Impact of Hybrid Biomass Fillers on the Physico-Mechanical and Degradation Properties of Utility Polymers

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ABSTRACT

The impact of cassava peel-rice husk hybrid fillers on the physico-mechanical and degradation properties of utility polymers were studied. Fine powders of cassava peel and rice husk of 75µm mesh size were homogeneously mixed at the ratio of 1:1 to form the hybrid filler. The virgin crystalline pellets of Low-Density Polyethylene and Polypropylene were filled with varying weight percentages (5, 10, 15, and 20) of the hybridized filler and the composites produced via the injection moulding technique at 288^{o}C. The mechanical properties were studied according to ASTM standards. The surface morphological properties and thermal properties were studied with Scanning Electron Microscope and Differential Scanning Calorimeter respectively. The results of the mechanical properties showed improved tensile strength, compression strength and hardness as the filler load increases till optimum filler load was attained, while the percentage elongation at break decreased with increase in filler load. The shear modulus was found to be irregular. The creep behaviour with the PP composites was irregular but linear with LDPE composites. The solvent imbibition showed no increase in water, but less than 1% increase in toluene. The DSC result showed the hybrid filler had positive impact on LDPE composite but no effect on PP composite. The micrographs showed improved properties as the filler loading increases. Biodegradation test in soil revealed a reduction in the mass of the composites after a 6- month burial period indicating that the composite is degradable and eco- friendly. From the results, the cassava peel-rice husk hybrid filler can be employed in formulation of polymers where strength, water resistance and biodegradability is required such as plastic tiles. Thus, it is suggested that agro-wastes such as cassava peel and rice husk could be used as fillers in production of degradable plastics as they are accessible, cheap, easy to use and eco-friendly.

Keywords: Cassava peel, Rice-husk, Low density polyethylene, Polypropylene, Degradation properties, Mechanical properties.

INTRODUCTION

Virtually all man's daily activities and needs involve one polymer or another for various uses such as clothing, shopping bags, cooking utensils. The diversity of polymers and the versatility of their properties are used to make a vast array of products that initiate medical and technological advances, energy savings and numerous other societal benefits, (Andrady and Neal, 2009). Low density polyethylene and polypropylene being the most widely used. These polymers when used and discarded can last thousands of years in the ecosystem causing environmental and health related issues due to release of flue gases (NO_X and SO_X), as well as dioxin, the by-products from the process of the disposal method as garbage in landfill disposal areas or incineration (Shaharuddin et al., 2017). The presence of the microplastics in our environment and its contact with humans through skin contact, inhalation and ingestion cannot be overemphasised. These chemicals within our ecosystem are capable of inducing different types of cancer, metabolic disorder, respiratory problems (Kehinde et al., 2020; Adeniran et al., 2022). To reduce the longevity and problems associated with these polymers in the ecosystem, test alternatives were considered by incorporation of agricultural waste into polymer matrix (Thompson et al., 2009).

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Thus, this research is aimed at studying the impact of hybrid fillers of cassava peel and rice husk on the mechanical, morphological, thermal and degradation properties of lowdensity polyethylene and polypropylene. The result will add value to other researches to assist some other young researchers in the field of polymer chemistry or material science.

LITERATURE REVIEW

Nwanonenyi and Ohanuzue, (2011) observed in their study on the effect of rice husk filler on some mechanical and end-use properties of LDPE that the tensile modulus and hardness increased with increase in filler loading, while tensile strength and percentage elongation decreased with increase in filler loading. Aridi et al., (2016) studied the mechanical and morphological properties of injection – molded rice husk polypropylene composites using various filler loading and strukol as coupling agent. Their observation showed that at 35wt% filler loading Young's modulus, flexural strength, flexural modulus and impact strength were the best, while 50 wt% filler load composite had optimum tensile strength, flexural strength and flexural modulus. The micrograph showed that as filler loading increases, more void and fibre pullout occurred. Chris-Okafor et al., (2017) studied the effects of local fillers; rice husk and corn cob, on flexible polyether foam using fillers particle size of 0.25mm mixed in equal ratio of 50:50 with varying loads of the mixed fillers viz-a-viz 5%, 10%, 15%, 20% and 25% incorporated into the foam. They observed that increase in filler load increased the density and tensile strength of the foam, while the compression strength increased but in an irregular pattern and the elongation at break decreased with an increase in filler load. Anggraeni et al., (2021) studied the effects of particle size and composition of cassava peels (CPs) and rice husks (RHs) on the briquette performance using combination of CPs and RHs in ratios of 90:10; 70:30; 50:50; 30:70; and 10:90. The result showed the optimum compressed and relaxed density was obtained for briquette with small particles and a CPs:RHs ratio of 70:30 and 50:50.

