American Journal of Engineering Research (AJER)
e-ISSN : 2320-0847 p-ISSN : 2320-0936
Volume-03, Issue-02, pp-96-104
www.ajer.org

Research Paper Open Access

Effects of Native Cassava Starch and Compatibilizer on Biodegradable and Tensile Properties of Polypropylene

*Obasi, H. C., and Igwe, I. O.
Department of Polymer and Textile Engineering, Federal University of Technology, P.M.B. 1526, Owerri.

Abstract: **-** The effects of starch content and polypropylene-graft-maleic anhydride (PP-g-MA) as a compatibilizer on the properties of indigenous cassava starch filled polypropylene blends have been investigated. The blends were prepared by the addition of cassava starch of particle size 0.075 mm to polypropylene matrix using an injection machine with a screw speed of 50 rpm and at a temperature range of 160 - 190°C. Starch contents ranged between 0 and 50 wt. % and PP-g-MA was 10 wt. % based on starch content. Tensile, water absorption, weight loss and morphological properties were studied. Tensile strength and elongation at break decreased, while Young's modulus, water absorption and weight loss percent increased with increasing starch content. However, on addition of PP-g-MA, these properties were improved due to enhanced interfacial adhesion between the starch and the matrix though tensile strength and elongation at break were still lower than the neat PP. The morphological studies of fractured surfaces using SEM corroborated the deterioration in the properties.

Keywords: *- Cassava starch, polypropylene, PP-g-MA, tensile properties, water absorption, weight loss, SEM.*

I. INTRODUCTION

The advent of biodegradable polymers can be considered a best approach to solving the menace of municipal solid wastes in our environment. As a result, a great number of biodegradable polymers have been synthesized and microorganisms and enzymes capable of degrading them have also been identified [1]. In Nigeria and other developing countries, environmental degradation and pollution by synthetic polymers have assumed alarming proportions. Attempts therefore have been made to solve these problems through structural modifications of the synthetic polymers to enhance their biodegradability.

The combination of synthetic polymers such as polyethylene, polystyrene, polypropylene and natural additives like cellulose, starch, and chitin is an important way to improve biodegradability of polymers [2-5]. The bioplastics obtained offer great benefits over conventional materials - socially, economically and much more environmentally friendly. The fast pace of these bioplastics have endeared the chemical and plastics industries to invest heavily in this sector, and have high expectations of the new generations of bioplastics which are now competing favourably with the traditional petroleum-based plastics.

These bioplastics can be degraded into natural ecosystems such as active sludge, natural soil, lake and marine [6]. Accordingly, the biodegradability of polymers corresponds to the ability to be chemically transferred by the action o biological enzymes or microorganisms [7, 8]. Biodegradation for limited periods is a reasonable approach for the complete assimilation and disappearance of an article leaving no toxic or environmental harmful residue [1]. Biodegradable polymers have been found very useful in medical, agriculture, drug release and packaging applications.

Polypropylene is one of the most widely used plastics for packaging and production of bags and other consumer products. It has high melting point (160°C) with combination of properties such as strength, lightness, stability, flexibility, moisture and chemical resistance and ease of processability [9]. Polypropylene is also employed in the production of automotive interiors, fibres and non-absorbable sutures and in composites with other materials [10]. Starch is a natural polymer obtained from crops which include corn, rice, potatoes, cassava and wheat. Starch has been extensively used as a raw material in bioplastics production due to increasing prices and declining availability of conventional polymer resins.

Starch itself is difficult to process with poor dimension stability and inferior mechanical properties for its end products hence native starch is not used directly.

Starch therefore can either physically be mixed in with its native granules, kept intact or melted and blended on a molecular level with suitable polymer [1]. Bioplastic materials that are formed from starch-based blends may be injection molded, extruded, blown or compression molded.

The blend material composed of a mixture of synthetic polymer with natural biopolymer like starch is believed to obtain a plastic material with different properties [11]. The quantity of starch in the blend affects its properties. It has been observed that increasing the starch content is shown to worsen the mechanical and rheological properties and the processability of the blend [12-14]. As a way of improving the properties of the blend material, a compatibilizer, polypropylene-graft-maleic anhydride (PP-g-MA) containing groups capable of hydrogen bonding with starch hydroxyls is used. It forms suitable complexes with starch due to hydrogen bond formation between anhydride groups of the compatibilizer and hydroxyl groups of starch.

In this study, indigenous raw cassava starch was incorporated into polypropylene matrix in the presence of a compatibilizer as a means of enhancing the tensile and biodegradable properties of the blends formed. Tensile, water absorption and biodegradable properties were investigated as a function of starch content. Fractured surfaces of the blends were investigated by scanning electron microscope (SEM) providing the information for the evaluation of interfacial fibre/matrix adhesion.

II. EXPERIMENTAL

Materials

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. Cassava starch (CS) 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 CS/PP Blends

Cassava Starch (CS) 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 cassava starch (CS) or compatibilized cassava starch (CCS) 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 CS/PP of CCS/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 a 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,

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

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 stirred in a desiccator until testing. The percent weight loss of the samples was determined as follows,

$$\text{Weight loss} = [(W_b - W_a)/W_b] \times 100 \quad \ldots\ldots (2)$$

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

Tensile Properties

The tensile tests for the blends were conducted using universal tensile testing machine Instron 3366, according to ASTM D 638. The test on dumbbell shaped specimen of 3 mm thickness was performed at a cross-head shaped of 5mm/min at 23 ± 5°C. Five specimens were used to obtain the average values of the tensile properties.

