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PREPARATION OF COMPATIBLE AND BIODEGRADABLE ACETYLATED CASSAVA STARCH/POLY (STYRENE-alt-MALEIC ANHYDRIDE) BLENDS USING POLYETHYLENE GLYCOL (400) AS PLASTICIZER

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ABSTRACT

The study was carried out to investigate the compatibility and biodegradability profile of acetylated cassava starch/poly(styrene-alt-maleic anhydride) blends using Polyethylene glycol (400) as plasticizer**.** Native cassava starch (NCS) was successfully acetylated at room temperature using acetic anhydride and 1M NaOH. The percentage acetylation and degree of substitution were found to be 5.38 % and 0.21 % respectively. Polymer blend films of Acetylated cassava starch (ACS) and poly (styrene-alt-maleic anhydride) (PSAMA) were prepared by casting technique. Biodegradation profile of the polymer film was evaluated by soil burial method and % water absorption of polymer blend were also determined as 1.31 % and 9.38 % respectively. Native cassava starch (NCS), acetylated starch (ACS) and their corresponding blends were further characterized by FTIR (CARY 630 AGILENT). The results obtained indicated an interaction between the two polymers. Scanning electron micrographs (SEM) of the polymer blend indicated a very good compatibility.

Keywords: Acetylation, biodegradation, compatible, degree of substitution (DS).

INTRODUCTION

Most synthetic polymers could not be degraded by microorganism, so they remain in the environment. The increased release and accumulation of these synthetic plastics especially packaging materials into the environment especially water stream has necessitated the demand for biodegradable polymers that could, in the future, replace the bulk polymers of today. Biodegradation of synthetic polymers is a valuable solution to this environmental problem. Research on biodegradable petroleum based polymers began in the 1970s (Chiellini *et al*., 2003), production of biodegradable plastics is considered as a possible way to solve the solid waste problem. Compounding petroleum based polymers with natural polymers such as starch, cellulose, lignin, chitin and chitosan is a significant way to promote polymer biodegradation (Raj and Sankar, 2004).

Starch, as an abundant and low-cost raw material, has been applied in the field of biomaterials. However, packaging films (composed entirely of starch) lack the strength and rigidity to withstand the stresses to which many packaging materials are subjected during their lifetime. Starch-based biopolymers can be produced by blending or mixing them with man-made polymers. Many of these combinations involve incompatible components offering poor mechanical properties unless compatibilization techniques are employed. Modification of the interface between the incompatible components is one of the compabilization techniques which involve functionalizing one of the polymers and offer good adhesion to both phases by reducing the interfacial energy. The compatibilizer modifies the interfacial character there by stabilizes the morphologies (Lloyd, 2014). According to Chen *et al.*, (2005) compatibilizer does not only improve the mechanical properties but also improves the dispersion and adhesion forces between the filler and polymer. Modified starches with lower levels of chemical modification can significantly improve their hydrophobicity. Likewise, they change their chemical, physical and rheological properties. The introduction of a polysaccharide ester group is an important development that allows modification in the hydrophilic nature and produces significant changes in the mechanical and thermal properties (BeMiller and Whistler, 1984)

Ideally, starch and the second polymer should be covalently bonded through existing functional groups or by introduction of new functional groups. In line with this, several approaches have been proposed and developed to overcome the problem of incompatibility of starch and synthetic polymer blends (Ramkumar and Bhattacharya, 1997). Therefore, for a synthetic polymer to be reactively blended with starch it must have the following functional groups – carboxyl, anhydride, epoxy, urethane, or oxazoline – that can react with the hydroxyl or carboxyl groups in native and modified starches for better compatibility respectively. Compatibility is a function of the interaction of polymer molecules in the blend and can be detected using various methods including FTIR and Scanning Electron Microscopy (Paul and Bucknell, 2000). This work focuses on the chemical modification of cassava starch by acetylation and blending with poly (styrene-alt-maleic anhydride) using low molecular weight polyethylene glycol

(400) as plasticizer, its suitability as materials for making biodegradable films, with the best physicochemical properties.