From the literature review, it was seen that researches on rice husk–LDPE and rice husk -PP has been done, none is known of cassava peel with any matrix and the only hybrid cassava peel- rice husk done was on briquette which involved varying the ratio of the respective biomass and not the blend. In this work, the biomass ratio was constant and the blend –matrix ratio varied to ascertain the impact of the hybrid on the polymer matrices.

METHODOLOGY

Materials

Low Density Polyethylene (LDPE) (Indorama Eleme Petrochemicals NGL015FS) and Polypropylene (PP) produced by Exon Mobil Nigeria were used. The cassava peel from cassava tubers and the rice husk were obtained from farm and mill in Anambra State, Nigeria. The cassava peel was cut into smaller fragments and washed, while the rice husk was washed to remove impurities like sand and dust, then both were air dried for seven days. The samples were separately crushed using a grain mill machine M6FFC-270 and sieved locally using a muslin cloth to obtain fine powder sample of 75μm mesh size.

Preparation of Composites

The fine powders of cassava peel and rice husk were homogeneously mixed at the ratio of 1:1 at room temperature to form the hybrid filler. The virgin crystalline pellets of LDPE and PP were weighed at 200g, 190g, 180g, 170g, and 160g respectively and homogenously mixed with the hybrid filler of 0g, 10g, 20g, 30g, and 40g respectively, corresponding to 0%, 5%, 10%, 15%, and 20% filler loading. The homogenous filler and the matrices were mixed, and then fed into the hopper of a TU150 200 gram injection moulding machine. The composites were formed at 288^{o}C.

Mechanical Properties Analysis of the Composites

The mechanical properties of the composites considered in this work include; tensile strength, hardness, shear modulus, compression strength and creep, which were measured using the American Standard Testing and Measurement method.

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The tensile strength of the composites was measured according to the ASTM D-638-14 method, using the universal testing machine Hounsfield Monsanto Tensometer 8889 Made in England. The test piece was measured to 160mm x 19mm x 3.2 mm dimension.

The hardness of the composite was measured according to the ASTM D2240, using Shore Scale Durometer Hardness Tester, Made in England. The values were automatically measured and read. The test was measured to 20mm x 20mm x 3.2 mm dimension.

The compressive strengths of the composites were measured according to the ASTM D-695, using the universal testing machine Hounsfield Monsanto Tensometer 8889 Made in England. The test was measured to 20mm x 20mm x 3.2 mm dimension. The readings were automatically recorded and the values computed with the formula;

$$\text{Compressive strength, } (N/mm^2) = \frac{\text{maximum force, P (N)}}{\text{cross sectional area, } A_o\ (mm^2)} \qquad \text{Eqn. 3.1}$$

The shear modulus was measured according to the American Standard Testing and Measurement Method D-732, using the universal testing machine Hounsfield Monsanto Tensometer 8889 Made in England. The test was measured to 20mm x 20mm x 3.2 mm dimension.

The creep was measured according to the ASTM D-2990. It was calculated using the equation;

$$E_x = X/L_o \qquad \text{Eqn. 3.2}$$

Where; E_x = strain, X = extension ($L- L_o$) (mm), Lo = original length of the material (mm), L = deformed length (mm). The slope of the strain – time graph gives the creep value measured in per second (S^{-1}) which was then plotted against filler load.

Solvent Imbibition Analysis

Solvent imbibition of the composites was determined by ASTM D-570-98 method using deionized water and toluene respectively for three days at room temperature. It was calculated using the formula;

$$\%\ \text{imbibition} = (W_f- Wi)/ W_i \times 100 \qquad \text{Eqn. 3.3}$$

Where; W_f = weight after soaking in solvent, W_i = weight before soaking in solvent.

Thermal Analysis

This was achieved using Modulated Differential Scanning Calorimeter MDSC 2920 CE USA with aluminium pans and lids for both the samples and empty reference pans and heating rate of 10^oC per minute.

Surface Morphological Study

The microstructural arrangements of the composites were conducted using Scanning Electron Microscope (SEM) model: JEOL-JSM 7600F.

Degradation Study

Degradation of composites was achieved through soil burial method. Composites were buried 10 cm depth into soil obtained from an automobile mechanic workshop mixed with poultry waste for six months (180 days) and weighing done every 30 days interval. Degradation was measured from the mass reduction of composites and the percentage degradation calculated with the formula;

$$\text{Percentage degradation} = (W_f – W_i / W_i) \times 100 \qquad \text{Eqn. 3.4}$$

Where; W_f = Final weight, W_i = Initial weight

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RESULTS AND DISCUSSION

The results of the mechanical properties of the low density polyethylene and polypropylene with cassava peel-rice husk composites are shown in the figures below.