Morphological test

The scanning electron microscopy (SEM) was used to evaluate the samples microstructure. The samples were first dried in an oven to remove air moisture and then sputter coated with a thin layer of gold to avoid electrical charging.

III. RESULTS AND DISCUSSION

Water Absorption Behavior

The waste absorption behavior is crucial for understanding the performance of natural filler based composites, since the moisture uptake under immersion in water or exposure to humidity intimately relates to such material properties like mechanical strength, dimensional stability, and appearance [15]. The water absorption of PP/cassava starch blends at different starch contents are presented in Figures 1 and 2. From the figures, it is evident that water uptake increased gradually with increase in starch content for both unmodified and modified starch/PP blends. The hydrophilic characteristic of Cassava starch was due to the presence of hydroxyl groups.

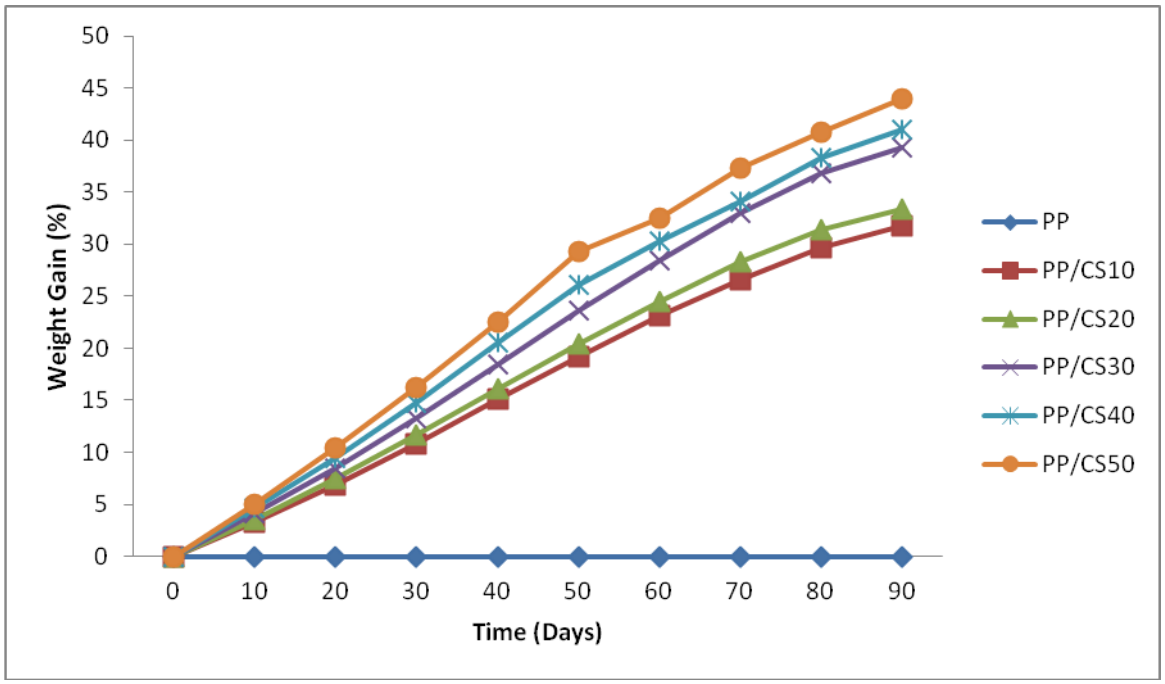


Fig. 1: Water absorption for PP/CS Blends

These hydroxyl groups increased with increasing starch content with the corresponding increase in water uptake. Again, the poor adhesion associated with high filler content may induce cracks and voids between the starch and matrix which increased penetration and high capillary action of water through the created interstice in the blend. Similar trends were observed by other researchers [16, 17]. The extent of water uptake however, decreased considerably on addition of compatibilizer to blends (Fig. 2). Compatibilized PP/starch blends showed considerable decrease in water uptake which corroborates a better adhesion between PP matrix and cassava starch. It is observed on comparison that at 70 days of immersion, % weight gain of CS was 3% greater than % weight gain of CCS at the end of 90 days test period. As reported by Bessadok et al. [18], modification of blend's constituents had resulted to blends with hydrophilic surfaces.