MATERIALS AND METHODS

Materials

Native cassava tuber (source Tofa), Poly(styrene-alt-maleic anhydride) 1.5KDa was supplied by Revolymer, UK and it was used as received, Acetic anhydride (99% BDH), Sodium Hydroxide (98% Aldrich), Hydrochloric acid (96% BDH), Tetra hydrofuran (99.9% Aldrich), polyethylene glycol (400) and Ethanol (96% Qualikem). All chemicals were of analytical grade and used without further purification. The FTIR spectra were acquired using CARY 630 AGILENT FT-IR spectrophotometer. The SEM images were obtained with Phenom Pro X Scanning Electron Microscope PW.

Extraction of Starch

Fresh cassava tubers were washed, peeled, crushed with blender and homogenized with 1M NaCl. The mixture was stirred with a stirring rod and then filtered using double layered nylon cloth. The filtrate was allowed to stand for 4 hours and the starch was separated by sedimentation and decantation. The starch was air dried on aluminium pan at room temperature for 48 hours.

Modification of Starch by Acetylation

The acetylation of native cassava starch was done using the modified method suggested by Phillips *et al* (1999). Native starch (25 g) was dispersed in 250 mL of distilled water, it was stirred using magnetic stirrer bar for 30 minutes to form a slurry. The pH of the slurry was adjusted to 8.0 by addition of 1M NaOH. Acetic anhydride (8.4mL) was added for a period of 40 minutes while the pH was maintained at 8.0-8.5 by addition of NaOH simultaneously. The reaction was allowed to proceed for 2 hours after the addition of Acetic Anhydrides. The pH of the slurry was then adjusted to 4.5 using 0.5M HCl and the slurry was filtered, washed 3 times with distilled water and air dried at room temperature for 48 hours.

Percentage Acetylation and Degree of Substitution (DS)

This was determined by saponification titration method as described by Elomaa *et al* (2004). Acetylated starch (1 g) was added to 50mL of aqueous solution of ethanol (75%). The slurry was kept in a water bath at 50ºC for 30 minutes. After the slurry was cooled down at room temperature, 40mL of 0.5M KOH was added to the mixture. The flask was sealed and kept for 72 hours with occasional swirling. Phenolphthalein indicator was added and titrated to end point with 0.5M HCl and solution was kept for 2 hours, any additional alkali that might leached out from the sample was titrated. A Blank containing native starch only was also prepared and titrated to end point.

$$\%\,\boldsymbol{acetylation} = \frac{(\boldsymbol{Blank} - \boldsymbol{sample})\boldsymbol{ml}\ \boldsymbol{X}\ \boldsymbol{M}\ \boldsymbol{of}\ \boldsymbol{HCl}\ \boldsymbol{X}\ \mathbf{0.043}}{\boldsymbol{sample}\ \boldsymbol{weight}(\boldsymbol{g})}\ \boldsymbol{X}\ \mathbf{100} \ldots\ldots\ldots\ldots(\mathbf{1})$$

Where: Blank = mL of HCl used in the Native Starch titration; Sample = mL of HCl used in the Acetylated Starch titration; 0.043 = milliequivalents of the acetyl group.

$$\boldsymbol{Degree\ of\ substitution\ (DS)} = \frac{\mathbf{162}\ \boldsymbol{X}\ \boldsymbol{acetylation}\ \%}{\mathbf{4300} - (\mathbf{42}\ \boldsymbol{X}\ \boldsymbol{acetylation}\ \%)} \ldots\ldots\ldots(\mathbf{2})$$

Where: 162 = molecular weight of glucose, 4300 = 100 x molecular weight of the acetyl group, 42 = molecular weight of the acetyl group-1.