Tensile Strength Result of the Ldpe and Pp Composites

Tensile strength measures the resistance of a material to breaking under tension. The result of the tensile strength of the composites is shown in Fig. 1.

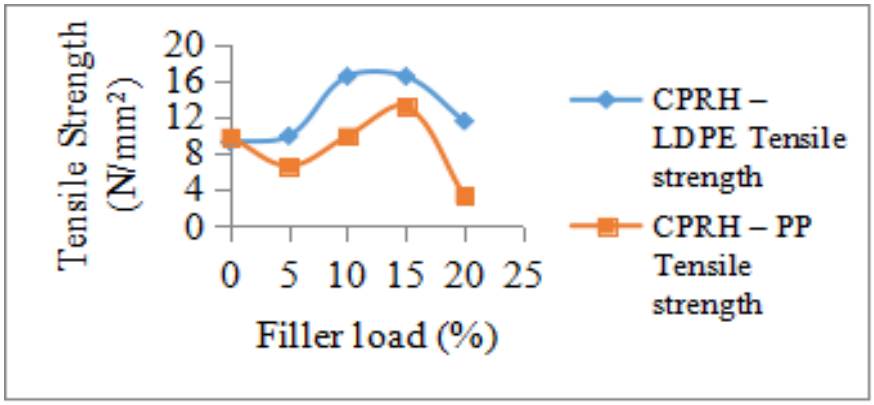

Fig. 1. Effect of filler loading on the Tensile Strength of LDPE and PP Composites

Figure1, shows an increase in the tensile strength as the filler load increases till saturation point before decreasing. The peak values were observed at 15wt% filler load for both LDPE and PP composites. This increase in the tensile strength of the composites could be as a result of stronger adhesion between filler and matrix interface which led to better stress transfer from the matrix to the filler. This is in line with Chris-Okafor et al., (2017) and Chris- Okafor et al., (2018) that attributed the increase in tensile strength to a better interfacial adhesion between the filler and polymer matrix. The gradual decrease after attainment of peak could be due to weakening of the interfacial attraction of the constituent composition as the fraction of the matrix is reduced with increasing weight fraction of filler that tends to alter the inherent properties of the matrix. This work is in agreement with the works of Morreale et al., (2008); Jacob and Mamza, (2021).

Percentage Elongation at Break

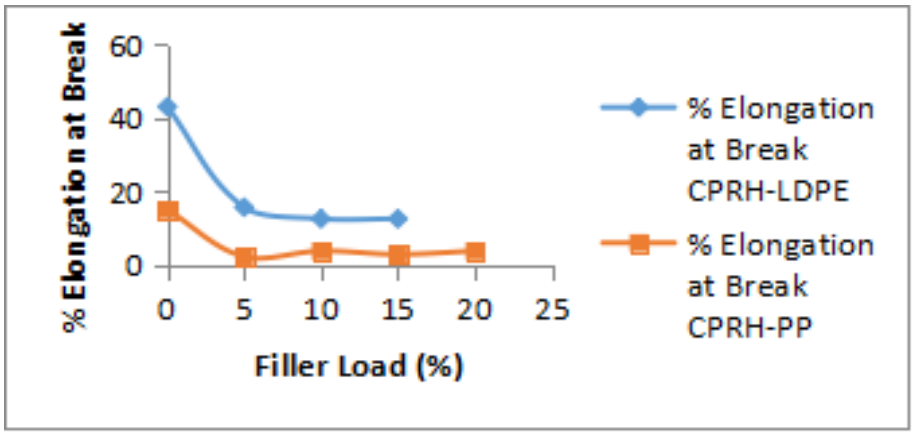

Fig. 2. Effect of filler loading on the Percentage Elongation at break of LDPE and PP Composites

Figure 2 shows that the percentage elongation at break decreased with increase in filler loading. This indicates that increase in filler loading decreased the ductility and/or elasticity but increases the toughness of the polymer composites. This is in line with Nwanonenyi and Ohanuzue, (2011) and Chris-Okafor et al., (2018) that observed decrease in percentage elongation at break and suggest that decrease was due to stiffening and hardening of the composite which reduced the composites resilience and toughness.

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Surface Hardness Result of the Ldpe and Pp Composites.

