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BIODEGRADABILITY OF MODIFIED NATURAL RUBBER BLENDS WITH MODIFIED CASSAVA STARCH

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ABSTRACT

Polymeric materials are widely used packaging materials, they are not easily biodegradable hence their disposability is of major concern. Recently researches are being geared towards the development of biodegradable polymeric materials from natural resource as alternatives to petroleum-derived polymeric materials. This study was carried out to assess and establish the biodegradability of the blends of modified natural rubber (epoxidized (ENR), deproteinized (DPNR) and depolymerized (DPLNR)) and modified cassava starch via acetylation. The natural rubber (NR) latex used was first characterised via total solid content, dry rubber content, ash content volatile matter and mechanical stability test before modification. The modified natural rubber (MNR) and acetylated starch (AS) were prepared and characterised using Fourier Transform Infrared Spectrophotometer (FTIR). Biodegradable polymer blends were prepared by blending the modified starch (from acetylated cassava starch) with each of the modified natural rubbers in the presence of glycerol as plasticizer using solution casting method. Biodegradability of the blends were then investigated via water absorption, solubility, mechanical analysis, thermal tests and soil burial test for twelve weeks. The progress of biodegradation under soil burial test was determined through weight loss measurement at two weeks interval. The results obtained showed that NR and MNR did not show any significant weight loss while starch and acetylated starch showed appreciable weight loss during the period of the test. Also observed was an increase in the biodegradability of the blends as the percentage of AS was increased with blend containing 30% ENR and 70% AS (ENRAS30) having the highest weight loss of 82.4%. The blends containing epoxidized natural rubber were also found to have the highest percentage weight loss. All the blends were found to be soluble in the following solvents; toluene, chloroform, petrol and kerosene used in this study. The tensile strength of the MNRs were found to be higher than that of the NR while those of the various blends were found to be lower than that of NR. The MNR have lower elongation at break than the NR. The elongation at break of the blends were also found to decrease with increase in the percentage of starch or acetylated starch in the blends. The study showed that blending NR, ENR, DPNR and DPLNR with AS will increase the rate of their biodegradability.

KEYWORDS: Natural rubber, epoxidized, depolymerized, deproteinized, acetylated, biodegradability.

INTRODUCTION

Polymers are substances whose molecules have high molar masses and are composed of a large number of repeating units. There are both naturally occurring and synthetic polymers. Among naturally occurring polymers are proteins, starches, cellulose, and latex. Synthetic polymers are produced commercially on a very large scale and have a wide range of properties and uses. The materials commonly called plastics are all synthetic polymers.

Indeed, it was only in the 1920s that the concept of a polymer or macromolecule came to be grudgingly accepted, slowly displacing the colloid theory that suggested that macromolecules were nothing more than aggregates of small molecules [8].

The subsequent two decades witnessed the rapid development of many types of synthetic fibers, plastics, and elastomers, including Dacron, nylon, and Spandex. Also, guiding principles for the successful linking of monomers into high-molecular-weight polymers were established [8].

Over the past few decades, the use of polymers in disposable consumer goods has grown tremendously. This growth is proving to be taxing on the waste disposal system, consuming a large fraction of available landfill space. Furthermore, the raw materials for these polymers are obtained from petroleum, a limited, non-renewable resource.

The use of biodegradable polymers can offer effective solution to this scenario as they are degradable in the presence of naturally occurring microorganisms.

Stimulated by environmental concerns, recent research by Scientists are geared towards the development of biodegradable polymeric materials from natural resources as alternatives to petroleum-derived plastics.

Bio-plastics can be made from many different sources and materials such as plant oil, cellulose, cassava starch, corn starch, potato starch etc.

Cassava is an important and cheap source of starch in tropical regions. The crop has growth advantages and production can take place in poor soil where other crops such as maize, sorghum and sweet potatoes cannot grow. Consequently, the manufacture of cassava-based industrial products may be of interest as a potential way of boosting the economic value of the crop.

Starch is a naturally occurring, biodegradable, inexpensive and abundantly available polysaccharide molecule. It is widely distributed in the form of tiny granules as the reserve carbohydrate in stems, roots, grains and fruits of all forms of green leafed plants [12]. It offers several prospective advantages as a raw material for plastics applications because it is renewable, biodegradable and obtained from a variety of plant sources and is a low-cost material. It is a versatile and useful polymer not only because it is low cost and obtained from natural resources, but also because its physicochemical properties can be altered through chemical or enzymatic modification.

There has been a widespread interest in films made from renewable and natural polymers which can degrade naturally and more rapidly than the petroleum-based plastics. Among all biopolymers, starch is being investigated as a potential material for biodegradable films [15].

Acetylation is a modification of polymeric starch molecules through the introduction of functional acetylated groups (CH_3CO) that react with free hydroxyl groups present in the branched chains of the starch polymer to produce a specific ester [20]. The introduction of acetyl groups reduces the resistance of bonds between the starch molecules. Acetylated starch increases the swelling capacity and solubility compared to native starch [6].

