

EFFECTS OF STARCH CONTENT AND COMPATIBILIZER ON THE METHANICAL, WATER ABSORPTION AND BIODEGRADABLE PROPERTIES OF POTATO STARCH FILLED POLYPROPYLENE BLENDS

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Abstract. Tensile, water absorption and biodegradable properties of potato starch filled polypropylene blends have been investigated. Polypropylene grafted maleic anhydride (PP-g-MA) was used as compatibilizer. It was observed that the tensile strength and elongation at break are inversely related to the starch content but Young's modulus followed a direct relationship with the starch content. However, the addition of PP-g-MA to the blends improved the tensile strength and elongation at break even though they were still lower than the neat polymer but the Young's modulus increased progressively. This is as a result of the enhanced interfacial bonding between the starch and matrix which can be proved by the SEM images. The tensile strength and elongation at break of the compatibilized blends increased by 30.59%; 42.62% and 23.36%; 24.62% in comparison with the uncompatibilized blends at 10 wt.% and 50 wt.% respectively. The percent water absorbed and weight loss of the PS/PP were higher than the CPS/PP blends due to poor interfacial bonding. Biodegradation products of the blends showed no deleterious effects on the growth of plants.

Keywords: *potato starch, polypropylene, compatibilizer, tensile properties, water absorption, weight loss*

Introduction

The environmental effect of continued persistence of plastics wastes is generating global concern, and disposal mechanisms to combat the trend seem to be limited. Incineration may generate toxic air pollutions; on its part, landfill sites are inadequate; recycling methods are energy intensive and besides not all plastics are recyclable while pyrolysis may not serve best due to the cost implications. As a result of the increasing environmental pressure generated by the accumulation of these plastic wastes, there has been a stimulated interest in the development of biodegradable or environmentally acceptable materials (Gasper et al., 2005; Bogoeva-Gaceva et al., 2007) as alternatives to conventional non-degradable polymers such as polyethylene, polypropylene, polystyrene etc.

These environmentally acceptable plastics are produced from natural polymers (such as starch, cellulose, chitin etc.) or synthetic polymers (such as polylactic acid, polycaprolactone, polyethylene succinate etc.) that can used individually, or as a blend, However, the production cost of synthetic biodegradable polymers is about five to six times greater than that of conventional synthetic polymers. Hence, researchers have

attempted to make commercially attractive biodegradable plastics through the use of natural and renewable materials.

Starch is a natural and renewable polymer obtained from a variety of botanical resources. Among its advantages, starch is inexpensive, abundant and biodegrades quickly (Fama et al., 2006; Teixeira et al., 2009). In recent years, starch has been identified as a key natural product for the production of biodegradable plastics. Reducing the amount of the synthetic polymer blending with starch is a strategy widely adopted for research (Pranamuda et al., 1996; Lawton and Fenta, 1994; Swanson et al., 1993; Koeing and Huang, 1995; Takagi et al., 1994). When is used in blend with non-biodegradable polymers, it increases surface for microbial activity on the matrix (Koeing an Huang, 1995) and also used as fillers with biopolymers where economics is the main objectives (Otey and Doane, 1984; Kotnis et al., 1995). However, the poor mechanical properties and relatively hydrophilic nature of starch compared to most conventional synthetic polymers have limited its widespread applications (Funke et al., 1998).

Polypropylene (PP) is a thermoplastic polymer produced commercially as plastic materials and difficult to be degraded by microorganisms in the environment as it is the case for all plastics. Notwithstanding its myriads of applications, polypropylene suffers a major limitation due to poor interaction with other materials (Arcana et al., 2007). Without any specific interactions, PP is unlikely to form miscible blends or even to adhere to other polymers (Chung and Rhubright, 1993).

Most of the physical and mechanical properties of the starch/plastic blends depend greatly on the interaction between the starch and the thermoplastic material. One way to improve this interaction is by the incorporation of a compatibilizer. Several studies showed that using PP modified maleic anhydride as compatibilizer in the starch/plastic blends greatly improved interfacial bonding between the starch fillers and the plastics (Waryat et al., 2013; Brent et al., 2012; Obasi and Igwe, 2014).