Water Abosrption Test

This was determined according to the method described by Fahmida *et al* (2010), 2 x 2 cm size polymer blend films were dried at 40°C until a constant weight (W_o) was obtained, submerged in a beaker with 20mL of distilled water, and the beaker was coverd, kept at room temperature with some agitation for 24 hours. After this time, samples were removed and dried at 40°C until a constant weight (W_1) was obtained. The percentage water absorption (% WA) was calculated as follows:

$$\%\boldsymbol{WA} = \frac{\boldsymbol{W1} - \boldsymbol{WOX100}}{\boldsymbol{WO}} \ldots\ldots\ldots(\mathbf{3})$$

Biodegradation by Soil Burial Test

This was also determined as described by Fahmida *et al* (2010). Garden soil was mixed with manure (1:0.25). The films (4 x 2 cm) were placed in soil contained in a stainless steel at 3 inches dept and kept for 2 weeks. The weights were taken at intervals of 4, 7, 10 and 14 days respectively. The degradation of the films was studied by determining the percentage weight loss of the polymer film after soil burial using the following equation.

$$\%\,\boldsymbol{weight\ loss} = \frac{\boldsymbol{Wo} - \boldsymbol{W1}}{\boldsymbol{Wo}}\ \boldsymbol{X}\ \mathbf{100} \ldots\ldots\ldots (4)$$

Where W_o, W_1 were the weight of the sample before and after soil burial treatment respectively.

Solubility Test

Samples with a size of 1x1 cm were immersed in sealed boiling tubes containing 10mL of different organic solvents and maintained at room temperature with eventual stirring. The solubility of the films was determined at time intervals.

RESULTS AND DISCUSSION

Degree of Substitution (DS)

The acetylation of cassava starch was successfully carried out at room temperature for 1 and 2 hours respectively with acetic anhydride and 1M NaOH as catalyst. The percentages acetylation were found to be 2.1 and 5.38 % at 1 hour and 2 hours reaction time respectively and their degree of substitutions were 0.07 and 0.21 respectively as shown in Table 1. This result indicates that acetylation increases with increase in reaction time and similar result was reported by Singh *et al* (2004).

Table 1: Percentage Acetylation and Degree of Substitution (DS)

Time	% Acetylation	DS
1 Hour	2.1	0.07
2 Hours	5.38	0.21

Infrared Spectra of NCS, ACS, PSAMA and ACS/PSAMA Blend

Figure 1 shows the FTIR spectrum of NCS, the stretching vibration of the hydroxyl group O-H appears as a broad band at 3270 cm^{-1}. The stretching vibration of the C-O bond of secondary hydroxyls appears at 1078 cm^{-1} and the C-O-C stretching vibration appears at 1151 cm^{-1}; tension bands corresponding to O-H, are located at 1343 cm^{-1}, and C-H alkane stretching at 2929cm^{-1}, C-H alkane bending at 1423cm^{-1}and O-H bending of retain water appears at 1639cm^{-1}**.** Two new bands appear in the ACS FTIR spectrum Fig. 2: Peak at 1721 cm^{-1}, this is attributed to the vibration of the carbonyl group, formed from the acetylation of hydroxyl groups on the NCS and the peak at 1246 cm^{-1} is characteristic of tension vibration of the ester function C-O bonds, indicating successful acetylation of NCS.

