and rheological properties depend on the type of agro fiber type utilized.

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