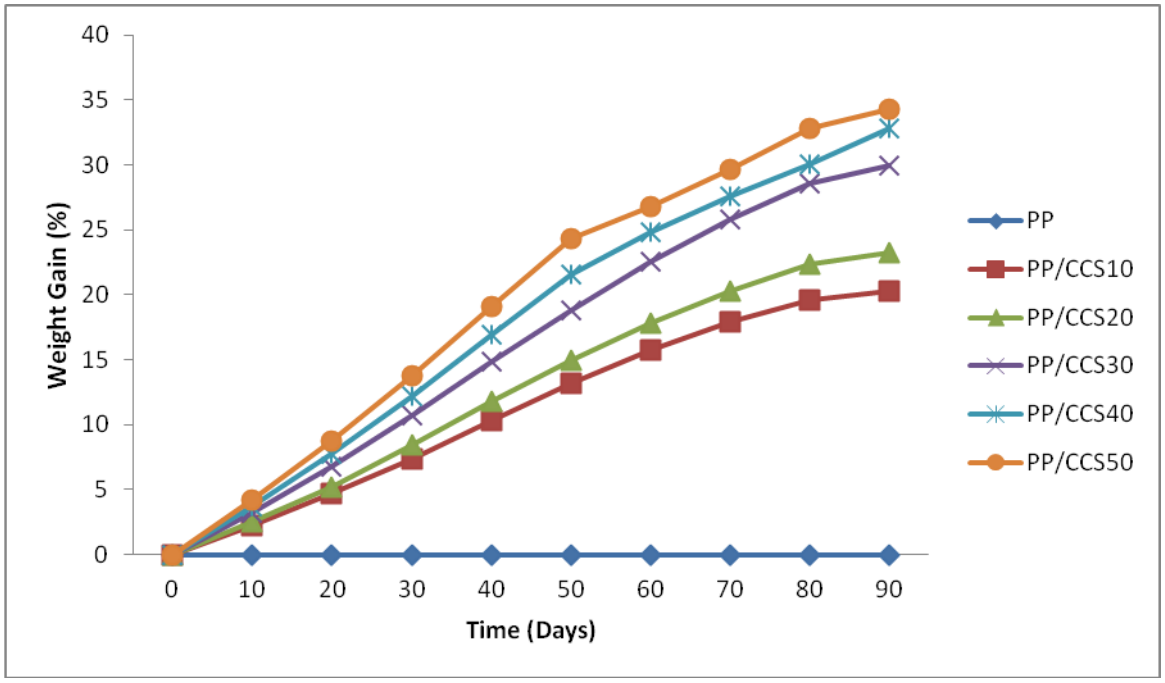


Fig. 2: Water absorption for PP/CCS Blends

Weight Loss

The biodegradation studies on composite behavior are of vital importance on the environmental application of biocomposites. Figures 3 and 4 represent weight loss of various blends as a function of starch content and biodegradation time for uncompatibilized and compatibilized blends.

