Effects of Starch on Tensile Properties and Bio-Degradation of Polypropylene

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Abstract Polypropylene is a polymer used extensively in a wide variety of applications. In this research polypropylene (PP) is the polymer selected to be mixed with cassava starch. The starch was added in the range of 0%, 2%, 4%, 6%, 8% and 10%. Some of the samples 20% hardener was added and others hardener was not added. The samples prepared were for Tensile tests, Microscopic examinations and Degradation behaviours. The results of the tensile tests revealed that; in the tensile test, for the samples without 0% starch content, the sample with 20% hardener is more ductile than the sample without hardener, as it failed at higher stress ($45 \times 10^3 N/cm^2$) and much more percentage elongation compared to the sample without hardener ($30 \times 10^3 N/cm^2$). The least is the sample with 10% starch content, where the one with hardener failed at a stress of ($25 \times 10^3 N/cm^2$), with higher elongation than the sample without hardener with a stress of ($20 \times 10^3 N/cm^2$). The rate of decay increases with increase in starch content. Such that the sample with zero starch had no degradation with the weight remaining 50g at the end of the period of 30days. The sample with the highest decay rate is the sample with 10% starch, which is the highest starch content for the research, which reduced to 30g at the end of the 30 days period. The hardner has serious effect on the degradation of the polymer, the sample with the highest starch content (10%) reduced to 34g at the end of the 30 days period.

Keywords Polymer, Thermoplastic, Polypropylene, Starch, Hardener, Tensile-property, Degradation

Introduction

Averous, Moro, Dole and Fringant, [1], has stated that polymers have undergone numerous modifications and improvements tothe extent that they can now compare favourably with other applied engineering materials since polymers are known. Polymer materials can be modified with ease by the addition of a variety of additives and fillers to give desired end-use properties. However, their use has been limited by their non-biodegradable nature, which causes environmental pollutions. Most countries are working on reducing the amount of plastic waste by means of recycling, but this has proved to be unsuitable and uneconomical for certain end-use applications. This global environmental awareness has caused an interest in the development of polymers that will be attacked by micro-organisms and degrade into benign by-products under composting environments. The use of starch material is considered a cheap way of developing biodegradable materials. The main challenge is to make the properties of such a material comparable to those of conventional polymers.

According to Cordelia [2], Starch is a natural polymer occurring in the seeds, tubers and stems of many plants, including maize. It is a mixture of two polymers: linear amylose and highly branched amylopectin. The ratio and the molar masses of the two polymers depend on the starch source, giving rise to different starch properties.

Thermoplastic starch (TPS) was obtained by gelatinizing a dry-blend mixture of maize starch, water, plasticizers and additives in a single-screw laboratory extruder. The TPS formed is a translucent amorphous material that could be shaped into pellets and injection-moulded into a variety of articles, just like conventional plastics.

Polyethylene or polythene (abbreviated PE; IUPAC name polyethene or poly(methylene)) is a thermoplastic polymer used extensively in a wide variety of applications [3]. As of 2017, over 100 million tons of polyethylene resins are produced annually, accounting for 34% of the total plastics market. In 2013, the global market for polypropylene was about 55 million tons [3-4]. Kenneth *et al.*, [5], has stated that it is produced via chain growth polymerization from the monomer propylene. Polypropylene belongs to the group of polyolefins and is partially crystalline and non-polar. Its properties are similar to polyethylene, but it is slightly harder and more heat resistant. It is a white, mechanically rugged material and has a high chemical resistance. Polypropylene is the second-most widely produced commodity plastic (after polyethylene) and it is often used in packaging and labeling [6]. Its primary use is in packaging (plastic bags, plastic films, geomembranes, containers including bottles, etc.). Many kinds of polyethylene are known, with most having the chemical formula $(C_2H_4)_n$. PE is usually a mixture of similar polymers of ethylene with various values of n. Polyethylene is a thermoplastic; however, it can become a thermoset plastic when modified (such as cross-linked polyethylene) [7].