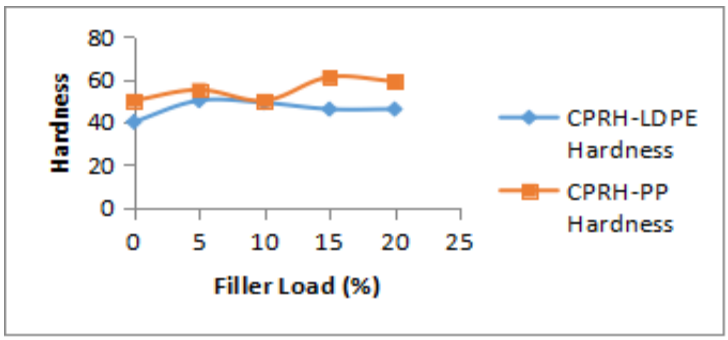

Fig. 3. Effect of filler loading on the Hardness of LDPE and PP Composites

Figure 3 reveals that the LDPE composites exhibited gradual increase in hardness as the filler load increases, while the PP composites showed fluctuating property although the hardness improved. This is an indication that the fillers enhanced the stiffness and strength as well as reduced the elasticity of the composites. Thus, yield a more rigid composite with enhanced surface resistance to indentation. This is in line with the works of Muhammad et al., (2011); Nwanonenyi and Ohanuzue, (2011) and Chris-Okafor et al., (2018); where there was observed increase in hardness of the composite as the filler load increases.

Compressive Strengths Result of the Ldpe and Pp Composites

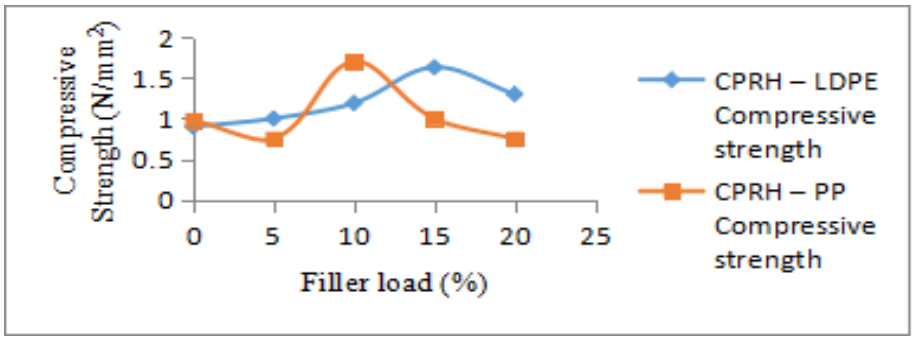

Fig. 4. Effect of filler loading on the Compressive Strength of LDPE and PP Composites

Figure 4 features an increase in the compressive strength as the filler load increases for LDPE composites, while the PP composites showed initial decrease followed by an increase at 10wt% then decrease continue. This increase could be attributed to the filler reinforcing characteristics, which due to its cellulosic nature was able to improve the composite's ability to be compressed. This is in agreement with the works of Ofora et al., (2016) where increased compression strength was observed and Chris-Okafor et al., (2017) that witnessed increased tensile strength in an irregular manner.

Shear Modulus Result of the Ldpe and Pp Composites

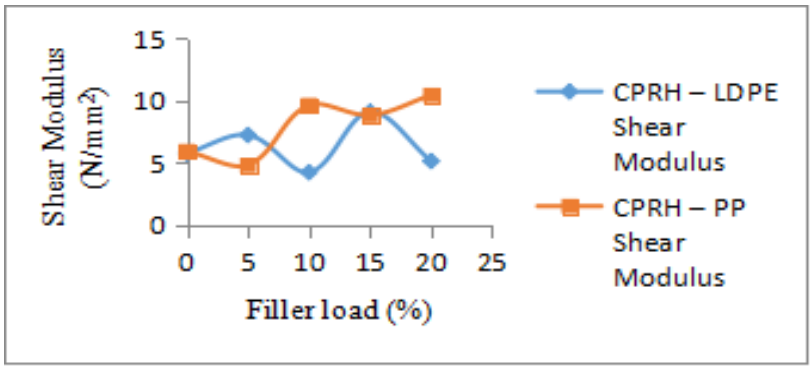

Fig. 5. Effect of filler loading on the Shear Modulus of LDPE and PP Composites

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From figure 5, the shear modulus of the composites showed irregular results as the filler loading increases. The shear modulus was found to be highest at 15wt% for LDPE and 10wt% for PP composites respectively. This increase suggests that the fillers increased the rigidity of the composites and enhanced the load-bearing capability of the material thus a larger force is required to deform the composites along the plane of the direction of the force. This is in agreement with the work of Ogudo et al., (2021) where there was observed increase in shear modulus with increase in filler load.