Natural rubber (NR) is obtained from the Hevea brasiliensis tree as a latex. It is primarily cis-1, 4-polyisoprene with small amounts of bound proteins and other contaminants.

Natural rubber products have very useful technical characteristics of good tensile strength, high resilience and excellent flexibility, and resistance to impact and tear.

Biodegradable plastic is an innovative means of solving the plastic disposal problem from the standpoint of development of new materials. Blending of polymeric materials has proved to be a successful method for preparing and developing material with properties superior to those of individual constituents. Hence, the blending technique becomes a desirable one and of commercial interest.

MATERIALS AND METHODS

Natural rubber used for this research was obtained from Rubber Research Institute of Nigeria, Benin City, Nigeria. Cassava tuber was obtained from Institute of Food Security, Environmental Resources and Agricultural Research, Federal University of Agriculture, Abeokuta. Distilled water, acetone, sodium sulphate, sodium hydroxide, hydrochloric acid, glacial acetic acid, formic acid, hydrogen peroxide, sodium nitrite, sodium dodecyl sulphate, methanol, toluene, urea, sodium carbonate, Chloroform used were analytical grade reagents. Petrol and kerosene were also used as purchased from the Nigeria National Petroleum Corporation.

Production of Cassava Starch

The procedure described by Kamaljit *et al*., 2016 [10] was adopted.

Preparation of Acetylated Starch

The acetylation was carried out using the method of Afolabi *et al*., 2012 [1] with slight modification.

Determination of Pasting Properties of Starch and Acetylated Starch

Pasting properties was determined with the Rapid Visco Analyser (RVA) [1].

Characterization of Natural Rubber Latex

The natural rubber latex used was first characterized via total solid content, dry rubber content, ash content, volatile matter and mechanical stability test before modification.[5]

Dry Rubber Content

The dry rubber content (DRC) of natural rubber latex is the actual amount of the rubber hydrocarbon present in the latex. The DRC was determined using the method of Akinlabi *et al.,* 2007 [2].

Total Solid Content (TSC)

TSC of natural rubber latex is the amount of solid materials present in the rubber latex. It was determined according to the method of Akinlabi et al., 2007 [2].

Volatile Matter (VM)

The volatile matter was determined using the method of Akinlabi et al. [2].

Modification of Natural Rubber Latex

The natural rubber latex was modified via epoxidation, deproteinization and depolymerisation.

Preparation of Epoxidized Natural Rubber (ENR)

The method of Akinlabi et al.[2] was adopted.

Preparation of Deproteinized Natural Rubber

The method of Akinlabi et al.[2] was adopted.

Preparation of Depolymerized Natural Rubber

The method of Akinlabi et al.[2] was adopted.

Preparation of the Blends

The blends were prepared by solution casting method. The natural rubber and modified natural rubber were separately dissolved in chloroform to form 5% (w/w) solutions. Cassava starch and acetylated starch (5% wt/wt) were gelatinized at 75˚C. Glycerol was added as plasticizer with 10% w/w relative to starch (dry basis). Thermoplastic starch/acetylated starch-natural rubber/modified natural rubber blends in the ratios of 100:0, 70:30, 50:50, 30:70 and 0:100 were prepared by mixing the solution together. The mixture was then homogenized by stirring for 10 minutes. The blends were casted onto glass petri dishes and oven dried at 50 ^{o}C overnight [21].

Determination of soil pH

Air dried soil (20.00 g) was measured and 0.01M $CaCl_2$ (20.00 mL) was added to it. The solution was allowed to absorb $CaCl_2$ without stirring. Then the solution was stirred for a few seconds. The soil sample was filtered and pH was measured using pH meter [9].

Determination of Biodegradability of Samples

The method of Cheong et al., 2010 [7] was used in the determination of biodegradability with modification. In situ environmental degradation was conducted on site on fertile garden soil (Morekete, Abeokuta). Initial weights of the samples were taken before they were buried at 15 cm below the soil surface. Samples were taken out of the soil every two weeks to measure their weights. This was taken for 3 months. The weight loss was used as the parameter for determination of the biodegradability.

The weight loss was calculated using the equation:

$$\text{Weight Loss \%} = \frac{(W_i - W_f)}{W_i} \times 100$$

Where W_i represents the initial weight and W_f represents the weight after each 2 week time

Water Absorption Test

Pieces of samples were cut and initial weights were measured using an analytical balance. Each sample was completely immersed in distilled water and after one hour, weight of each sample was measured [9].