Therefore, the main objective of this work is to investigate the effects of starch content and compatibilizer on the mechanical, water absorption and biodegradable properties of potato starch filled polypropylene blends. Scanning Electron Microscopic (SEM) was used to provide the information to evaluate the filler/matrix interaction.

Materials and methods

Polypropylene (PP) granules (Melt flow index: 70 g/10 min; melting temperature: 165°C) were obtained from CeePlast Industries Ltd, Aba, Abia State, Nigeria. Compatibilizer polypropylene-graft-maleic anhydride (PP-g-MA) was supplied by Sigma-Aldrich Chemicals Germany (melting point: 156°C; density: 0.934gcm⁻³). Cassava tubers were purchased from local market in Ehime Mbano, Imo State, Nigeria. Potato starch (PS) was extracted from the tubers according to the method used by integrated cassava project (ICP) of the Federal Ministry of Agriculture and Rural Development, Nigeria. It was sieved to a particle size of 0.075 mm.

Preparation of PS/PP Blends

Potato Starch (PS) was dried to 1 – 2 % moisture content using an oven at 80°C for 24 h and then stored in sealed polyethylene bags to avoid moisture infiltration. Compounds of potato starch (PS) or compatibilized potato starch (CPS) and polypropylene (PP) were melt blending similar to polymer blending in an injection

machine with a screw speed of 50rpm and at a temperature of 160 - 190°C to obtain PS/PP or CPS/PP blends. These blends with five different starch contents (10, 20, 30, 40 and 50 wt. %) were prepared for tensile properties and biodegradability whereas polypropylene-graft-maleic anhydride (PP-g-MA) at 10 wt. % based on the starch content was used as compatibilizer. After injection molding, the sheets were conditioned for 24 h at 70°C and stored in desiccator prior to testing.

Water Absorption Test

Water uptake by the various blend samples were determined using cut samples of dimensions, 2 cm x 2 cm. Before the absorption test, cut samples were thoroughly washed, over-dried at 50°C for 12 h, cooled in desiccators, and immediately weighed to the nearest 0.001 g to obtain the sample initial weight (W_0). The conditioned samples were then immersed in distilled water at room temperature range 32 - 36°C. At predetermined intervals (10 days), samples were taken out from the water and weighed using determined balance to obtain the weight of the sample after immersion in water (W_1). Excess water on the surface of the samples was removed before weighing. The percentage (%) of water absorption by the samples was calculated as follows;

$$\% \text{Water absorbed} = \left[\frac{W_1 - W_0}{W_0} \right] \times 100 \quad (1)$$

Biodegradability Test

The biodegradability of the samples was carried out at ambient temperature under moisture-controlled conditions. Samples of known dimensions, 2 cm x 2 cm were placed in a perforated plastics boxes containing moisturized alluvial soil. The samples were buried 10 cm below the surface of soil which was regularly moistened with water. The samples were removed at predetermined time intervals (10 days), washed with distilled water, dried at room temperature to a constant weight and stored in a desiccator until testing. The percent weight loss of the samples was determined as follows;

$$\text{Weight loss} = \left[\frac{W_b - W_a}{W_b} \right] \times 100 \quad (2)$$

where W_b is the initial mass before degradation and W_a is the mass after degradation to the soil.

Morphology Test

The microstructure of the PS/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.

Results and Discussion

Tensile properties

Tensile strength (TS), Young's modulus (YM) and Elongation at break (EB) are important parameters to describe mechanical properties of materials. TS and EB represent the resistance of a material to elongation and its stretching capacity whereas YM denotes a measure of the rigidity of the material. *Figure 1* and *Figure 2* present the tensile properties of PS/PP and CPS/PP blends. From the figures, it was observed that

TS and EB are inversely related to the starch content. This means that TS and EB decrease with increase in starch content and became significant when the starch concentration increased. It is evident that the values of TS and EB dropped from 38.902 N/mm² to 14.947 N/mm² and 17.2% to 5.3% at 50 wt. % starch content respectively. This may be attributed to high filler-filler interaction at the expense of low matrix-filler interaction. The results agree with those found by other authors (Rosa et al., 2007; Wahab and Mottabeb, 2001).