Polyethylene, like other synthetic plastics, is not readily biodegradable, and thus accumulates in landfills. However, there are a number of species of bacteria and animals that are able to degrade polyethylene. In May 2008, Daniel Burd, a 16-year-old Canadian, won the Canada-Wide Science Fair in Ottawa after discovering that *Pseudomonas fluorescens*, with the help of *Sphingomonas*, can degrade over 40% of the weight of plastic bags in less than three months [8]. The thermophilic bacterium *Brevibacillus borstelensis* (strain 707) was isolated from a soil sample and found to use low-density polyethylene as a sole carbon source when incubated together at 50 °C. Biodegradation increased with time exposed to ultraviolet radiation [9]. *Acinetobacter* sp. 351 can degrade lower molecular-weight PE oligomers. When PE is subjected to thermo- and photo-oxidization, products including alkanes, alkenes, ketones, aldehydes, alcohols, carboxylic acid, keto-acids, dicarboxylic acids, lactones, and esters are released [8]. In 2014, a Chinese researcher discovered that Indian mealmoth larvae could metabolize polyethylene from observing that plastic bags at his home had small holes in them. Deducing that the hungry larvae must have digested the plastic somehow, he and his team analyzed their gut bacteria and found a few that could use plastic as their only carbon source. Not only could the bacteria from the guts of the *Plodia interpunctella* moth larvae metabolize polyethylene, they degraded it significantly, dropping its tensile strength by 50%, its mass by 10% and the molecular weights of its polymeric chains by 13% [7]. In 2017, researchers reported that the caterpillar of *Galleria mellonella* eats plastic garbage such as polyethylene [4].

Due to polypropylene structure's rigidity and relative cheapness, it's used in various applications. It has good chemical resistance and weldability, which makes it ideal for the automotive industry, consumer goods, furniture market, and industrial applications such as custom wire baskets. Some common uses of polypropylene include[10], [11]:

- **Packaging Applications:** Polypropylene's structure and strength make it a cheap and ideal packing application.
- **Consumer Goods:** Polypropylene is used for many consumer goods—including translucent parts, housewares, furniture, appliances, luggage, toys and more.
- **Automotive Applications:** Polypropylene is widely used in automotive parts because of its low cost, weldability, and mechanical properties. It can mostly be found in battery cases and trays, bumpers, fender liners, interior trim, instrumental panels and door trims.
- **Fibers and Fabrics:** Polypropylene is utilized in a host of fiber and fabrics applications including raffia/slit-film, tape, strapping, bulk continuous filament, staple fibers, spun bond, and continuous filament.
- **Medical Applications**: Due to polypropylene's chemical and bacterial resistance, it is used for medical applications including medical vials, diagnostic devices, petri dishes, intravenous bottles, specimen bottles, food trays, pans, pill containers, and disposable syringes.

- **Industrial Applications:** The high tensile strength of polypropylene's structure, combined with its resistance to high temperatures and chemicals, makes it ideal for chemical tanks, sheets, pipes, and Returnable Transport Packaging (RTP).

Problems Statement

The menace of Polymers as environmental pollutant cannot be over emphasized. This is because polymers products do no decayed or degrade after being disposed. The alternatives have been to recycle it to reduce their availability in the environment as waste products. The danger to that have been cited that some of the recycled products of the waste polymer materials are not hygienic to human life. What is then the best alternative is to make them degrade into microscopic matters and thereby contribute to replenishing farmlands they happened to be disposed on.

Objectives of the Research

The aim of this research is to develop a polymer using cassava flour as starch material on Polypropylene polymer. The objectives are:

- ➢ To develop cassava-polypropylene resin blended polymer using percentage ranges of cassava flour of 2%, 4%, 6%, 8% and 10%.
- ➢ To add 20% hardener to some and leave some without the addition of hardener.
- ➢ To test the tensile properties of each sample developed.
- ➢ To carry out microscopic observation of the structure of each sample developed.
- ➢ To observe the degradation behaviour of the various samples

Scope of the Research

The scope of this research is to develop a biodegradable polymer using cassava flour-polypropylene blend in order to investigate the various properties modification of the blended cassava flour and the degradability of the developed samples.