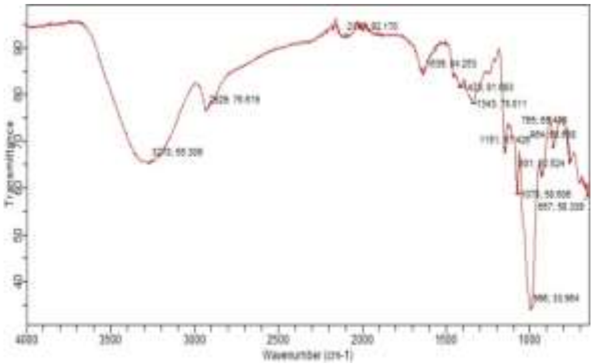

Fig. 1: FTIR spectrum of native Cassava starch

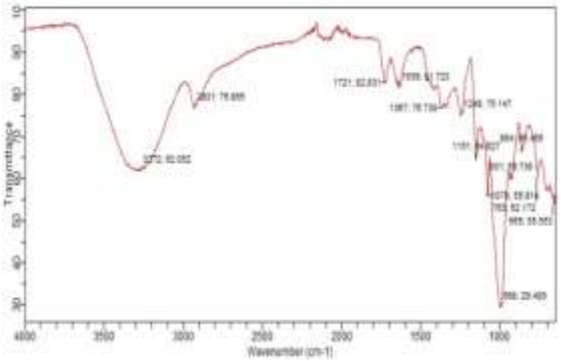

Fig. 2: FTIR spectrum of ACS

Fig. 3 shows the FTIR spectrum of poly (styrene-alt-maleic anhydride) [PSAMA] : the vibration at 3030cm^{-1} indicate C-H stretching due aromatic, vibration at 1847cm^{-1} and 1775cm^{-1} are due to five membered ring anhydride carbonyl, 1620cm^{-1} and 1495 cm^{-1} are vibration of C=C aromatic, 1456cm^{-1} is C-H alkane bending, 2956cm^{-1} corresponds to SP^3 C-H alkane stretching, 1220cm^{-1} is attributed to C-O absorption frequency of ester.

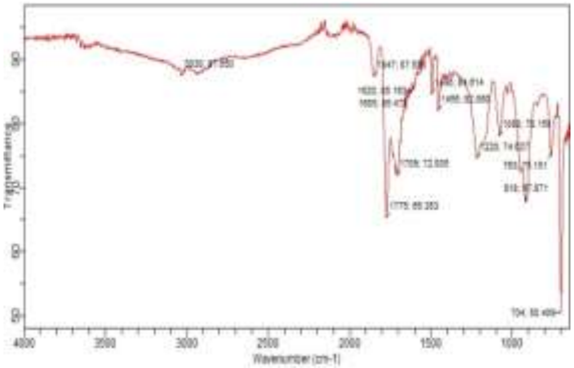

Fig 3: FTIR spectrum of PSAMA

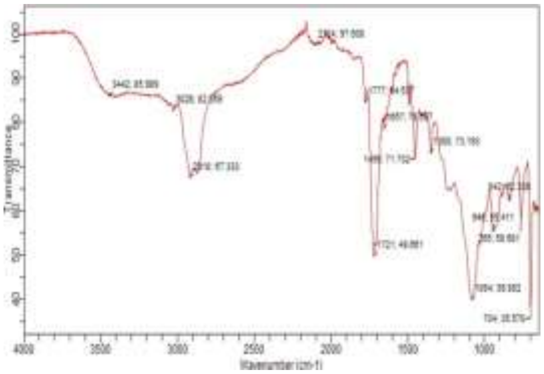

Fig 4: FTIR spectrum of ACS/PSAMA blend

Figure 4 shows the FTIR spectrum of acetylated starch/poly(styrene-alt-maleic anhydride) blend (ACS/PSAMA): some major differences were observed , absence of vibration at 1847 cm^{-1} and 1775cm^{-1} due to anhydride carbonyl, shifting of vibrational band from 3270 cm^{-1} to 3442 cm^{-1} indicating the appearance of O-H due to carboxylic acid, appearance of a strong intensity stretching vibration at 1721 cm^{-1} due to carbonyl . The reduced intensity of O-H and shifting of C-O due to ester vibration from 1220 cm^{-1} to 1250 cm^{-1} was observed, presence of vibration at 1456 cm^{-1} due to acetyl C-H bending and vibration at 3028 cm^{-1} due to sp^2 C-H stretching of aromatics were also observed. Finally, the intensity of the band corresponding to the OH group decreases considerably due to the high degree of substitution.