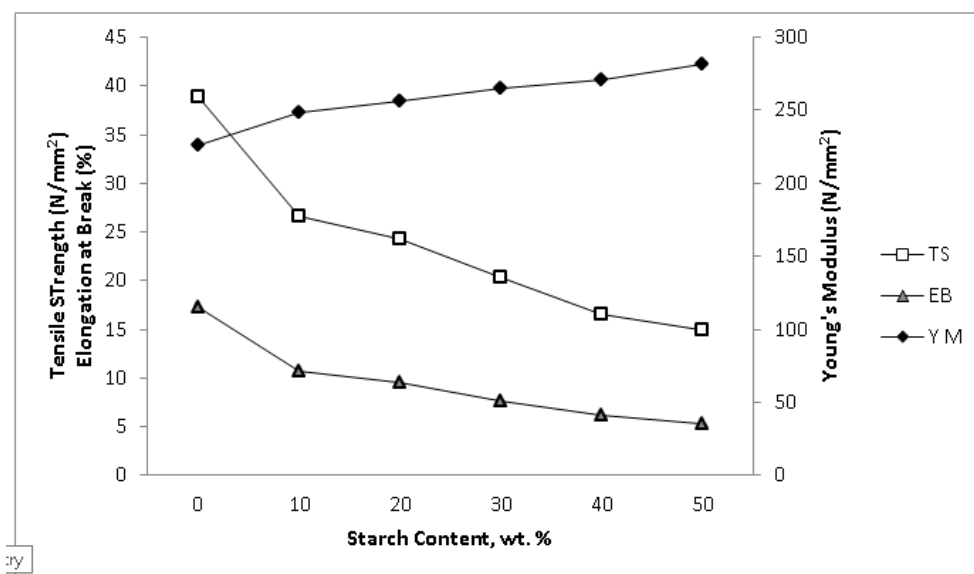


Figure 1. Tensile properties of PS/PP blends.

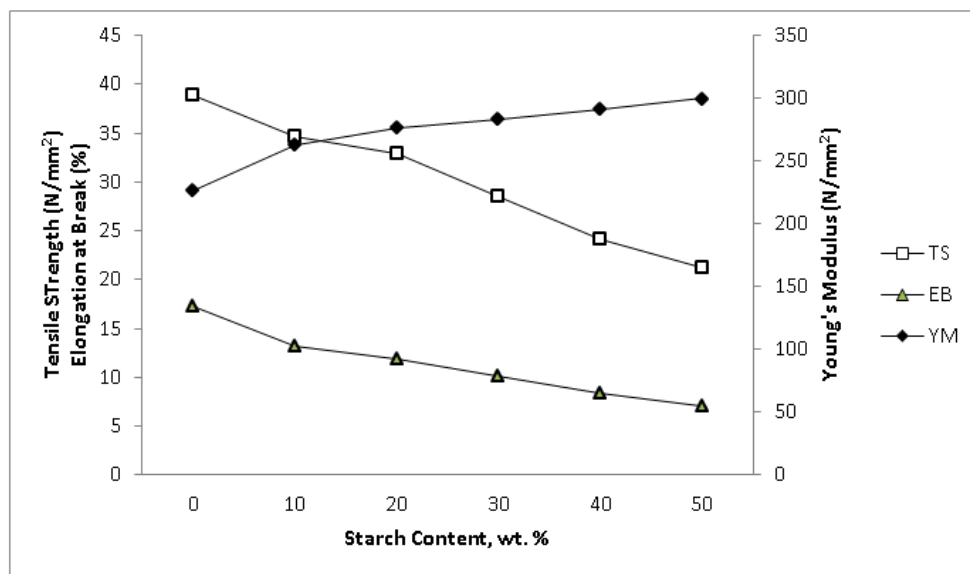


Figure 2. Tensile properties of CPS/PP blends.

The addition of potato starch increased the rigidity (greater YM values) of the blends in comparison with the pure PP matrix. The YM increased from 226.174 N/mm² to 282.019 N/mm² when starch content was raised from 0 wt. % to 50 wt. %. This may link to the stiffening effect which gave rise to low stretchability. This phenomenon is

probably due to presence of structural discontinuities in the polymer network and as well as the lack of the interactions between the starch components and PP matrix.