Water absorption was calculated using Equation:

$$\text{Weight gain \%} = \frac{(W_f - W_i) \times 100}{W_i}$$

Where W_i represents the initial weight and W_f represents the weight after each 1 hour time

RESULTS AND DISCUSSION

The NR was characterized to determine the quality of the rubber and the results obtained is as shown in Table 1. The dry rubber content (DRC) was found to be 32.42 %, while the total solid content (TSC) which gives the total amount of solid materials in the rubber latex was found to be 37.96 %. The mechanical stability test (MST) which signifies the time for flocculation was found to be 7.8 min while the volatile matter and ash content were found to be 21.83 % and 2.72 % respectively.

Table 1: Characteristics of Natural Rubber Latex

Parameters	TSC (%)	DRC (%)	AC (%)	MST (min)	VM
	37.96	32.42	2.72	7.8	21.83

TSC = Total solid content, DRC = dry rubber content, AC = ash content, MST = mechanical stability test, VM = volatile matter

The pasting properties were determined using Rapid Visco Analyser (RVA) [1]. There was significant change in the pasting properties of the starch after acetylation as shown in table 2. The peak viscosity, final viscosity, breakdown viscosity and through of the acetylated starch (ACS) increased while the setback decreased. The higher pasting properties of the acetylated starch is due to the introduction of the bulky acetyl group into the starch granules which weakens the starch–starch interactions and enhanced the viscosity of the starch granules. The setback of ACS was considerably lower than that of the native starch indicative of the starch to form a more stable paste.

Table 2: Pasting Properties of STS and ACS

Sample	Pasting Temp ^oC	Final Viscousity (RVU)	Peak (RVU)	Breakdown	Through	Setback
STS	73.4	239.33	423.45	298.83	170.33	68.58
ACS	74.4	258.74	469.17	307.32	182.64	57.75

STS = native starch, ACS = acetylated starch

From the FT-IR spectra of natural rubber (NR), epoxidized natural rubber (ENR), deproteinized natural rubber (DPR) and depolymerized natural rubber (DPL), the absorption bands of NR at 2854.75, 1644.56, 1453.72, 1376.08 and 836.90 cm-1 are assigned to the C-H stretching, C=C stretching, -CH_2- deformation, C-H deformation and =C-H deformation respectively. New absorption band at 1244.50 cm^{-1} is assigned to symmetric stretching of the epoxide ring. This confirmed the formation of oxirane ring (epoxide) from the reaction of performic acid (generated in situ by the reaction of formic acid and H_2O_2) with the C=C bond on the NR molecules. Peaks at 1644.56cm^{-1} and 1453.72cm^{-1} assigned to C=C stretching and -CH_2- deformation were found to have reduced in sample D (DPLNR) when compared to NR. This suggests that chain breaking had occurred at the C=C bond [16].