Water Absorption

Improvement in reducing water sensitivity and enhancing water resistance of thermoplastic starch materials is highly important. Water absorption of the PEG (400) plasticized acetylated cassava starch/poly(styrene-alt-maleic anhydride) blend films are shown in Table 2. Since grafting modifies the surface of a polymeric blend film, it is evident from the Table 2 that grafting with poly (styrene-alt-maleic anhydride) [PSAMA] has lowered the water absorption of the blend films. This is may be due to the fact that polysaccharide chain of starch and OH- groups of PEG (400) are mostly occupied with PSAMA. So, there is very little chance for the water molecule to be associated with or absorbed by film. The result shows that the percentage absorption was 9.40% which coincides with the literature reported by Emeje *et al* (2012) and was calculated using equation 3. This high water absorption value of the polymer blend sample may be due to the introduction of hydrophilic substituent groups (O=C-O-) that allow little retention of water molecules because of their ability to form hydrogen bonds. This high retention of water, that enters the granule, increases the swelling capacity of the film.

Table 2: Percentage Water Absorption of Polymer Blend

Initial weight (g)	Final weight (g)	% Absorption
0.84	0.919	9.40

Biodegradation of Polymer Blend

From the result presented in Figure 5 and Table 3 it shows that there was great loss of weight at the beginning which was due to loss of water and this continues as the number of days increased indicating that the sample is degrading with respect to time. Presence of starch made the blend a biodegradable material because the polymeric chain breakage occurred when the starch content was digested by the microorganisms. However, from the FTIR spectrum (figure 6), the intensity of carbonyl vibration (1721 cm^{-1}) reduced which is one of the hydrolytic group introduced into polymer backbone and disappearance of sp^2 C-H vibration due aromatic at 3028 cm^{-1} and also disappearance of C-O-C at 1151 cm^{-1} from the starch, all these are the bonds (labile groups) that were expected to be attacked by the microbes or enzymes present in the soil.

Table 3: Biodegradation Profile of Polymer Blend

Initial weight(g)	Final weight (g)	Days	% weight loss
1.11	1.105	4	0.45
1.105	1.102	7	0.72
1.102	1.1017	10	0.75
1.101	1.0955	14	1.31

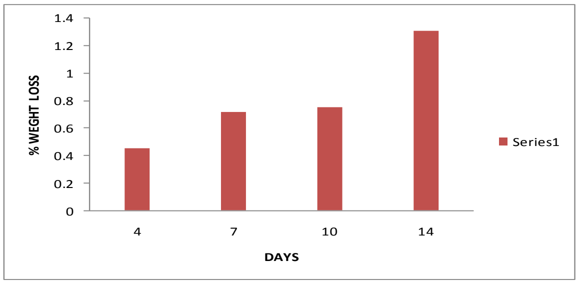

Fig 5: Biodegradation profile of ACS/PSAMA

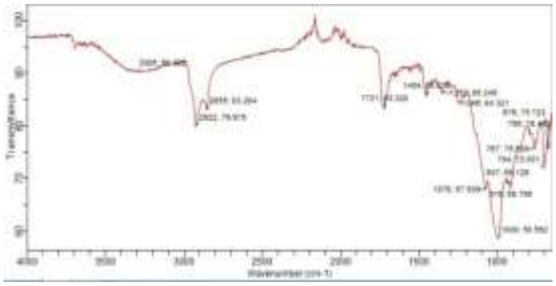

Fig 6: FTIR of ACS/PSAMA after burial

Solubility Behaviour of the Polymer Blend in Various Solvents

The solubilty of polymer blend was evaluated in solvents of varying polarity and the results obtained are presented in Table 4.