The effect of the PP-g-MA on the tensile properties (TS, YM and EB) of PS/PP blends is presented in Fig.2. Coupling agent (PP-g-MA) was used to provide compatibility between starch and PP to improve interfacial adhesion. It is observed that PS/PP compatibilized blends gave higher values than the uncompatibilized indicating good interfacial adhesion. The TS of the blends increased by 30.59% and 42.29% while EB improved by 23.36% and 24.62% in comparison with the uncompatibilized blends at 10 wt.% and 50 wt.% respectively. It is worthy. to note that the values of both the TS and EB for both compatibilized and uncompatibilized blends were lower than the neat PP indicating that potato starch is non-reinforcing filler. On other hand, YM experienced higher increase on addition of PP-g-MA. The values of YM increased by 5.73% and 6.22% relative to the untreated blends at 10 wt.% and 50 wt% starch content respectively. Similar to our findings are the works of (Wu, 2003; Bikiaris et al., 1998). The increase in the tensile properties of the blends could be attributed to improved stress transfer resulting in reduced interfacial debonding between the polar starch and non-polar PP matrix.

Water Absorptions Test

For many applications, dimensional changes caused by water absorption are major concerns when working with hydrophilic materials. *Figure 3* presents the water absorption of potato starch-filled PP blends for compatibilized and uncompatibilized at varying starch content. As can be observed, the water absorption gradually increased with increasing starch content as well as immersion time. This scenario is due to the hydrophilic nature of sweet potato starch which contains hydroxyl groups; therefore strong hydrogen bonds are formed between the starch fillers and water molecules. This means that at higher starch content, a higher amount of water is being absorbed (Kale et al., 2007).

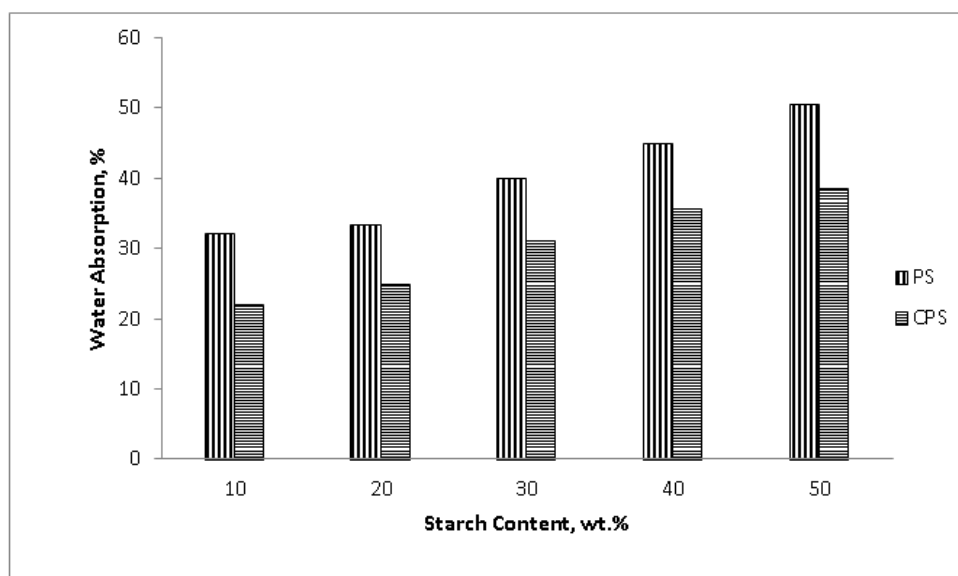


Figure 3. Water absorption of PS/PP and CPS/PP blends after 90 days of immersion.

The PS/PP blends showed lower water resistance index than the CPS/PP blends. The increment of water absorption for PS/PP blends compared with CPS/PP blends was about 45.95% and 30.95% at 10 wt. % and 50 wt. % filler content respectively. It is worthy to note that after 90 days of immersion, the percentage water absorbed by PS at 30 wt. % (40.131%) starch content is higher than that absorbed by CPS at 50 wt. % (38.595%) starch content indicating good stress transfer at the filler/matrix interface. Again, the blends after 90 days of water immersion did not equilibrate. This is an agreement with the works of (Willet, 1994), demonstrating that the equilibration time for starch/PE blend is the period of months even when immersed in water.

