

The use of plasticizing agents (such as glycerol) in starch blend films is required to overcome film brittleness, occasioned by high intermolecular forces. Plasticizers function by interspersing and intercalating among and between polymer chains, disrupting hydrogen bonding and spreading the chains apart, which not only increase flexibility, but also water vapor and gas permeabilities [11], [12], [13].

On the other hand, the incorporation of starch into synthetic polymers causes a reduction in the mechanical strength of the resultant products [14], [15], [16]. To overcome this problem of mechanical strength reduction, a number of approaches such as the chemical modification of starch [17], [18], [19], [20], [21], the use of compatibilizers [16], [22], [23], fatty acids [17], and ethylene-co-acrylic acid [24] is adopted. Furthermore, it has been observed that the amount of starch in the blend also affects its mechanical properties. The mechanical and rheological properties and processability of the blend system have shown to worsen on increasing the starch content [25], [26], [27]. Studies have shown that the size and type of starch in the plastic blends [28] and the ratio of amylose to amylopectin of starch [29] affect the physical and mechanical properties of the starch/plastic blends.

In this study, the incorporation of plasticized and compatibilized indigenous potato starch into polyethylene has been considered as a means of improving the mechanical and biodegradable properties of the starch/pp blends. In this regard, the effects of starch content, plasticizer and compatibilizer on the mechanical properties, water absorption, biodegradability and fracture surface morphology of the blends have been investigated.

II. METHODS AND MATERIAL

Materials

Polypropylene pellets with properties (melting temperature, 165°C and melt flow index (MFI), 70g/10min) were obtained from Ceeplast industries Ltd, Nigeria. Maleic anhydride-graft-polypropylene (MA-g-PP) with properties (melting point, 156°C and density, 0.934g/cm³), obtained from Sigma-Aldrich corporation was used as a compatibilizer. Glycerol plasticizer was purchased from Ajax chemicals. Sweet potato starch

extracted from sweet potato tubers (*Ipomoea batatas*) which were purchased from Natural Root Crop Research Institute, Umudike, Abia State, Nigeria. It was sieved to a particle size of 0.075mm.

Preparation of Plasticized Potato Starch

Potato Starch (PS) was converted to plasticized potato starch (PPS) by adopting the method employed by St-Pierre *et al.*, [30] using a high speed laboratory mixer. Homogeneous mixture of starch, water and glycerol was obtained at 70°C and 50 rpm. The modified starch was then oven dried at 90°C for 12 h to reduce moisture content.

Preparation of PPS/PP blends: Blends of plasticized potato starch and polypropylene were obtained with an injection molding machine at a temperature of 160-190°C and screw speed of 50 rpm. The PPS loadings ranged from 0-50 wt. % whereas MA-g-PP was used at 10wt. % based on the starch content. The injection molded sheets were over dried for 24 h at 70°C to reduce moisture content to barest minimum.

Tensile Properties

The universal tensile testing machine, Instron 3366 was used to carry out the tensile tests for the PPS/PP blend samples according to ASTM D 638. The test was performed at a cross-head speed of 5mm/min at 23±5°C on a dog bone shaped specimen of 3mm thickness. Five specimens were used to obtain the average values of the tensile properties.

Water Absorption Study

Water uptake study of the various PPS/PP blends was conducted using cut samples of known dimensions (20 x 20 mm). These cut samples first were carefully washed with distilled water, over dried at 50°C for 12 h, cooled in a desiccator, and immediately weighed to the nearest 0.001g to obtain the initial weight (W_0). Afterwards, the samples were immersed in distilled water at room temperature range 32-36°C. Samples were removed from the water at definite time intervals (10 days) and weighed to obtain the weight after immersion in water (W_2). The percent (%) water absorbed by the samples was calculated using,

$$\% \text{ Water Absorbed} = [(W_1 - W_0)/W_0] \times 100 \dots\dots\dots (1)$$

Soil Burial Test

PPS/PP blend samples of dimensions, 20 mm x 20 mm were used to undertake the soil burial test at room temperature to determine the biodegradability of the PPS/PP blends. The samples were buried 100 mm below the surface of alluvial soil placed in perforated plastic boxes which was regularly moistened with water. The samples were removed at regular time intervals (10 days), washed with distilled water, dried at room temperature prior to weighing. The percent weight loss of the samples measured after every 10 days and that got after every tenth day were determined respectively as follows,

$$\% \text{ Weight Loss} = [(W_2 - W_3)/W_2] \times 100 \dots \dots \dots (2)$$

Where W_2 and W_3 are initial mass before and after degradation in the soil respectively

$$\% \text{ weight loss (after every 10days)} = \frac{\text{Initial wt. before 10days} - \text{final wt. after 10days}}{\text{Initial wt. at the beginning}} \times 100 \dots \dots (3)$$

Growth of Plants

The growth of some annual plants (soya bean and wheat) was monitored from the germination stage to find out whether or not degradation products from the PPS/PP samples would affect their growth. The plant seeds were placed in different pots containing the already removed PPS/PP samples, and were allowed to grow in the open for 30days. The length of the roots and height of the shoots of the growing plants were measured.