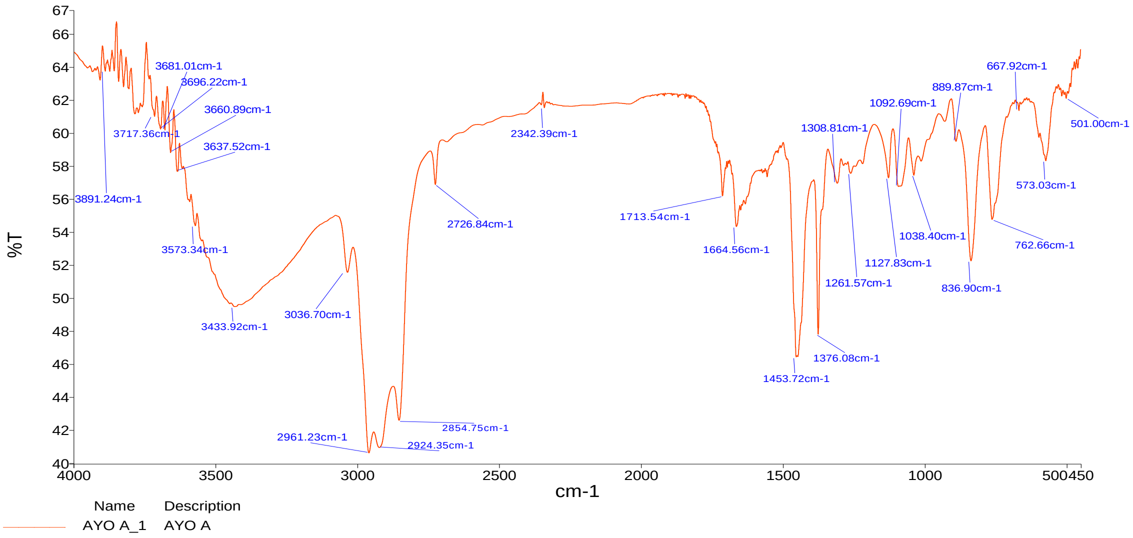

Figure 1: FT IR spectrum of natural rubber

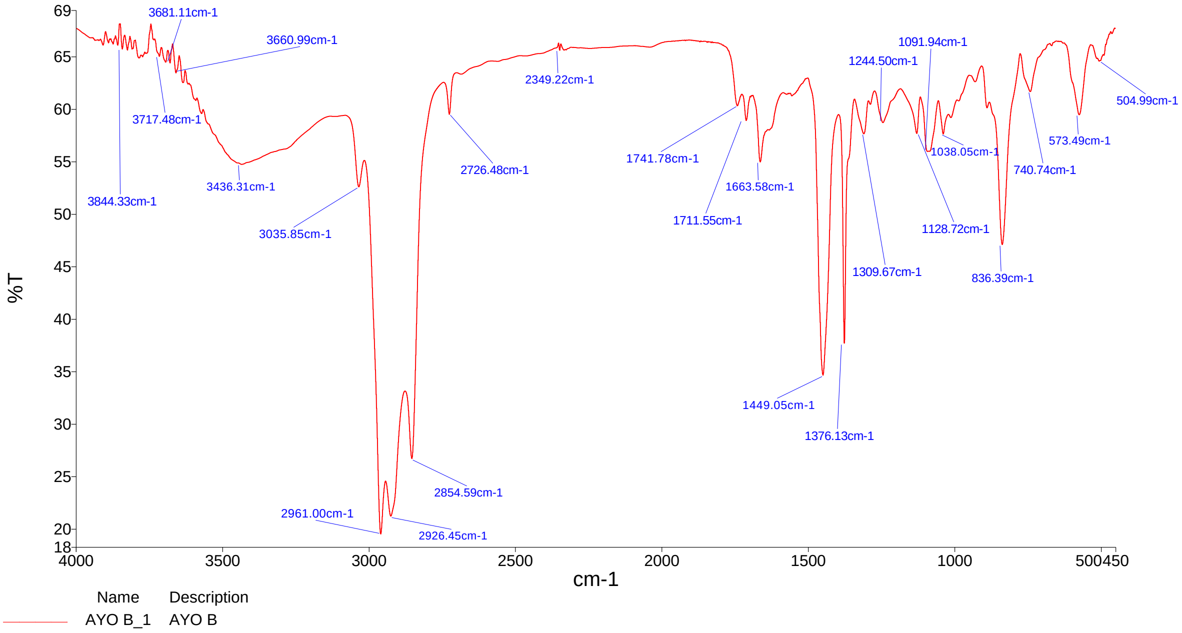

Figure 2: FT IR spectrum of epoxidized natural rubber (ENR)

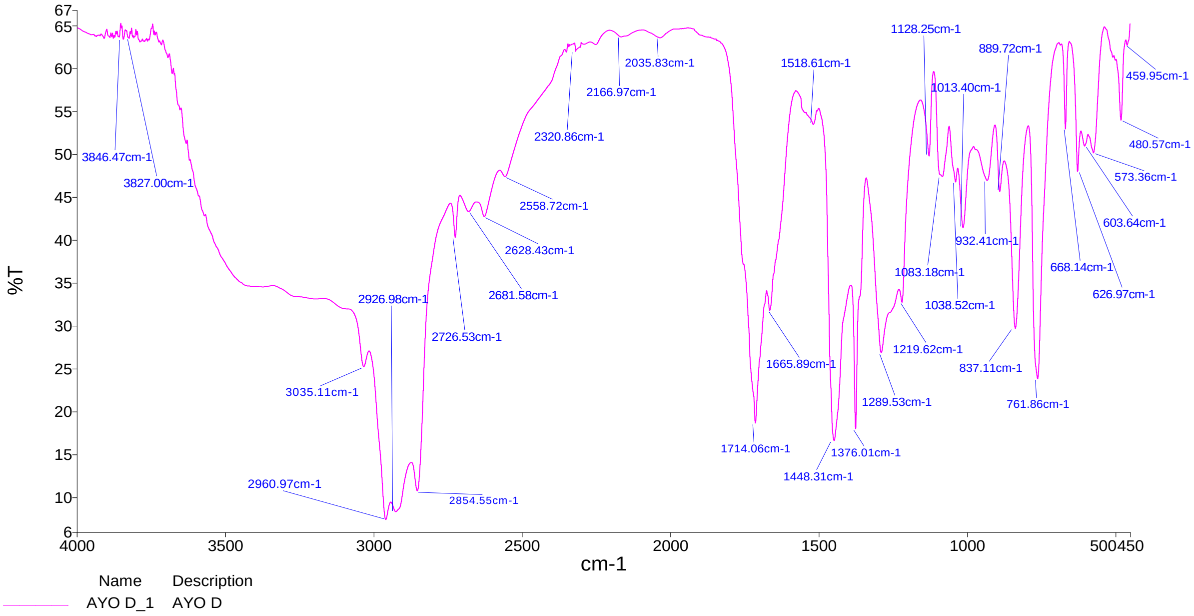

Figure 3: FT IR spectrum of depolymerized natural rubber (DPLNR)

Biodegradability test result is shown in Figures 4-10

Biodegradability of the blends was indicated by the loss in their total weight after soil burial for the three-month period. There were black spots on the surface of the blends indicating the soil microbial invasion. NR and all the modified NR did not give significant changes in weight during the period of the test. On the other hand, starch and acetylated starch gave appreciable change in weight with both of them giving 100% weight loss as indicated in Figure 4.