Biodegradability Test

The biodegradability study of the blends which indicates the weight loss of PS/PP and CPS/PP blends defines the extent of biodegradation of the blends and is presented graphically in *Figure 4*. It is evident from the figure that the weight loss of PS/PP and CPS/PP blends increased with increase in starch content as well as burial time. Again, PS/PP blends had a higher weight loss percent than CPS/PP, with an incremental index of about 7.81% at 10 wt. % and 26.70% at 50 wt. % starch content. This behaviour is similar to that observed in water. Thereafter, the rate of biodegradation increased with PS/PP blends having a higher reduction in weight. At 50 wt. % starch content, the CPS/PP blends had weight loss percent value of about 2.33% which is little higher than that obtained for PS/PP blends at 30 wt. % starch content. This behaviour may be attributed to the absorption study and same factors earlier advanced might still be responsible where higher water absorption was recorded.

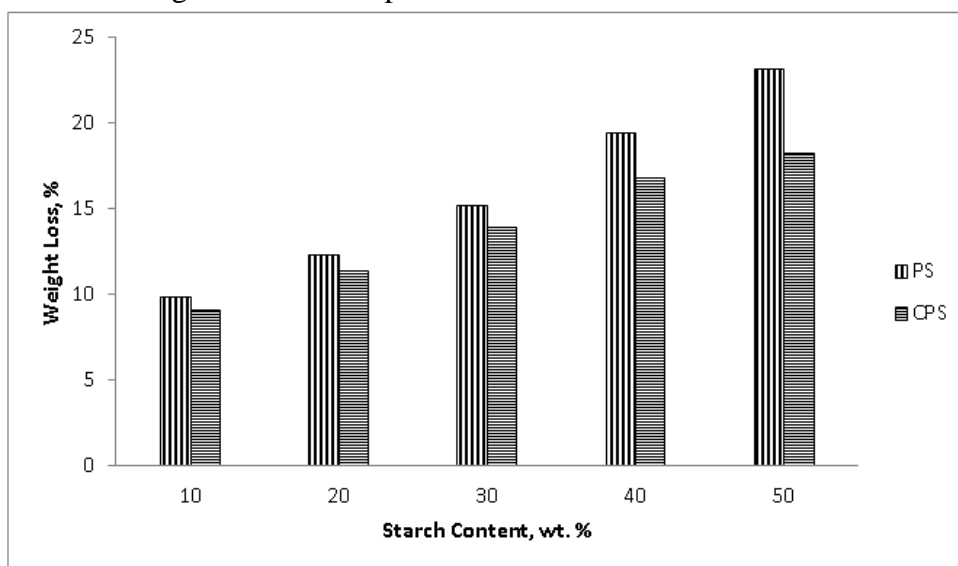


Figure 4. Weight loss of PS/PP and CPS/PP blends after 90 days of soil burial.

In another arrangement, the weight loss percent of the PS/PP and CPS/PP blends was taken after every 10 days and is shown in *Figure 5*. This was measured as the weight difference after each 10th day prior to 10 days which indicates specifically the rate of weight loss by each blend sample at any given time. From the results, it is clear that the rate of biodegradation was low at lower starch content (≤ 20 wt. %) for all the blends. Thereafter, the rate of biodegradation increased with PS/PP blends having a higher reduction in weight. At 50 wt. % starch content, the CPS/PP blends had weight loss

percent value of about 2.33% which is little higher than that obtained for PS/PP blends at 30 wt. % starch content. This behaviour may be attributed to the improved stress transfer and good interfacial adhesion between the starch filler and the matrix in CPS/PP blends.