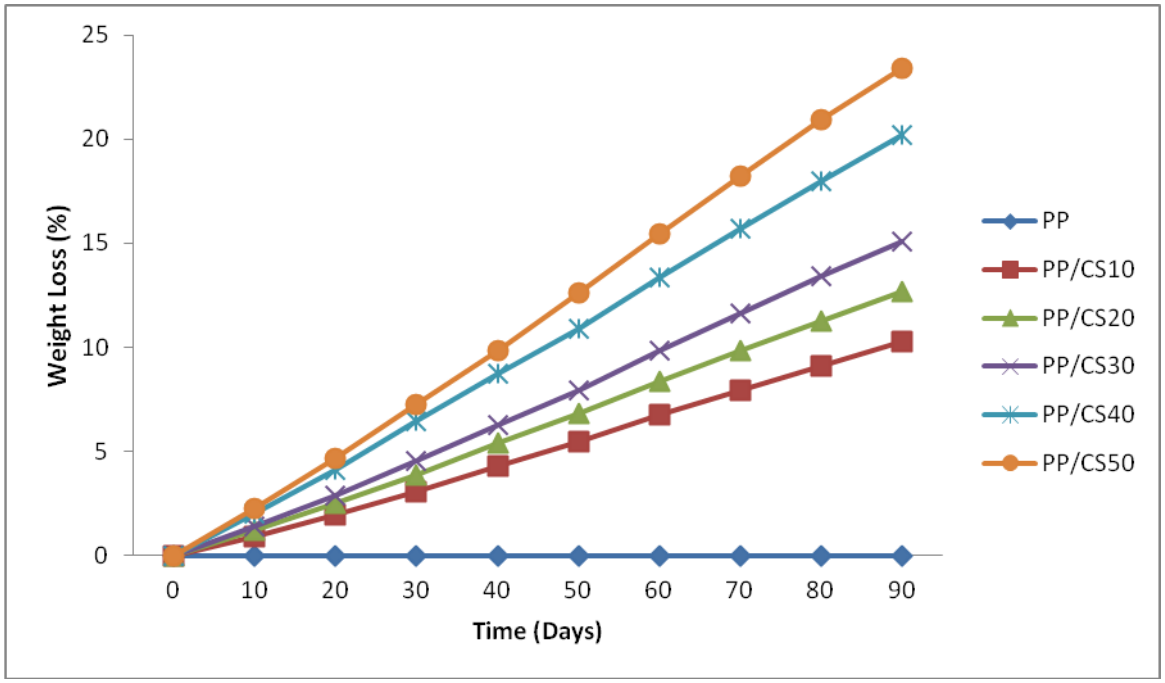


Fig. 3: Weight Loss for PP/CS Blends

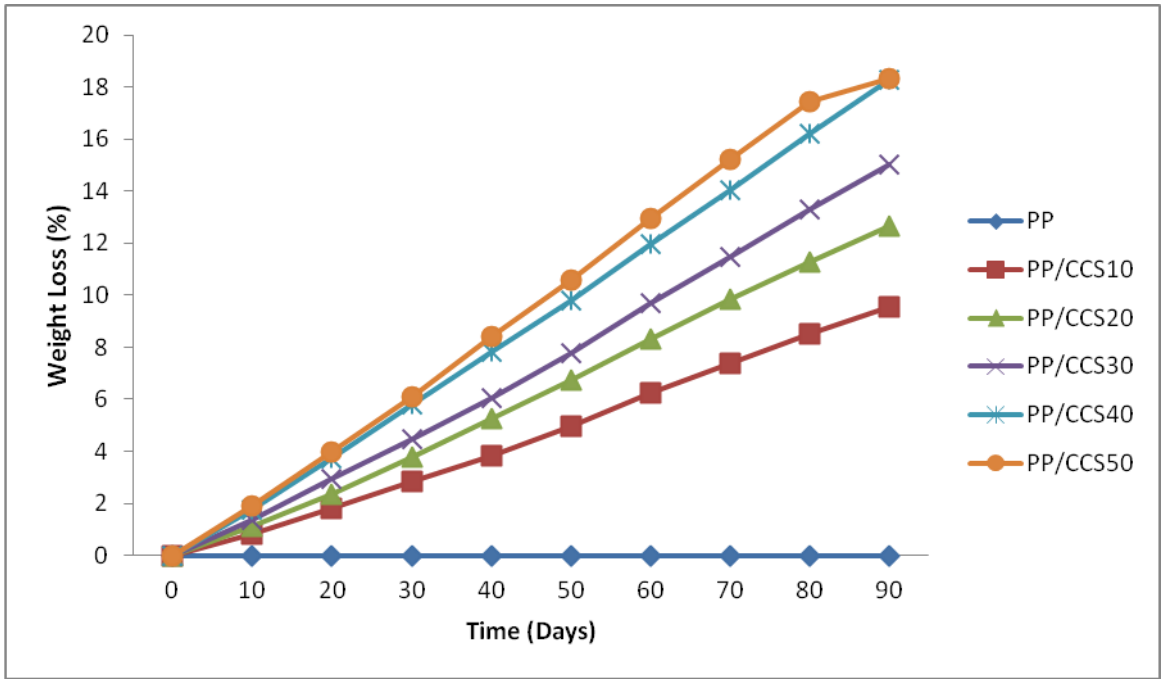


Fig. 4: Weight Loss for PP/CCS Blends

It can be seen that for both blends the weight loss percent increased with increase in starch content as well as burial time and continued as the burial time progressed. This may be attributed to the hydrolytic depolymerization of starch materials leading to monomeric units and possible blend deterioration caused by microorganisms [19, 20]. For both blends studied, weight reduction for 50 wt. % starch content after the first 10 days are 2.24 % and 1.92 % for PP/CS and PP/CCS respectively. The weight loss decreases gradually as the burial time progresses and after 90 days of study, the percent weight loss are 23 % and 18% accordingly. Again, it is noticed that after 70 days of study, the PP/CS blends had weight decrease of over 18 % which corresponds to the overall weight reduction percent for PP/CCS. The lower weight loss of PP/CCS may be linked to the improved interfacial bonding between PP matrix and starch and other similar factors leading to lower uptake.

Tensile Properties

Natural filler such as starch plays a vital function in defining mechanical properties of biofilled thermoplastic blends. A biodegradable polymer is expected to withstand normal stress encountered during its application [10]. The filler/matrix interfacial bonding is an essential factor that affects the mechanical properties of biopolymer blends.

Tensile tests were carried out to evaluate the tensile properties of both compatibilized and uncompatibilized PP/CS and PP/CS blends respectively. Figures 5 - 7 represent the effect of starch content on the tensile strength, elongation at break and Young's modulus of the blends. In the case of uncompatibilized PP/starch blends, adhesion between the two materials was expected to be lower than compatibilized PP/starch blends due to hydrophobic nature of PP and hydrophilic character of the starch to PP matrix showed a common phenomenal decrease in tensile strength (Fig.5) as shown by conventional biodegradable blends [10, 21, 22]. The decrease in tensile strength of the blends with increase in starch content was due to poor interfacial adhesion and low compatibility between the starch and PP [23]. The tensile strength of PP/CCS blends increased significantly than the PP/CS blends but however, lower than the neat PP. This is probably because of a better interfacial bonding that took place between the starch filler and the PP matrix after the addition of compatibilizer, PP-g-MA. This occurrence is further explained in the morphological sturdy. It was also noticed that on addition of 10 wt. % starch content to the PP matrix, the tensile strength dropped by 38 % and 28 % for uncompatibilized and compatibilized blends and was greater at 50 wt. % content given rise to 67 % and 59 % compared to the neat PP respectively. The polar nature of starch hindered its ability to develop strong bonding with non-polar PP. at high filler content, filler-filler interaction predominates over filler-matrix interaction leading to the agglomeration of starch filler within the PP matrix. This behavior indicated poor stress transfer due to inadequate wettability of starch filler by the matrix material [16, 24].