Creep Result of the Ldpe and Pp Composites

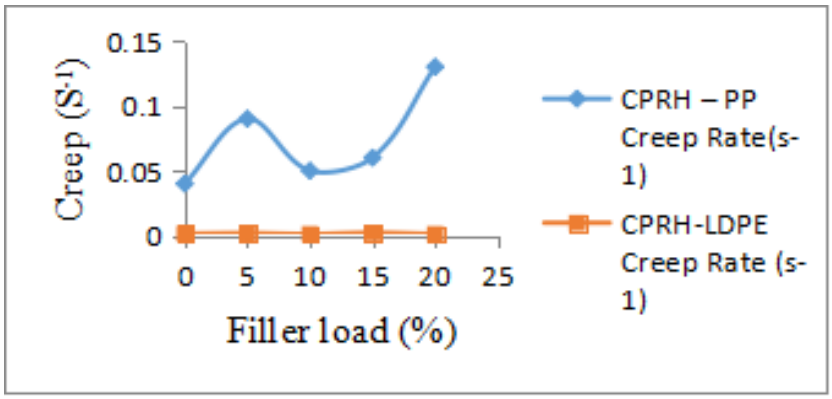

Fig. 6 Effect of filler loading on the creep of LDPE and PP Composites

Figure 6, shows the LDPE has linear creep behaviour, thus there was neither increase nor decrease in the creep behaviour of the LDPE composites. The PP composites showed irregular creep behaviour as the filler load increases. The increase in creep rate means increased deformation and reduced stiffness, while decrease in creep rate indicates improved stiffness.

Solvent Imbibition Result of the Ldpe and Pp Composites

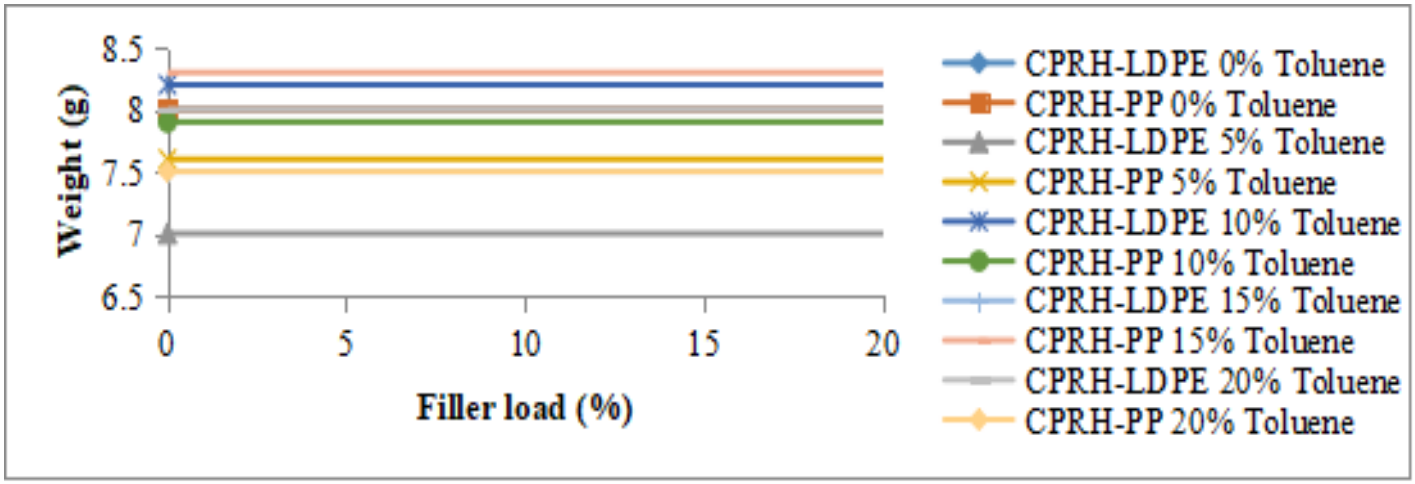

Fig. 7. Effect of filler loading on the Solvent Imbibition of LDPE and PP Composites

From the experiment, the water imbibition of the composites showed no increase to the final weight of the composites after complete immersion in water for seventy-two hours at room temperature. This could be due to some factors like: the hydrophobic nature of the polymer matrix and presence of lignin-a component of the filler, temperature variation effect; the low concentration of the fillers compared to the polymer matrix or the degree of homogeneity in the dispersion of fillers. This is in agreement with Ogudo et al., (2021). The imbibition in toluene showed slight increase in weight of about less than 1% as could be seen in figure 7. This result suggests that the composites can be used in wet environment; as water storage tanks, bathroom interior, etc. Water and toluene were chosen because of the difference in their nature and polarity. While water is a universal/polar solvent, toluene is an organic non-polar solvent. Also, the difference in boiling point is not much.