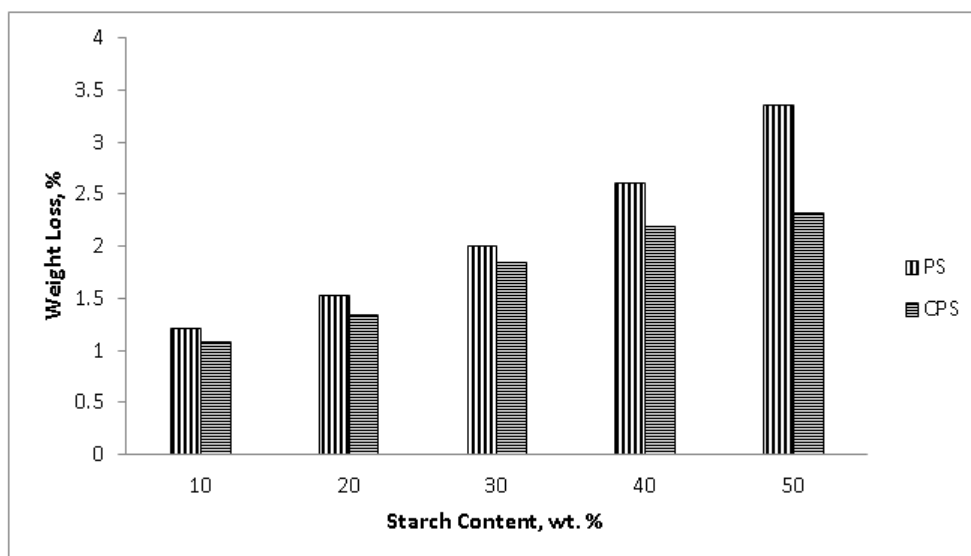


Figure 5. Weight loss after every 10 days of PS/PP and CPS/PP blends after 90 days of soil burial.

Growth of Plants

The effects of biodegradation products on the growth of wheat and soya bean plants have been studied and the results obtained are presented in *Figures 6* and *Figure 7*. These plants were planted in the containers where PS/PP and CPS/PP blends were buried in the soil and were monitored from germination stage. The shoots of these plants were measured every 10 days for a period of 30 days and average length of the shoots obtained. The graphs indicate that the plants germinated as planted, and with varying growth rates and independent of starch content. The results also show that the growth rate was rapid at early stages and later decreased. This later phenomenon may be linked to the fact that the plants might be approaching maturity.

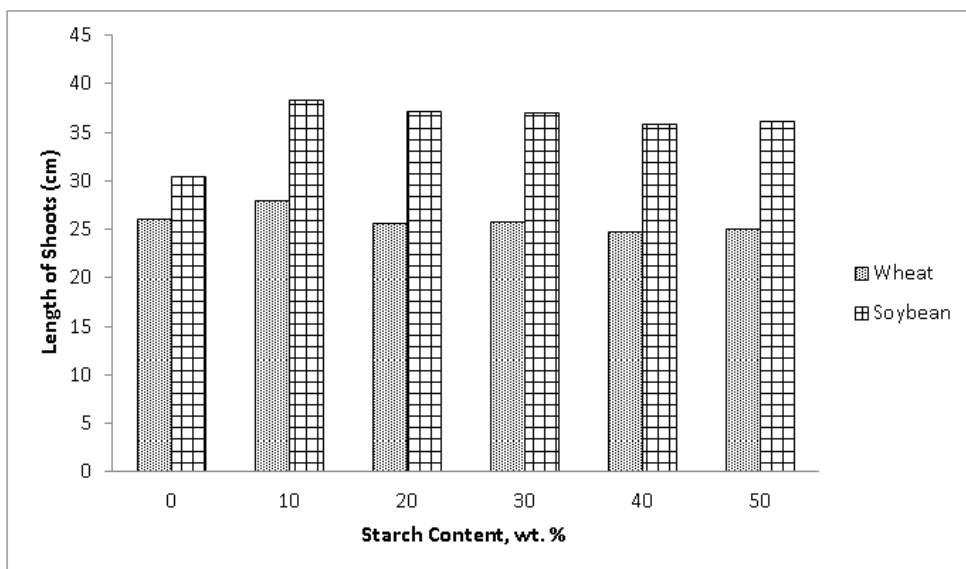


Figure 6. Average length of wheat and soya bean plants for PS/PP blends at the end of 30days.