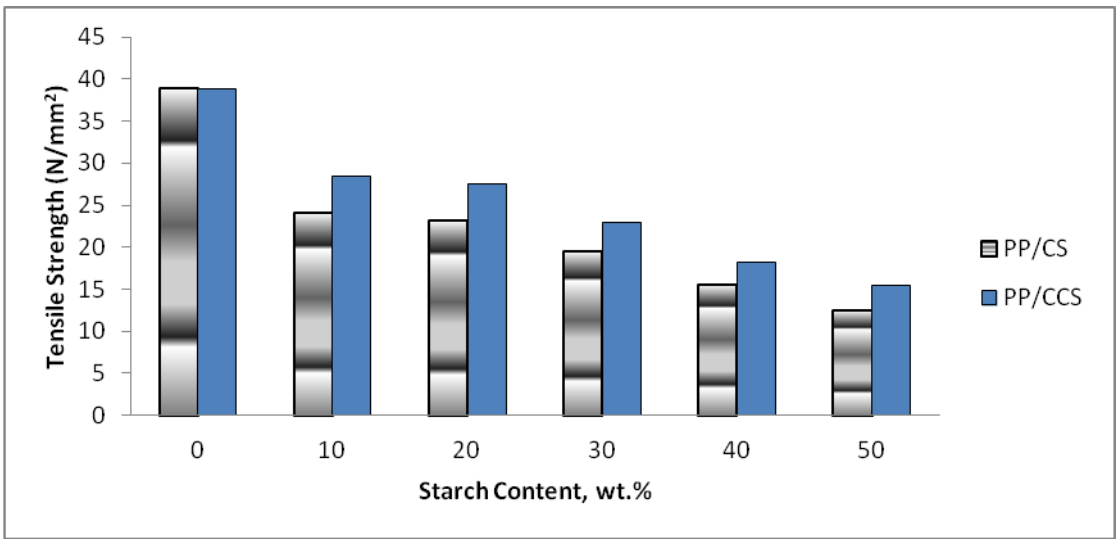


Fig. 5: Tensile Strength of PP/CS Blends

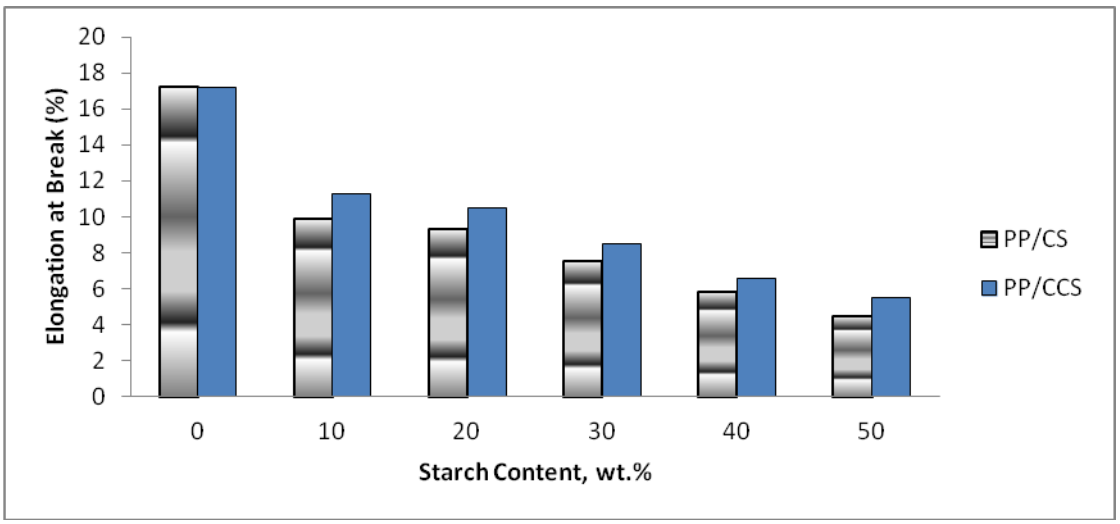


Fig. 6: Elongation at Break of PP/CS Blends

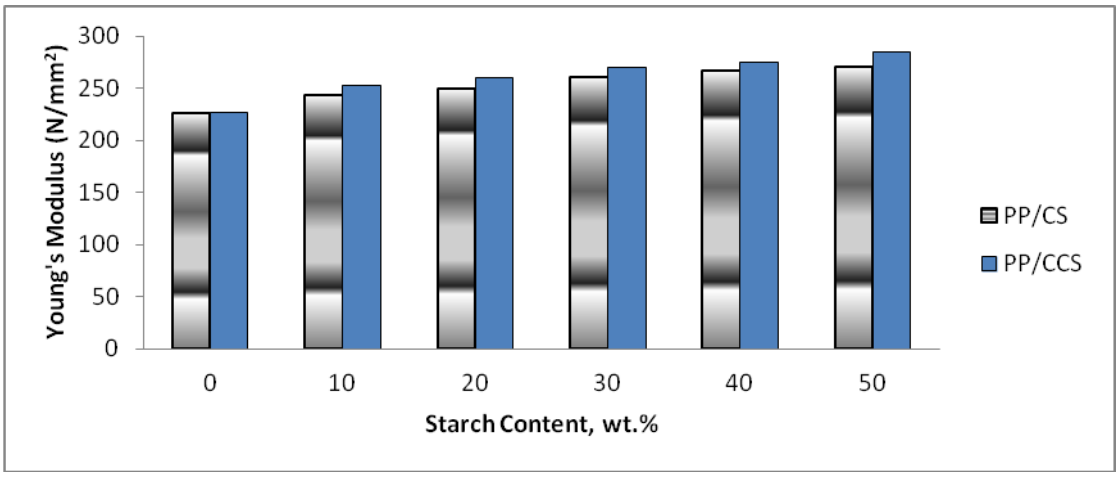


Fig. 7: Young's Modulus of PP/CS Blends

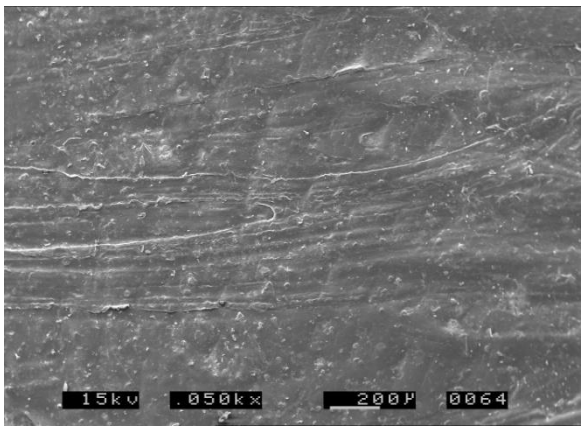
The effect of starch content on the elongation at break of PP/starch blends is presented in Fig.6. Elongation at break was observed to decrease on addition of 10 wt. % starch content and continued to decrease with increasing starch content. This may be attributed to the hydrophilic nature of the starch filler that may have

absorbed moisture and interfered with the adsorption effect by lowering the effect of physical bonding between the interfaces of PP/cassava starch [25]. As earlier mentioned, at high filler content, agglomeration may occur leading to high points of stress concentration which will readily initiate crack propagation in the blends. This induced the elongation at break of the blends to decrease with increasing starch content. Balakrishna et al., [16] and Karima et al., [26] observed similar trends with natural filler filled PP blends.

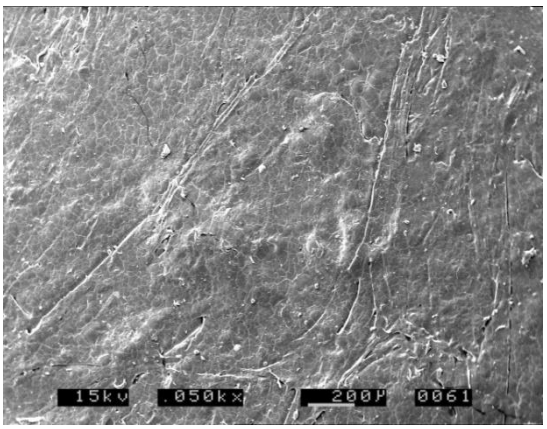
However, the addition of 10 wt. % cassava starch to the PP matrix increased the Young's modulus by 8 % and 11 % whereas 20 % and 26 % increment were observed at 50 wt. % starch content for uncompatibilized and compatibilized PP blends respectively (Fig.7). The incorporation of the starch into the blends hindered the mobility of the polymer chain of the PP matrix thus contributing to the rigidity of the blends [22, 27]. Supri et al [28] attributed the