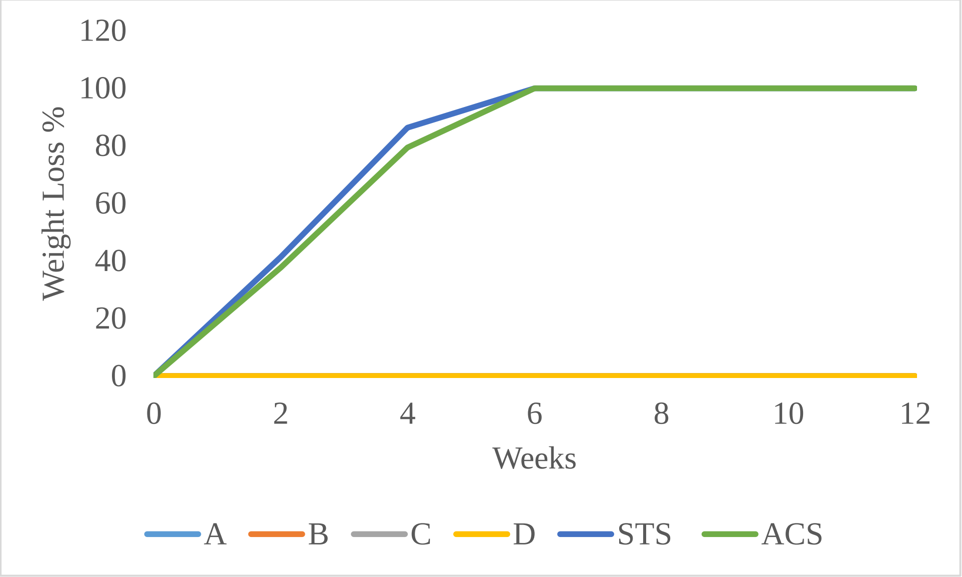

Figure 4: biodegradability of NR (A), modified NR (B, C & D), starch film (STS) and acetylated starch (ACS)

Moreover, all the blends gave appreciable changes in weight during the period of the test as indicated in Figures 5-10. It was observed from the result that an increase in the percentage of the natural rubber and modified NR in the blends resulted in a decrease in the percentage weight loss. Also observed was an increase in the biodegradability of the blends as the percentage of AS was increased with blend containing 30% ENR and 70% AS (ENRAS30) having the highest weight loss of 82.4%. The blends containing epoxidized natural rubber were also found to have the higher percentage weight loss than other blends.

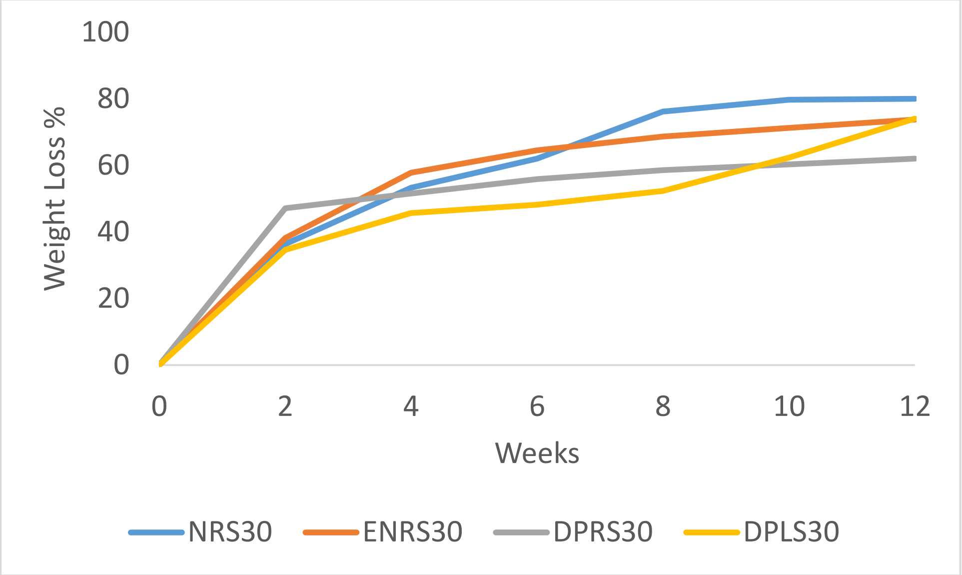

Figure 5: Biodegradability of Blends of NR and modified NR with starch at ratio 30:70