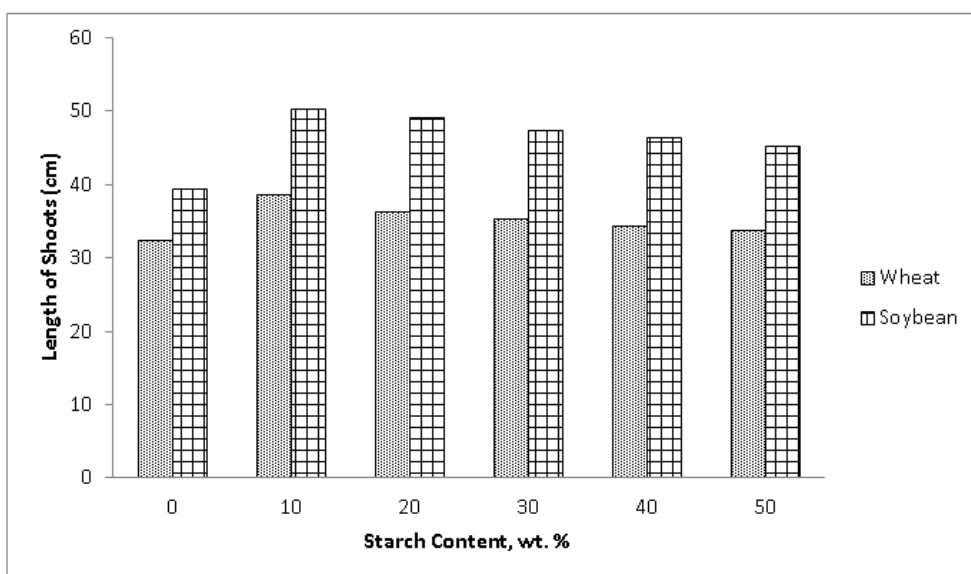


Figure 7. Length of wheat and soya bean plants for PCPS/PP blends at the end of 30days.

In the same vein, the behaviour of the plants' roots was also observed since they were directly in contact with the soil sample, though the roots were not edible parts of the plants under study. The results obtained in terms of average determined length of the roots were presented in Table 1 for PS/PP and CPS/PP blends. The growth rates were progressive and also an indication that the degradation products are not deleterious to the growth of plants.

Table 1. Average length of plants roots for PS/PP and CPS/PP blends.

| Starch Content WL (%) | PPS/PP Blends | | PCP/PP Blends | |
|-----------------------|---------------|----------------|---------------|----------------|
| | Wheat (cm) | Soya Bean (cm) | Wheat (cm) | Soya Bean (cm) |
| 10 | 11.30 | 19.50 | 10.90 | 18.70 |
| 20 | 12.10 | 18.40 | 13.30 | 17.30 |
| 30 | 14.30 | 18.80 | 12.40 | 16.90 |
| 40 | 13.90 | 19.20 | 13.50 | 17.80 |
| 50 | 12.20 | 18.30 | 12.20 | 17.40 |

Morphology Test

Scanning Electron Microscopy (SEM) was used to determine the surface morphology of the fractured surfaces of PS/PP and CPS/PP blends and also to visualize the extent of dispersion of the starch filler in the polymer matrix. *Figure 8* and *Figure 9* present the surface micrographs of PS/PP and CPS/PP blends before and after soil burial at 10 wt. % and 50 wt. % starch contents respectively.