Morphology Test

The microstructure of the PPS/PP blend sample was evaluated using Scanning Electron Microscope (SEM). The samples were oven dried to remove moisture prior to sputter coating with a thin layer of gold to avoid electrical charging.

III. RESULTS AND DISCUSSION

Tensile Properties

The properties of tensile strength (TS), Young Modulus (YM) and elongation of break (EB) of both compatibilized and uncompatibilized plasticized potato starch /PP blends at different starch content are presented in Figures 1 and 2. It can be seen that the

behaviour of the tensile strength and elongation at break is inversely related to the starch content. This trend indicates that the tensile strength and elongation at break decrease with increase in starch loading. It is evident that the tensile strength and elongation at break of PPS/PP blends decreased from 38.902 N/mm² to 12.670 N/mm² and 17.2% to 4.9% respectively (Fig.1). The observed reduction is due to the poor interfacial adhesion between the two polymers with differing polarities which results in poor stress transfer between the matrix and the dispersed phase which possibly formed pockets of agglomerates.

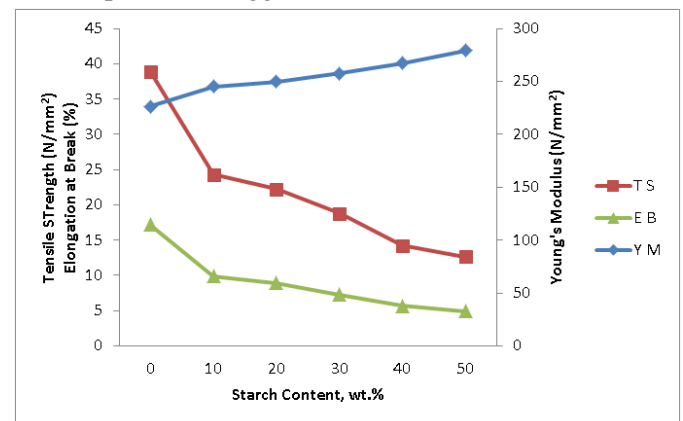


Figure: 1. Tensile properties of PPS/PP blends

On the other hand, the Young's modulus had a direct relationship with the starch contents on addition to PP matrix as envisaged. The modulus increased from 226.174 N/mm² to 278.980 N/mm² when the starch concentration was increased from 0 to 50 wt. %. Rosa *et al.*, [31], Wahab and Mottaleb [32] and Hanafi *et al.*, [33] have observed similar scenario in their respective studies. However, as the compatibilizer (MA-g-PP) was added into the PPS/PP blends, up to 50 wt. % starch content, the tensile strength and elongation at break of the blends significantly increased even though the values are still below the values of the pure PP (Fig.2). This is due to the ability of the MA-g-PP to improve interfacial adhesion and enhance the interaction between starch and PP components. This has been corroborated by SEM micrographs. It is observed that the TS of the blends increased by 42.69% and 67.86% while EB increased by 33.33% and 44.90% with reference to the uncompatibilized blends at 10wt.% and 50 wt.% starch content respectively. Again, with the same starch content, the PPS/PP blend with MA-g-PP showed higher Young's modulus than the uncompatibilized blend counterparts (Fig.1). This outcome is tied to the cross linking and the better interactions between starch and PP

in the presence of MA-g-PP. The Young's modulus at 10 wt. % and 50wt.% increased by 7.04% and 7.38% relative to the uncompatibilized blends respectively. Similar to our findings are the results obtained using hydrophilic fillers [33], [34], [35], [36], [37].