increment in Young's modulus to the intrinsic properties of the filler, where the filler may show its high stiffness. The high Young's modulus recorded by the PP/CCS blends may be linked to the presence of PP-g-MA which improved the bond characteristics of the starch and PP matrix. Moreover, the high percent decrease in tensile strength and moderate increase in Young's modulus of the PP/starch blends on addition of starch filler to the PP matrix suggest that the filler is not reinforcing filler. This is in concordance with the assertion of Billmeryer [29], who stated that non-reinforcing fillers produce reducing effect on the properties of polymers by weakening their rigidity. The effect of poor starch wetting by the matrix was demonstrated by the easy detachment starch from matrix as shown in the SEM micrographs in Figs. 8 and 9.

Morphology

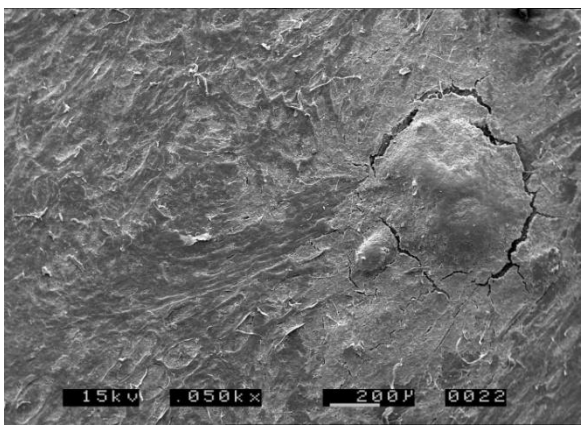
Figures 8 and 9 show the SEM images of PP/starch blends for both uncompatibilized and compatibilized blends before and after soil burial respectively. From the micrographs, the blends show specific morphology, rough surface with many air voids, though particles of starch seemed to be well embedded in the PP matrix. The rough surface nature of the blends may be associated with starch content, the higher the starch content, the more the surface roughness of the blends. The images here illustrate the increase in porosity of the blends due to fungal growth leading to formation of holes and voids. This is associated with uncompatibilized blends at higher starch content due to poor wettability compared to compatibilized ones with better interfacial adhesion.