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Dsc Result of the Ldpe and Pp Composites

For research purpose, DSC analyses of only composites with highest tensile strength were done and the results were as follows;

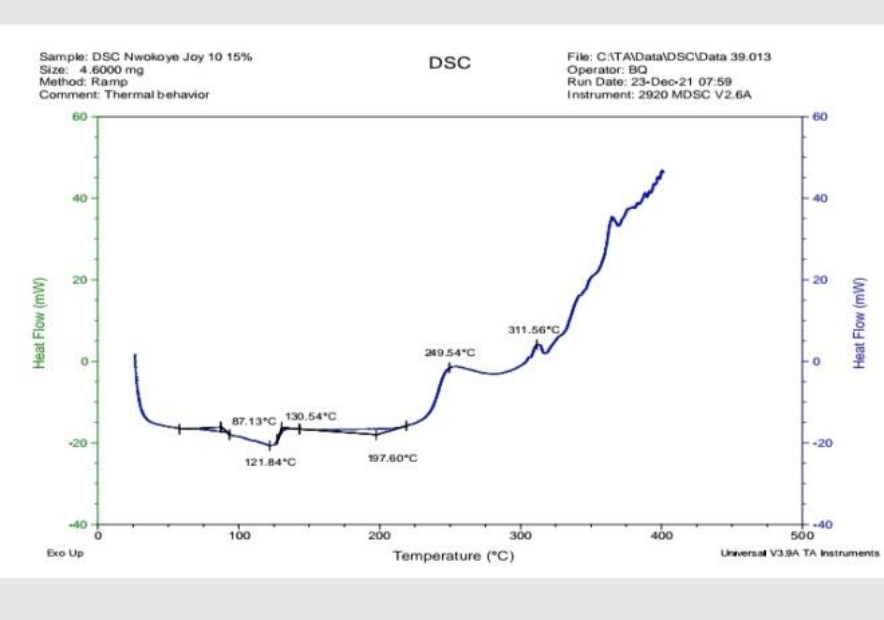
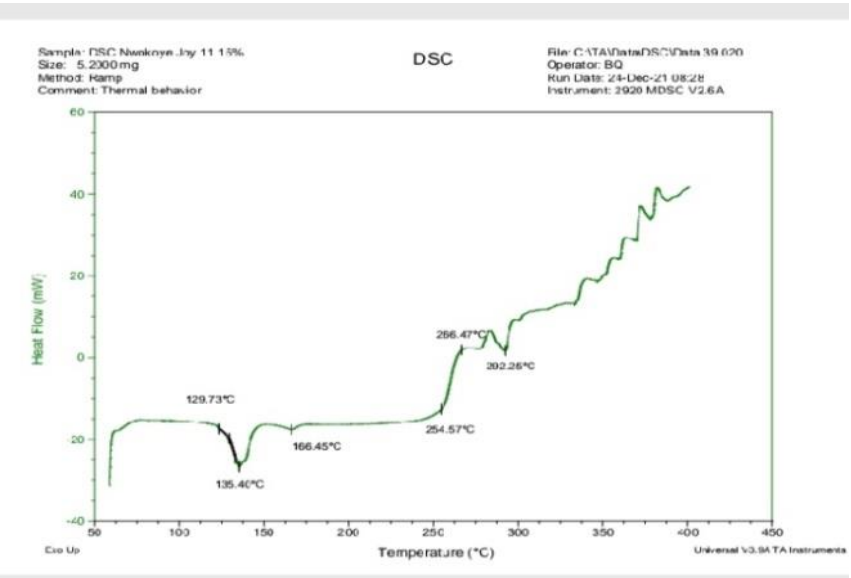


Fig. 8a. DSC thermogram of 15wt% CPRH-LDPE



8b. DSC thermogram of 15wt% CPRH-PP

For CPRH-LDPE composite, the glass transition temperature was obtained at 58.19^{o}C and the peak melting temperature was obtained at 121.84^{o} C indicating an increase in the melting temperature as against the commercial LDPE with melting temperature range from 105^{o}C to 115^{o}C, while the CPRH-PP composite had its melting temperature at 135.40^{o}C which falls in the range of commercial PP melting temperature of 130^{o}C to 171^{o}C. CPRH–PP composite experienced exothermic reaction at 266.47^{o}C indicating crystallization or aggregation but CPRH –LDPE did not experience exothermic reaction. This indicates that the agro-waste fillers had no effect on the PP composite temperature that is within the range of commercial PP, but improved the melting temperature of LDPE composites by 6%.

Morphology Result of the Ldpe and Pp Composites

Micrographs of the LDPE and PP composites via Scanning Electron Microscope.