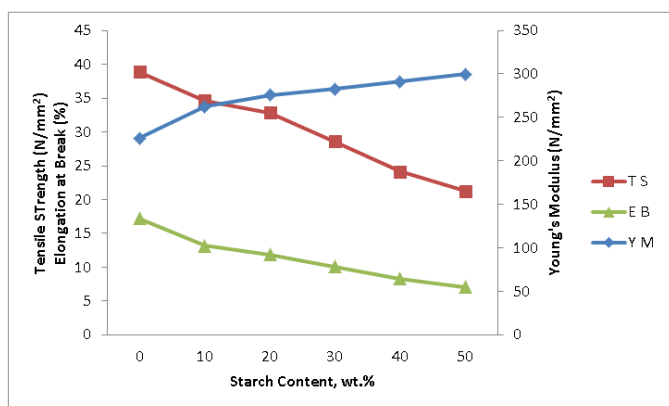


Figure 2. Tensile properties of PCPS/PP blends

Water Absorption Study

The water absorption characteristics of the PPS/PP and PCPS/PP blends against filler content as a function of time are presented in Figure 3. Results show that water uptake gradually increased with increasing starch content as well as immersion time. The hygroscopic nature of starch filler is due to the presence of hydroxyl groups. These hydroxyl groups increased with increasing starch content hence formation of hydrogen bonds between the fillers and the water molecules increased leading to high water uptake [38], [39], [40]. Again, poor interfacial adhesion associated with high filler content may generate anticipated cracks and voids between the starch filler and the matrix resulting to increase in water absorption [34]. However, PCPS/PP blend exhibited low water absorption behavior than the PPS/PP blends due to positive interaction between the PCPS/PP blends that resulted in cracks and voids minimization. The difference in water absorption rate for PPS/PP blends relative to PCPS/PP blends was about 38.02% and 13.61% at 10 wt. % and 50 wt. % filler content respectively. The maximum percentage water uptake increment at 50 wt. % starch content may be linked to the percolation of starch particles from the samples at high starch content with time [15].

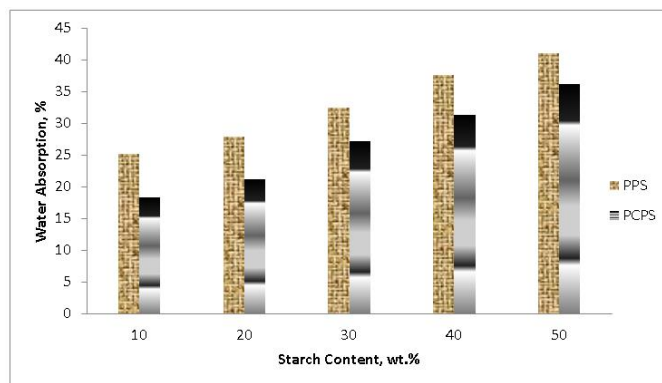


Figure 3. Water absorption of PPS/PP and PCPS/PP blends after 90 days of immersion

Soil Burial Test

The weight loss of PPS/PP and PCPS/PP blends as a result of the changes in weight with time is clearly highlighted in Fig 4. As it is the case with plastic matrix where starch is used as an additive, blend in contact with the soil and /or water is attacked by the soil microorganisms. It could be observed that biodegradation of the blends increases with increase in starch content and time for both PPS/PP and PCPS/PP blends up to 24%. Further observation indicates that PPS blends showed higher weight loss than PCPS blends, with an index of about 36% at 10wt. % and 34% at 50wt. %. This may be linked to higher interfacial adhesion existing in PCPS/PP blends. The weight losses percent of PPS/PP and PCPS/PP blends measured after every ten days have been investigated and are illustrated graphically in Fig 5. This was taken as the weight of the sample on each 10th day minus the proceeding weight of the sample prior to ten days. It is shown that at lower starch (≤ 20 wt. %) content, the weight loss was low but increased with starch content for both blends. The PCPS blends showed lower rate of weight loss and may be attributed to improved interfacial adhesion between the filler and matrix in the blends.