Significant of the Research

The importance of research of this nature can never be over emphasized, owing to their local, national and global importance. All over the globe, polymer products have been used in one form or the other. But the greatest menace imposed by the products of polymer are their inability to decay or degrade into microscopic size after disposed. This research found out property modification of the addition of cassava flour into polypropylene polymer as an additive to introduce degradability into the product. This will go along way into bringing a lasting solution to the environmental problems of polymer materials.

Materials and Methods

Materials

The materials used for the research were:

- ➢ Dry cassava was obtained from Kara Market in Sokoto and grinded in the same market. The flour was then sieved to remove coarse materials to make it suitable for the application.
- ➢ Polypropylene Resin and hardener obtained from Philips Sumika (Chevron Philips Chemical Company) with trade name Martex®, through CEMAN VENTURES LTD, Kano, Kano State, Nigeria
- ➢ The Polymer hardener was obtained from Alfa Chemistry, 2200 Smithtown Avenue. Room 1 Ronkonkoma, NY 1178-7329 USA, through CEMAN VENTURES LTD, Kano, Kano State, Nigeria

Preparation of Polymer-Starch mixture for Samples Production

The cassava flour was mixed at paste level with cool water as other water was on fire awaiting boiling. The boiled water was poured into the pasted flour up to a predetermined quantity and the starch was produced. Next was the

heating of the Polypropylene resins in a controlled furnace environment up to the melting point at $138^{\circ}C$. The content was kept at the melting temperature for mixture of the starch and the melted polymer to be done. The following calculations were followed in order to carry out the addition.

Sample preparation includes all the processing steps necessary to convert granular starch into thermoplastic pellets, such as mixing, extrusion, injection moulding and cutting.

PS1 = 100%PP + 0% Starch = 100% Melt weight was casted into a preheated metallic mold which was water cold after pouring of the molten polymer without adding hardener.

PS2 = 98%PP + 2%Starch

PS3 =   96%PP + 4%Starch

PS4 = 94% PP + 6% Starch

PS5 = 92% PP + 8% Starch

PS6 = 90% PP + 10% Starch

PHS1 = 80% PP + 20% Hardener + 0% Starch = 100% Melt weight

PHS2 = 78% PP + 20% Hardener + 2% Starch = 100% Melt weight.

PHS3 = 76%PP + 20% Hardener + 4% Starch = 100% Melt weight.

PHS4 = 74% PP + 20% Hardener + 6% Starch = 100% Melt weight.

PHS5 = 72% PP + 20% Hardener + 8% Starch = 100% Melt weight.

PHS6 = 70 % PP + 20% Hardener + 10% Starch = 100% Melt weight.

Tests, Results and Discussions

The various samples were prepared for tensile test, microscopic examination and biodegradation. The results of the tests and observations made are shown below:

Tensile Testing Results

The results of the tensile tests carried out on the various samples are displayed below on graphical chart.

(a)   (b)

(c)   (d)