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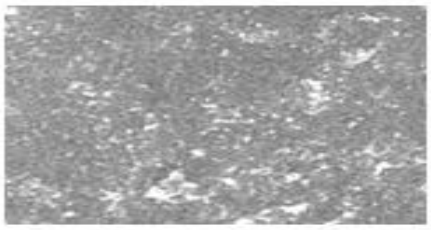
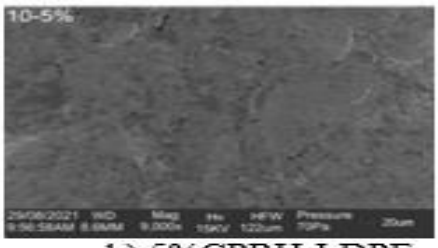
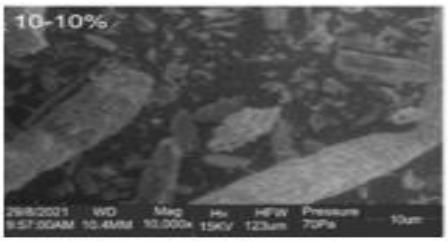


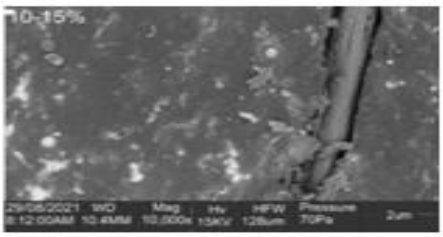
Fig. 9a) 0%CPRH-LDPE.



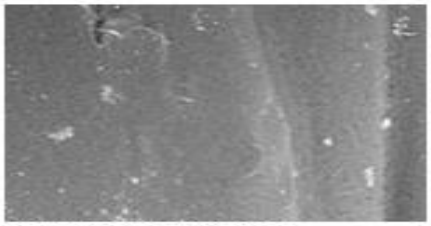
b) 5%CPRH-LDPE



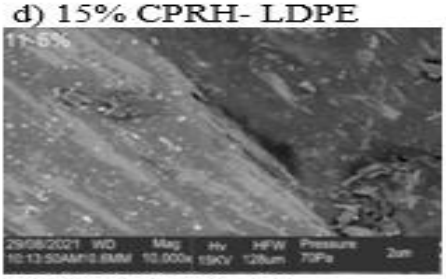
c) 10% CPRH-LDPE



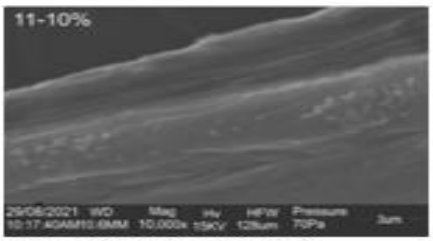
d) 15% CPRH- LDPE



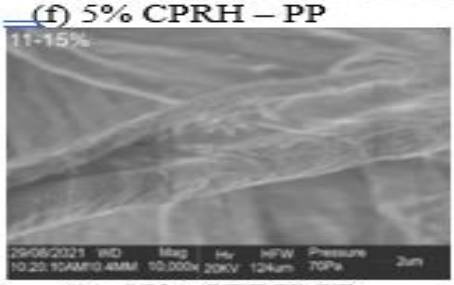
(e) 0% CPRH - PP



(f) 5% CPRH – PP



(g) 10% CPRH-PP



(h) 15% CPRH-PP

Figure 4.9a-h shows the micrographs of the LDPE and PP composites via Scanning Electron Microscope at 10,000 magnification and 70 Pa pressure. Figure 4.9a showed the morphology of virgin LDPE as homogeneous surface, while figures 4.9b-d showed the morphology of the composite (CPRH-LDPE) as the filler load increased from 5wt% to 15wt%. From the figures, there was no sign of presence of filler at 5wt% filler loading as the morphology seems to replicate that of pure LDPE but darker than the later. This means that the filler volume was inadequate to yield pronounced effect or could be that the interfacial bonding between the filler and the matrix was weak. As the filler loading increased to 10wt%, there was more interaction with the matrix to yield better bonding effect although there were signs of filler-filler interactions in form of fibre bundles, but the best morphology was obtained at 15wt% with greatest filler dispersion and single half-filled fibre pullout/ void, thus improved compatibility of the composites was observed. Figure 4.9e showed the morphology of virgin PP as homogeneous surface, while figures 4.9 f-h showed the morphology of the composites (CPRH-PP) as the filler load increased from 5wt% to 15wt%. From the figures, there was great sign of presence of filler at 5wt% filler loading. As the filler loading increased to 10wt%, there was more interaction with the matrix to yield better bonding effect as shown by the neat interactive surface, but the best morphology was obtained at 15wt% with greatest filler dispersion and homogenous surface, thus improved compatibility of the composites. From the SEM images, it could be inferred that as the filler loading increases, the filler dispersion improved and perfectly bonded to the matrix. The high interfacial contact between the hybrid fillers and the polymer matrix was attributed to the high mixing efficiency of the cassava peel and rice husk. Thus, CPRH-LDPE and CPRH-PP composites that showed higher tensile strength, was because the filler particles were well dispersed in the polymer matrix as both had excellent adhesion. This is in line with the works of Jumaidin et al., (2017) where observed homogenous structure without phase separation was observed in SEM image of some composites.