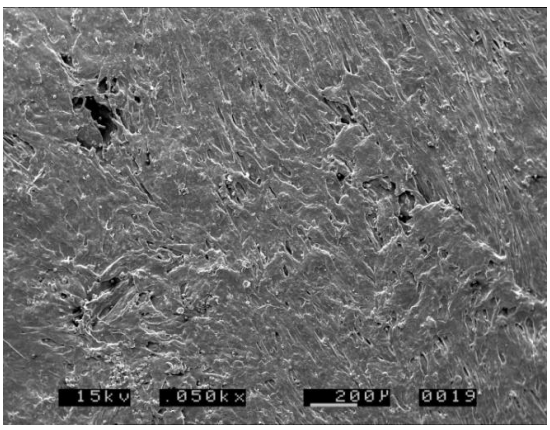
8(a)



8(c)

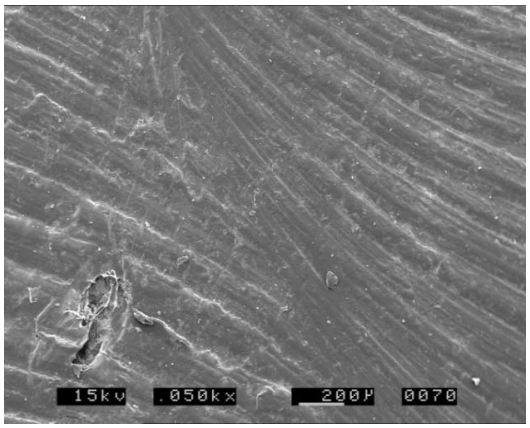


8(b)

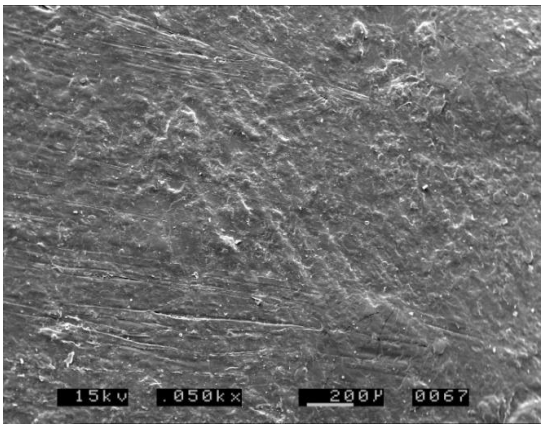


8(d)

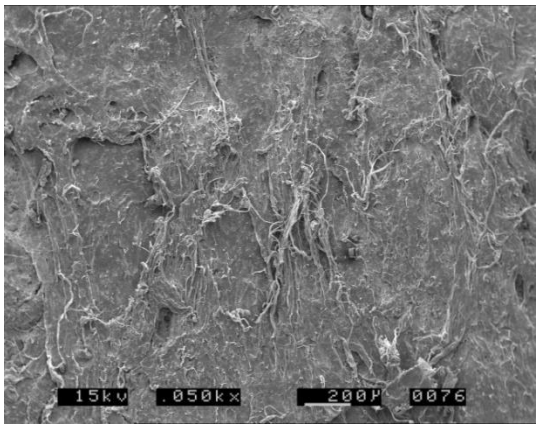
Fig. 8: SEM images of PP/CS blends, (a) 10 % CS and (b) 50 % CS before soil burial; (c) 10 % CS and (d) 50 % CS after soil burial.



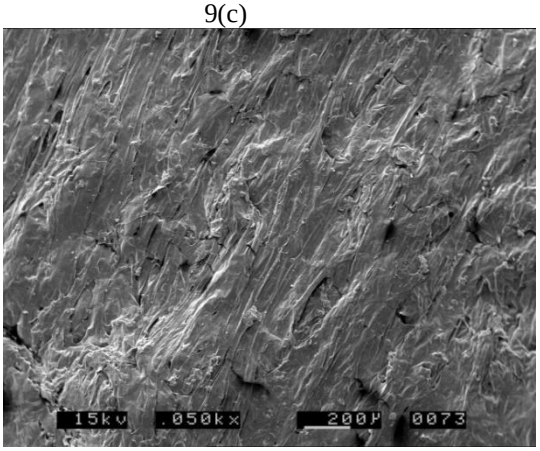
9(a)



9(c)



9(b)



9(d)

Fig. 9: SEM images of PP/CCS blends, (a) 10 % CCS and (b) 50 % CCS before soil burial; (c) 10 % CCS and (d) 50 % CCS after soil burial.

IV. CONCLUSION

The main conclusion drawn from this study can be summarized as follows:

1. Biodegradable blends have successfully been prepared using indigenous cassava starch blended with polypropylene.
2. Water absorption by the blends increased with increasing starch content as a result of increasing presence of hydroxyl groups in the blends.
3. Biodegradation rate of the blends increased with increasing starch content due to increased microbial invasion on the blends.
4. Higher starch content in polypropylene reduced the tensile strength and elongation at break due to poor interfacial adhesion between the starch and matrix.
5. The Young's modulus increased with increasing starch content due to reduction in mobility of the chains of PP matrix giving rise to the stiffness of the blends.
6. Determination of the tensile and biodegradable properties was confirmed by the SEM images.
7. The addition of PP-g-MA improved the properties under study due to enhanced interfacial adhesion between the starch and PP matrix.

REFERENCES

[1] Chandra R. and Rustgi R. (1998). Biodegradable polymers. Prog. Polym. Sci., 23, 1273 - 1335.
[2] Shahrzad K. (2011). Study of water absorption and biodegradation of potato starch based polyethylene. Adv. Environ. Biology, 5(10): 3156 - 3158.