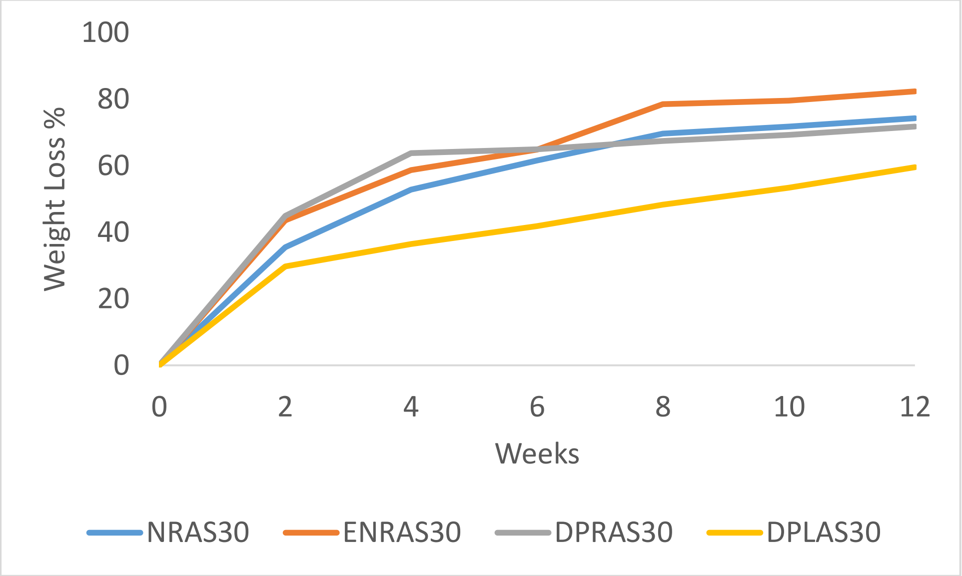

Figure 6: Biodegradability of Blends of NR and modified NR with acetylated starch at ratio 30:70

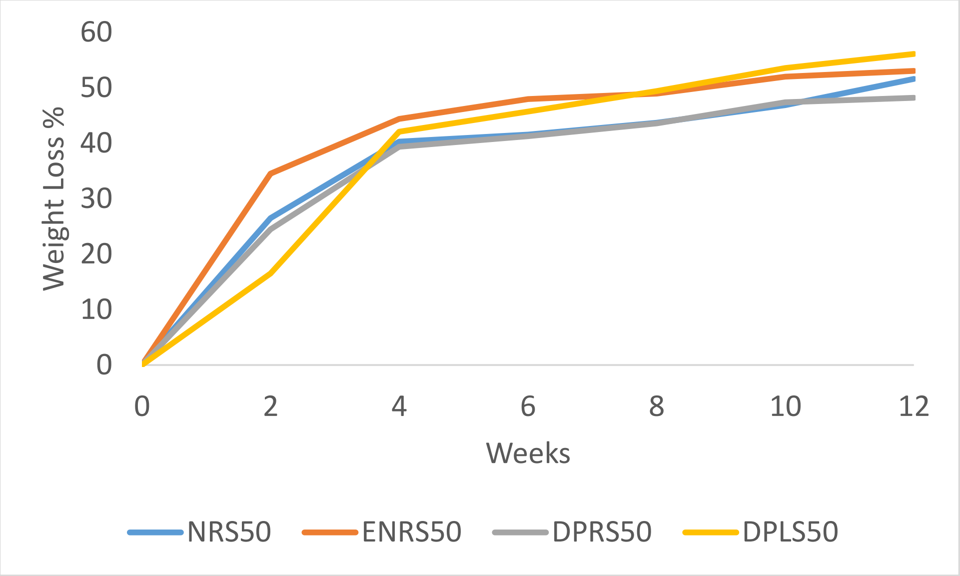

Figure 7: Biodegradability of blends of NR and modified NR with starch at ratio of 50:50