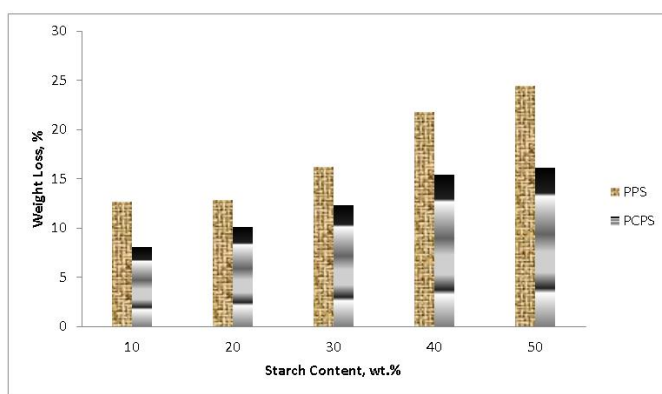


Figure 4. Weight loss of PPS/PP and PCPS/PP blends after 90 days of soil burial

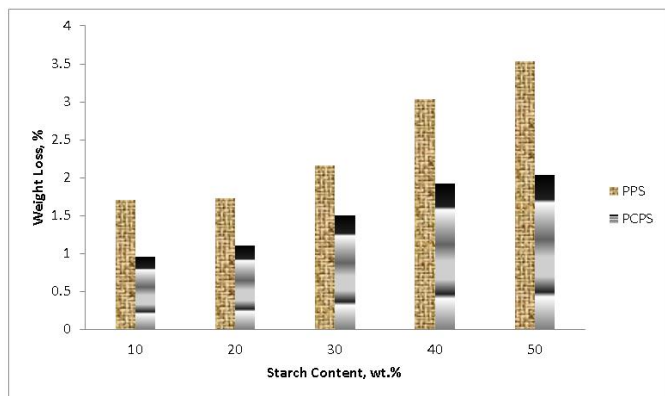


Figure 5. Weight loss after every 10 days for PPS/PCPS blends after 90 days of soil burial

Growth of Plants

In order to determine the effects of biodegradation products on the lives of the plants, wheat and soya bean plants were planted in plastic containers where PPS/PP and PCPS/PP blends. The plants were carefully watched from germination stage, and the shoots of the plants were measured as presented in Figs.6 and 7 respectively. It is seen that the plants under study germinated and with different growth rates irrespective of the starch contents. At early stages, the rate of growth was rapid and slowed down later. This phenomenon could be because the plants were approaching maturity. Furthermore, the response of the plants roots was also monitored since they were directly in contact with the soil sample. The determined average length of the roots for both PPS/PP and PCPS/PP blends is shown in Table 1. It could be observed that the roots were fresh and alive and were responsible for nutrients uptake which in turn promoted the growth of the plants. This phenomenon indicates that the degradation products are not detrimental to the growth of the plants.

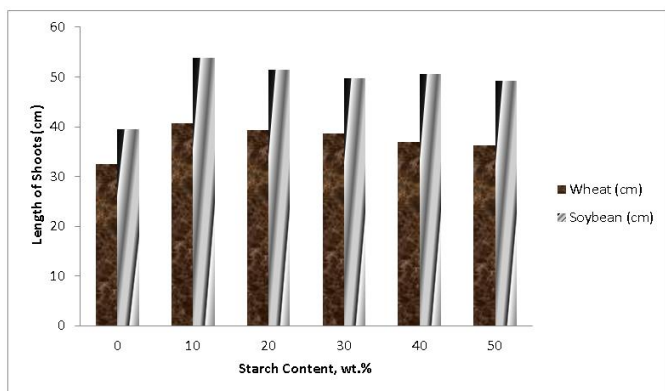


Figure 6. Length of wheat and soya bean plants for PPS/PP blends at the end of 30days

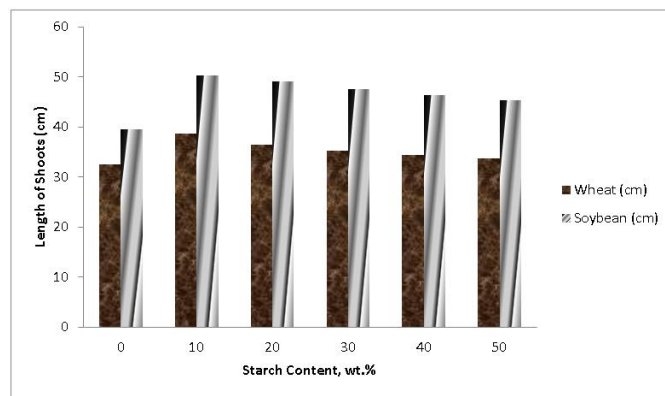


Figure 7. Length of wheat and soya bean plants for PCPS/PP blends at the end of 30days

Table 1: Average Length of plants roots for PPS/PP and PCPS/PP blends.