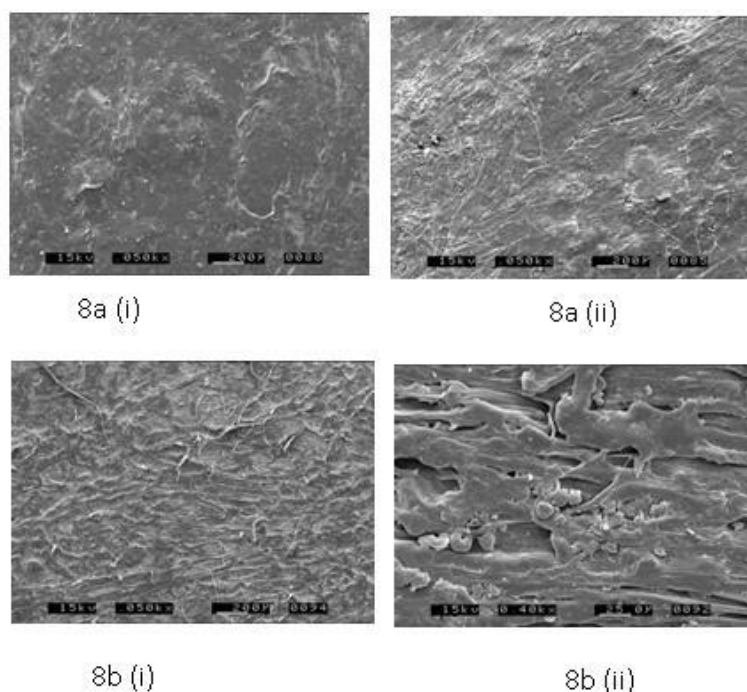


Figure 8. SEM micrographs of PS/PP blends. 8a (i & ii) 10 % PS and 8b (i & ii) 50% PS before and after soil burial.

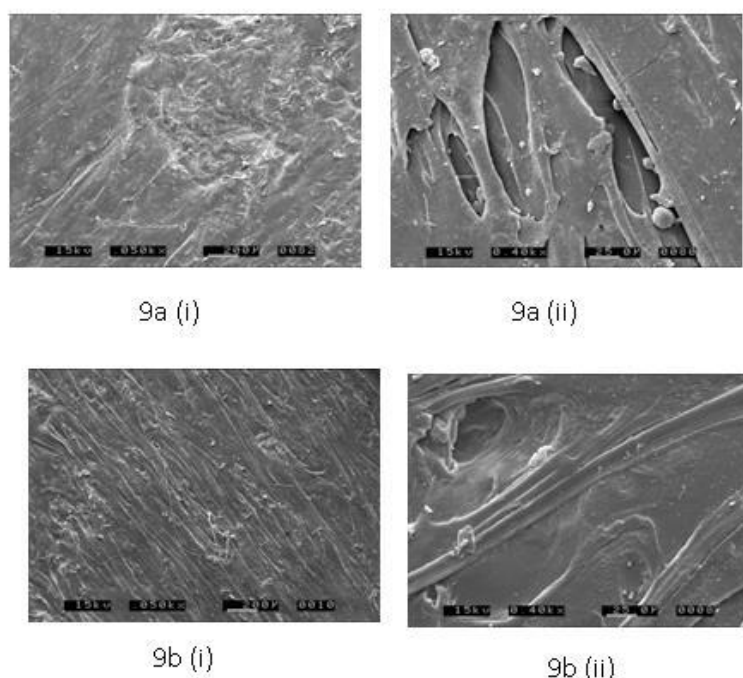


Figure 9. SEM micrographs of CPS/PP blends. 9a (i & ii) 10% CPS and 9b (I & ii) 50% CPS before and after soil burial.

Figure 8(a) and *Figure 9(a)* represent starch content at 10 wt. % in which starch is less visible due to poor dispersion of the starch in the PP matrix. However, a minimal effect was observed in *Figure 9(a)* due to the presence of compatibilizer. On the other hand, *Figure 8(b)* and *Figure 9(b)* represent starch content at 50 wt. % in which the starch particles are evidently visible; an indication that the particles of the starch are not completely covered by the matrix as displayed in *Figure 8(b)*, but a better distribution of starch in PP matrix was seen. This validated the improvement of tensile properties of PS/PP blends on the incorporation of PP-g-MA. As can be seen from the micrographs, majority of the starch particles seem to disappear because of microbial attack after 90 days of soil burial. This leaves a blend with a surface full of holes which appear very significant with increase in starch content as shown in *Figure 9(b)* for starch content at 50 wt. %.

Conclusion

The main conclusions drawn from this study were higher starch content in polypropylene lowered the tensile strength and elongation at break due to poor interfacial adhesion between the filler and the matrix, the Young's modulus increased with increase in starch content and the incorporation of PP-g-MA into the PS/PP blends is necessary to improve the tensile properties, water absorption by the blends increased with increasing starch content due to increasing presence of hydroxyl groups in the blends, the compatibilized PS/PP blends showed lower weight loss percent than the uncompatibilized PS/PP blends indicating good interfacial adhesion, biodegradation products of the various blends were found to be harmless on the growth of plants, and presence of compatibilizer (PP-g-MA) improved the interfacial adhesion between the starch filler and matrix as confirmed by the SEM images.

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