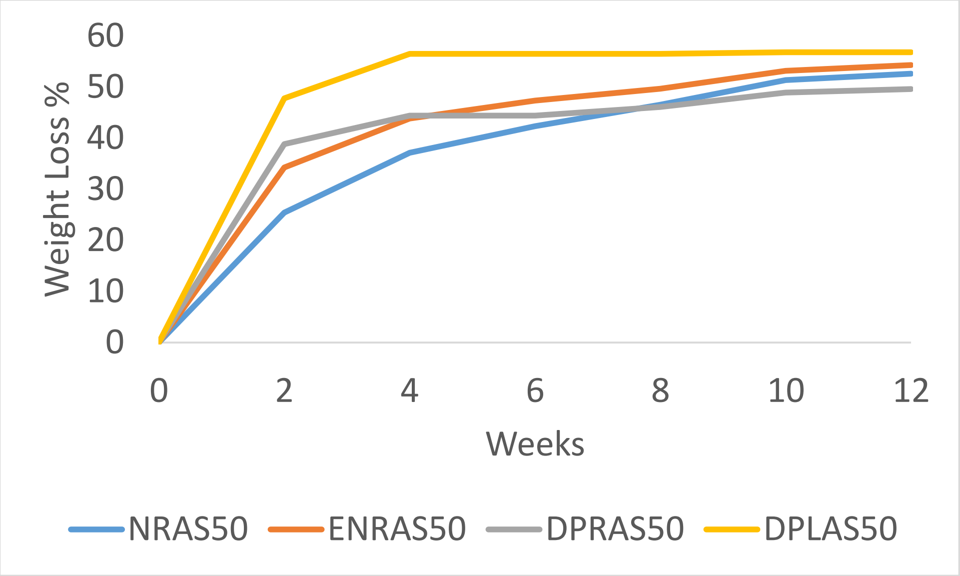

Figure 8: Biodegradability of blends of NR and modified NR with acetylated starch at ratio of 50:50

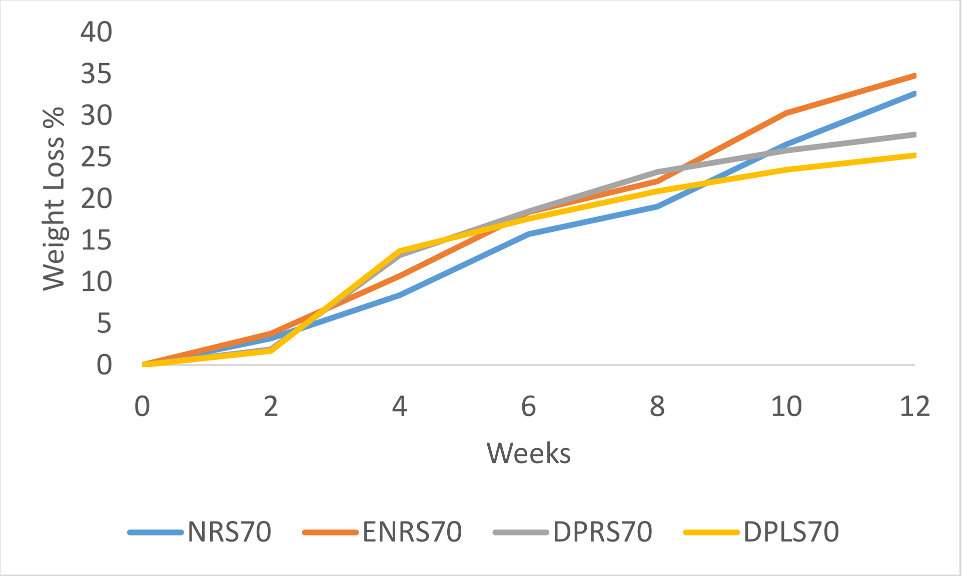

Figure 9: Biodegradability of blends of NR and modified NR with starch at ratio of 70:30

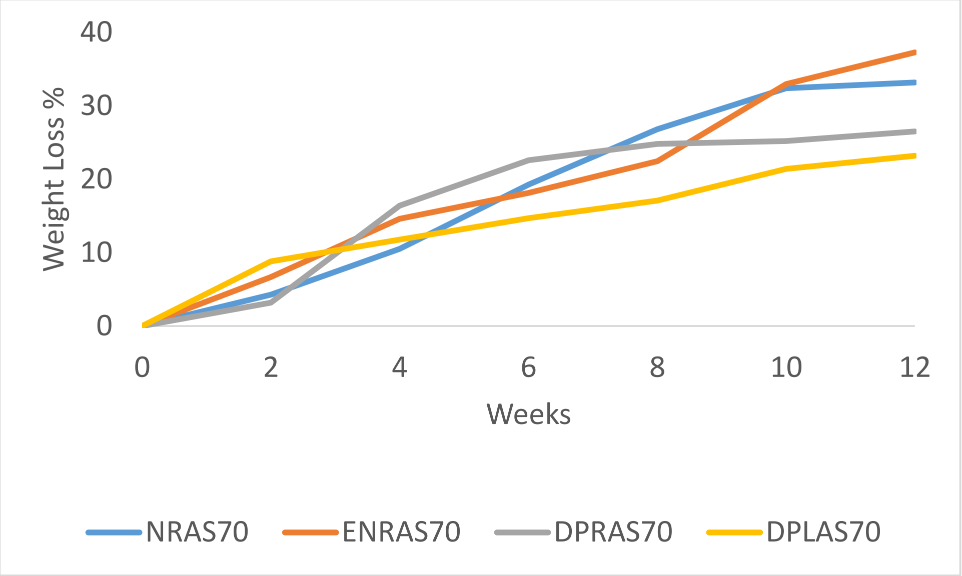

Figure 10: Biodegradability of blends of NR and modified NR with acetylated starch at ratio of 70:30