Starch Content Wt. (%)	PPS/PP Blends		PCPS/PP Blends	
	Wheat (cm)	Soya bean (cm)	Wheat (cm)	Soya bean (cm)
10	14.30	23.00	13.60	21.70
20	15.40	21.30	12.50	19.50
30	12.80	22.30	14.50	20.80
40	13.50	21.60	12.30	19.30
50	13.30	20.70	13.00	18.20

Morphology Test

Figures 8 and 9 show the SEM micrographs of fracture surfaces of PPS/PP and PCPS/PP blends for 10 and 50 wt.% starch loading before and after soil burial. The rough surface effects associated with plasticized starch could be observed as shown in the figures. However, the effect is minimal in PCPS/PP blends due to the presence of compatibilizer for both the 10 and 50 wt. % blends. Generally, the agglutination of blends at higher starch content can be reduced with the addition of a compatibilizer. This further suggested that improvement of tensile properties of PPS/PP blend on incorporation of PP-g-MA. All in all, majority of the grains seem to disappear because of microbial attack after 90 days of soil burial. This leaves a blend with a surface full of holes which are predominant with increase in starch loading and burial time as well as presence of compatibilizer as shown in Figure 9 showing enhanced interfacial adhesion between starch and polypropylene.

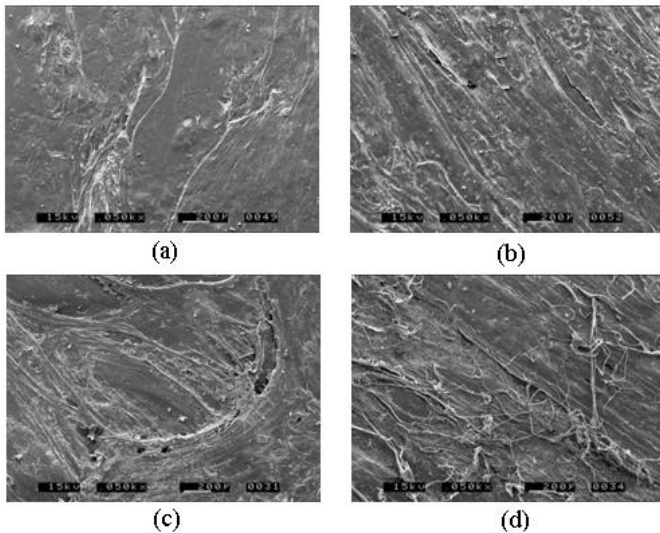


Figure 8. SEM micrographs of PPS/PP blends, 8 (a & b) at 10 %, 8 (c & d) at 50 % PPS before, and after soil burial

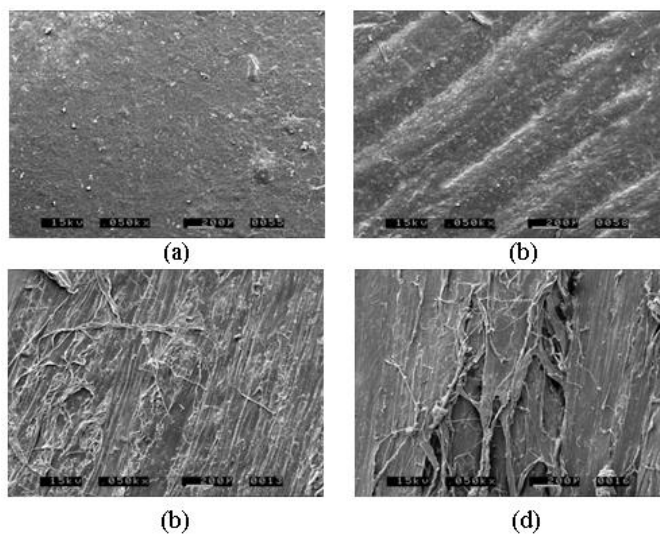


Figure 9. SEM micrographs of PCPS/PP blends, 9 (a & b) at 10 %, 9 (c & d) at 50 % PCPS before and after soil burial

IV. CONCLUSION

The addition of plasticized potato starch (PPS) into polypropylene matrix was found to be directly proportional to the Young's modulus and inversely related to the tensile strength and elongation at break of the blends. The incorporation of PP-g-MA into the PPS/PP blends is necessary to enhance the tensile properties.

Water absorption by the PPS/PP blends increased with the increase in starch content due to the hydrophilic nature of PPS but was however reduced on addition of compatibilizer.

The soil burial study revealed that the weight loss percent is higher for uncompatibilized than the

compatibilized PPS/PP blends indicating poor interfacial adhesion.

As for the growth of plants, the biodegradation products of the various blends presented no harmful effects on the plants. The fracture surfaces of the SEM micrographs of the blends indicate better presence of the compatibilizer

V. REFERENCES

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