Table 4: Solubilty of Polymer Blend

	Solvents							
Samples	**Acetone**	**DCM**	**DEE**	**DMSO**	**Ethanol**	**Methanol**	**THF**	**Water**
60/40	S	SS	IS	S	S	S	SS	IS

S = Soluble, **SS** = slightly soluble, **IS** = Insoluble

From the results presented in Table 4, the polymer film was found to be soluble in solvents of higher polarity as evident from the observed solubility behaviour of the polymer blend which is found to be readily soluble in DMSO, ethanol, methanol and acetone. But it takes up to 24 hours before it dissolved in DCM, 2 hours in THF and completely insoluble in water. This indicates that solubility of the blend depends on the polarity of the solvent. The solubility of ACS / PSAMA blend film in polar solvents may be due to the introduction of hydrophilic substituents that allow the retention of solvent molecules because of their ability to form hydrogen bonds**.** It also suggests that ACS/PSAMA blend have a comparable solubility parameter with the polar solvents used

Scanning Electron Microscopy (SEM)

Figure 7 shows the micrograph of native starch (NS) and reveals that the starch particles in the form of granules tends to be rounded, and some morphological irregularities (cuboids or deformed pyramids) and other truncated forms, which probably originated during the starch extraction process. Fig 8 shows the image of ACS in fused form, the fusion of starch granules was evident of acetylation. The acetylation reaction causes the disruption of the matrix, accompanied by a greater agglomeration of the granules and a modification of their size, shape and texture. In these conditions, the ACS likely suffered some destruction as it interacts with amylose and amylopectin, resulting in a different sort of chemical bonds. The size of the agglomerates in the ACS reveals a different type of inter-granular cohesion, which may be caused by changes in functional groups, which, in turn, results in increasing hydrogen bonds and a subsequent inter-granular agglomeration. This coincides with acetylated corn and potato starches with low degree of substitution as reported by Singh *et al,* 2004. It was also reported that increase in the anhydride acetic level produced higher granule fusion and that fusion granule after acetylation is attributed to the introduction of hydrophilic groups to the starch molecules, which resulted in increase of hydrogen bonding. Therefore, starch molecules coalescing together resulted in fusion of starch granules (Kaur *et al.,* 2004). Figure 7 and 8 also revealed the average size of the particles in the native starch and modified starch. 110 µm for the native starch, whereas for the acetylated starch was 130 µm respectively, this increase in the size is due to the introduction of the acetyl groups to the chains of starch, this was in accordance with Francisco *et al* (2012)