Water absorption capacity plays an important role in the degradability of bio-based materials. It was observed from the result as presented in Figure 11 that NR and all the modified NR absorbed an appreciable percentage of water. B (epoxidized natural rubber (ENR) however gave the highest percentage of water absorptivity of 12.6%. This could probably be due to the presence of epoxide group. Epoxidized natural rubber (ENR) shows a higher polarity than NR due to the epoxide groups in its structure. By its polar functional groups, ENR interacts with hydroxyl groups

Starch and acetylated starch films also readily absorbed water with starch film having the higher absorptivity due to the presence of hydroxyl group. It was also observed that the ability of blends to absorb water generally decreases with increase in the percentage of NR and modified NR present in the blends. It was discovered from the result that increase in the percentage of NR and MNR lead to a decrease in water absorptivity.

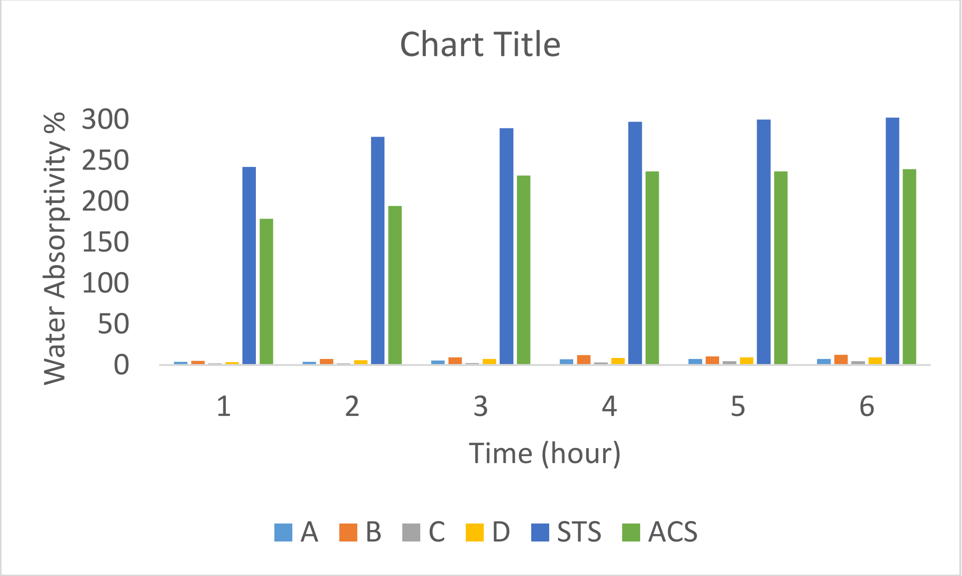

Figure 11: Water absorption capacity of NR (A), ENR (B), DPR (C), DPL (D), STS (Starch) and ACS (acetylated starch)

Table 3a: Tensile Strength of Samples

Sample	Tensile Strength (MPa)
A	0.73
B	0.82
C	0.89
D	0.96
NRS30	0.44
NRAS30	0.42
NRS50	0.46
NRAS50	0.6
DPRAS30	0.49
DPRAS50	0.69
DPLS50	0.35
DPLAS50	0.13
DPLS70	0.06
DPLAS70	0.04
ENRS30	0.48
ENRS50	0.44
ENRAS30	0.39
ENRAS50	0.62
ENRS70	0.59
ENRAS70	0.53
NRS70	0.52
NRAS70	0.56

Blends were tested for their tensile strength and elongation at break and Young's Modulus in accordance with the ASTM 412 standard. Tables 3a and 3b showed that all the modified NR gave higher tensile strength but lower elongation when compared to NR. On the other hand, all the blends showed lower tensile strength and elongation when compared to NR with DPLS70 having the lowest value of tensile strength of 0.06 MPa and NRS30 having the lowest elongation of 40 %. It was also observed that the tensile strength of the blends increase as the percentage of starch and acetylated starch in the blends was increased.

Table 3b: Elongation at break of Samples

Sample	Elongation at Break %
A	655.42
B	452.31
C	362.92
D	361.25
NRS30	40
NRAS30	63.08
NRS50	81.67
NRAS50	106.67
DPRAS30	94.26
DPRAS50	62.5
DPLS50	72.92
DPLAS50	68.02
DPLS70	184.58
DPLAS70	97.92
ENRS30	43.13
ENRS50	72.48
ENRAS30	61.15
ENRAS50	98.64
ENRS70	163.17
ENRAS70	152.36
NRS70	198.35
NRAS70	172.18

Conclusion

The result of this study showed that all the blends of modified natural rubber with starch and acetylated starch at different ratios of 30%, 50% and 70%, in general, biodegraded in real soil environment. Biodegradability of the blends increased as the percentage of the starch and acetylated starch was increased. The biodegradability was also enhanced due to the presence of modified NR in the blends most especially the blends that contained epoxidized natural rubber. The tensile strength and elongation were reduced in the blends.

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