[3] Huang J.C., Shetty A.S. and Wang S.W. (1990). Biodegradable Plastics: A review Adv. Polym. Tech., 10, 23 - 30.
[4] Doi Y. and Fukuda K. (1994). Biodegradable Plastics and Polymers. Elsevier Science B.V., 601 - 608.
[5] Potts J.E. (1981). Environmentally Degradable Plastics. In: Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Suppl. Vol., John-Wiley, New York, 638 - 668.
[6] Kim H.S., Kim H.J., Lee J.W. and Choi I.G. (2006). Biodegradability of Bio-flour filled biodegradable poly (butylenes succinate) bio-composites in natural and compost soil. Polym. Degrad. Stab., 91, 1117 - 1127.
[7] Okada M. (2002). Chemical Syntheses of Biodegradable Polymers. Prog. Polym. Sci., 27, 87 - 133.
[8] Mohanty A.K., Misra M. and Hinrichsen G. (2000). Biofibre, biodegradable polymer and biocomposite. Macromol mater. Eng., 266/277: 1 - 24.
[9] Mash K. and Bugusu B. (2007). Food Packaging-Roles, Materials and Environmental Issues. J. Food Sci., 72, 39 - 55.
[10] Obasi, H.C. (2013). Tensile and Biodegradable Properties of Extruded Sorghum Flour Filled High Density Polyethylene Films. Acad. Research Int., 4(5), 78 - 86.
[11] Rosen J.J. and Schway A.M. (1980). Kinetics of cell adhesion to a hydrophilic-hydrophobic copolymer model system. Polym. Sci. Technol. 12B, 667 - 686.
[12] Willet J.L. (1994). Mechanical Properties of LDPE/granular starch composite. J. Appl. Polym. Sci., 54, 1485 - 1695.
[13] Kim M. (2003). Evaluation of Degradability of Hydroxyl propylated potato starch/polyethylene blend films. Carbo. Polym., 54, 173 - 181.
[14] Lim S.T. and Jane J.L. (1992). Effect of Starch Granule size on Physical Properties of Starch-filled polyethylene film. Biotech. Prog, 8, 51 - 57.
[15] Sandeep S.L., Kumar D.J.M., Viveka S. and Nagaraja G.K. (2012). Preparation and Properties of Biodegradable Film Composites using Modified Cellulose Fibre Reinforced with PVA. ISRN polym. Sci., 1 - 7.
[16] Balakrishna N.S., Ismail H. and Othman N. (2012). The Effects of Rattan Filler Loadings on Properties of Rattan Power-Filler Polypropylene Composites. BioResources 7(4), 5677 - 5690.
[17] Demir H., Atikler U., Balkose D. and Tihminlioglu F. (2006). The effect of fibre surface treatments on the tensile and water sorption properties of polypropylene-luffa fibre composites. Composites Part A: Appl. Sci. Manufact., 37(3), 447 - 456.
[18] Bessadik S., Marais S. and Gouanve F. (2007). Effect of chemical treatments of Alfa (Stipa Tenacissima) fibres on water-sorption properties. Compos. Sci. Technol., 67 (3 - 4), 685 - 697.
[19] Kim H.S., Yang H.S. and Kim H.J. (2005). Biodegradability and Chemical Properties of Agro-Flour Filled Polybutylene Succinate Biocomposites. J.Appl. Polym. Sci. 97, 1513 - 1521.
[20] Ishiaku U.S., Pang K.W., Lee W.S. and Ishak A.M. (2002). Eur. Polym. Mater., 38, 393.
[21] Muhammad A.M., Sinin H., Muhammad R.R. and Muhammad S.I. (2011). Treated Tropical Wood Sawdust - Polypropylene Polymer Composite: Mechanical and Morphologica Study. J. Biomater Nanotechnol., 2, 435 - 444.
[22] Obasi H.C. and Onuegbu G.C. (2013). Biodegradability and Mechanical Properties of Low Density Polypropylen/Watse Maize Cob Flour Blends Int. J. Appl. Sci. Eng. Res., 2(3); 242 - 248.
[23] Oksman K. and Clemons C. (1998). Mechanical Properties and Morphology of Impact Modified Polypropylene-wood Flour Composites. J. Appl. Polym. Sci., 67(9), 1503 - 1513.
[24] Yew G.H., Mohd Yusuf A.M., Mohd Ishak Z.A. and Ishiaku U.S. (2005). Water absorption and enzymatic degradation of poly(lactic acid)/rice starch composites. Polym. Degrad. Stab., 90(3), 488 - 500.
[25] Febrianto F., Setyawati D., Karina M., bakar E.S. and Hadi Y.S. (2006). Influence of wood flour and modifier contents on the physical and mechanical properties of wood-recycle polypropylene composites. J. Biol. Sci., 6: 337 - 343.
[26] Karina M., onggo H. and Syampurwadi A. (2007). Physical and Mechanical Properties of Natural Fibres Filled Polypropylene Composites and it's Recycle. J. Biol. Sci. 7(2): 393 - 396.
[27] Sam S.T., Ismail H. and Ahmad Z. (2009). Linear Low Density Polyethylene/Soya powder Blends containing Polyethylene -g-(maleic anhydride) as a compatibilizer. J. Vinyl Addit. Technol., 15(4), 252 - 259.
[28] Supri A.G., Tan S.J., Ismail H. and The P.L. (2011). Effect of poly(methyl methacrylate) modified water hyacinth fibre on properties of Low Density Polyethylene/natural fibre/water hyacinth fibre composites. Polym. Plast. Technol. Eng., 50(9), 898 - 906.
[29] Billmeyer F.W. (1971). Textbook of Polymer Science (2nd ed. Pp 311, 499). New York: John Willey & Sons Inc.