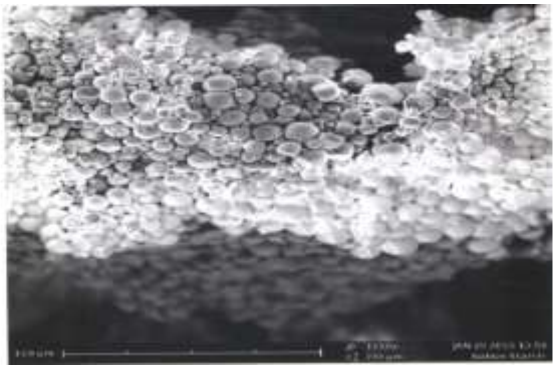
Fig 7: SEM image of NCS

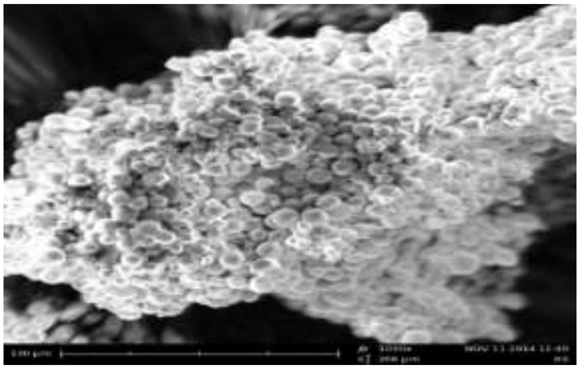
Fig 8: SEM image of ACS

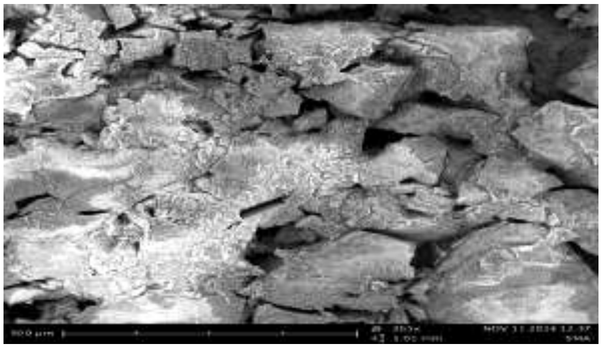

Fig 9: SEM image of PSAMA

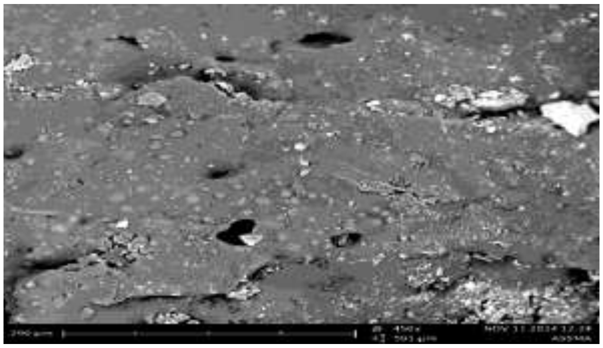

Fig 10: SEM image of ACS/PSAMA 60/40 blend

Fig 11 optical image of 80/20 blend

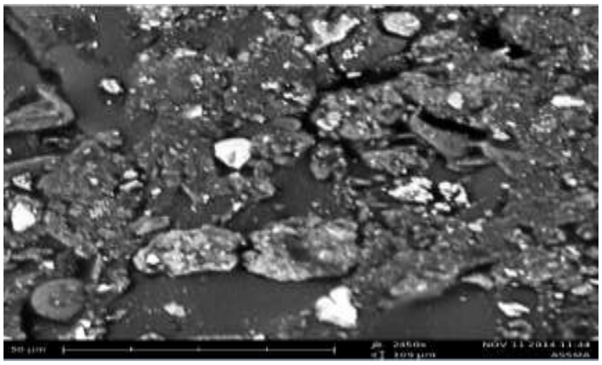

Fig 12 SEM image of ACS/PSAMA80/20 blend

Fig 10 shows the morphology of ACS/PSAMA blend which indicates the dispersion of ACS domain over the PSAMA domain without much rupture. The morphology of the blends changed where spherical domains of starch, dispersed in continuous matrix of the poly (styrene-alt-maleic anhydride), changed to a highly non homogeneous mixture of granules macro-domains of both components which indicates compatibility of the blend and also decrease in particles size as seen in (Fig 10), Lloyd (2014) reported similar observation. The SEM micrographs show very good compatible morphologies without the edge, cavity, and holes resulting from poor interfacial adhesion. It is possible that the good adhesion of this blend is due to the reaction between the hydroxyl group of starch molecule and anhydride group of PSAMA. This means the adhesion between ACS and PSAMA was achieved through maleic anhydride that functions as a bridge or a binding between the two different polymers; this also agrees with the findings of Prachayawarako *et al*., (2010).

CONCLUSION

Blends of ACS with PSAMA were found to be compatible in the composition range of ACS/PSAMA 60/40 confirmed by FTIR and SEM image of blend film. Several efforts were made to prepare blend of 80/20 in different solvents but proved abortive due brittle nature of both starch and PSAMA despite their modifications Fig 11 and 12. From the result of water absorption and soil burial experiments, the film was found to be biodegradable under the tested environmental conditions as also confirmed by FTIR. The physicochemical properties of the blend revealed that the film is soluble in polar organic solvents but relatively stable with water, hence considering these characteristics, it could potentially be used in packaging dry substances as single use disposable material.

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