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Degradation Result of the Ldpe and Pp Composites

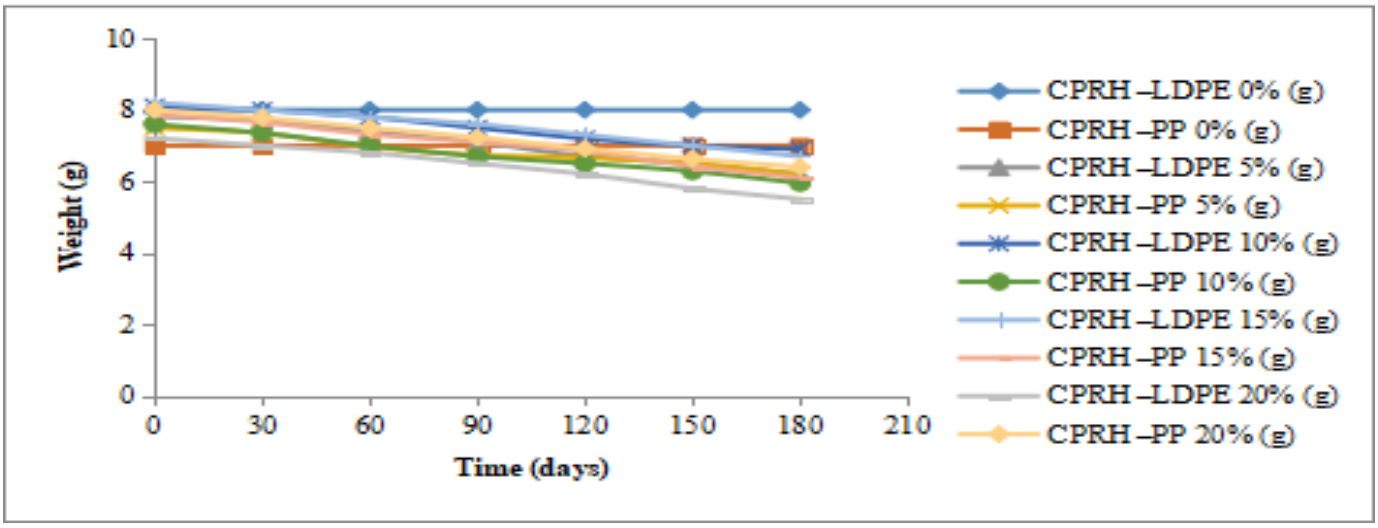

Fig. 10 Effect of filler load on the degradation properties of LDPE and PP composites

From figure 10, there was no reduction in weight for 0wt% PP during the 180 days test period, but there was a general reduction in weight after 30 days for 5wt%, 10wt%, 15wt% and 20wt% composites respectively. As the burial time increases, the weight reduction increases also. It was further observed from the figure that as the filler loading increases, the rate of degradation of the composites increases. This may be attributed to the relatively high cellulose content of cassava peel and rice husk. Increase in the lignocellulose content in the blend and increased underground temperature lead to increase moisture absorption and composite modification that aids faster degradation with consequent reduction in the mass of the composites (Abdul Amer and Saeed, 2019; Arutchelvi et al., 2008). Jumaidin et al., (2017) also observed increased in degradation as a result of addition of biomass which is in line with the present study result.

CONCLUSION

Cassava peel and rice husk blend have shown their effects on low density polyethylene and polypropylene composites at different filler loadings. The mechanical properties; tensile strength, compression strength and hardness were found to be improved while the percentage elongation at break decreased with increase in filler load. Thus, hybridization with cassava peel improved the tensile property of the rice husk which was seen to be reduced in the work of Nwanonenyi and Ohanuzue, (2011). This result also corroborates the work of Chris-Okafor et al., (2017) where increased tensile strength and compression strength with reduced percentage elongation was observed. The shear modulus was found to be irregular. The fillers had no effect on the LDPE composites creep rate and showed irregular creep behaviour with the PP composites. The solvent imbibition showed no result in water but less than 1 % increase in toluene. The DSC thermo gram showed the blend had positive impact on LDPE composite but no effect on PP composite. Micrographs at 10,000 magnification and degradation for 180 days demonstrated improved properties of the composites as the filler loading increases. Thus, it is accepted that agro-wastes like cassava peel and rice husk can be used as fillers in the manufacture of degradable plastics where strength and water resistance is required.

RECOMMENDATION

Further studies on degradation using direct microbial attack on the composite is recommended. More so, surface treatment of the biomass is recommended to see the effect on the polymer composites.

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