(e)   (f)
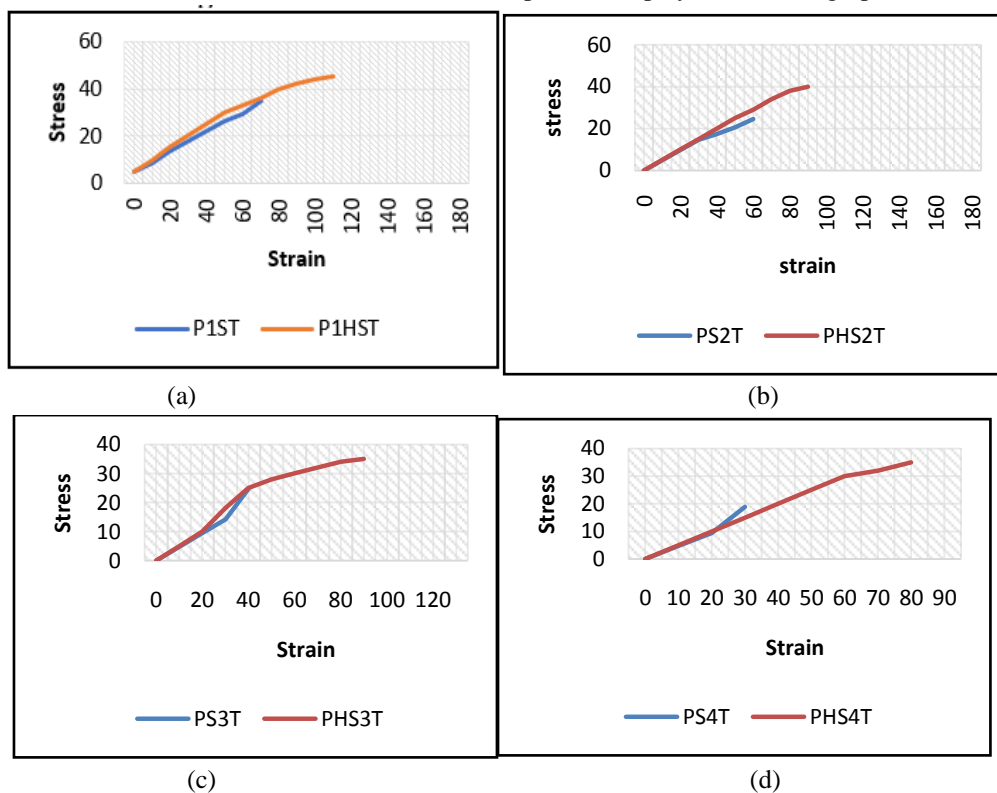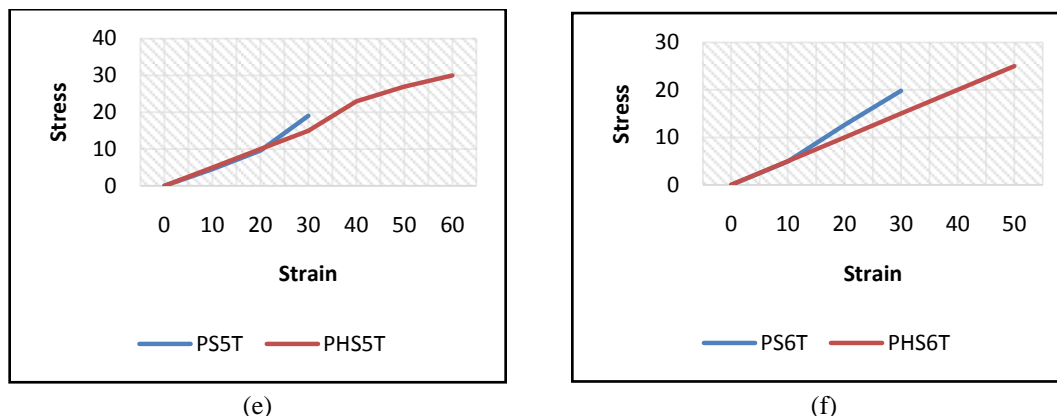
Figure 1: Comparative Stress-Strain Curves for Polypropylene without and with 20% Hardener

(a) Samples without starch content, (b) Samples with 2% starch contents, (c) Samples with 4% starch contents, (d) Samples with 6% starch content, (e) Samples with 8% starch contents, (f) Samples with 10% starch content.

From figure 1 above, six stress-strain curves can be observed. (a) is that of samples without 0% starch content. It can be seen from the two lines that the sample with 20% hardener is more ductile than the sample without hardener. Also, it failed at higher stress ($45 \times 10^3 N/cm^2$) and much more percentage elongation compared to the sample without hardener ($30 \times 10^3 N/cm^2$). (b) is for samples with 2% starch contents. Looking at the lines it can be observed that the sample with hardener still has higher breaking stress ($40 \times 10^3 N/cm^2$) and elongation compared to one without hardener ($25 \times 10^3 N/cm^2$). As for (c) with 4% starch contents, it is seen that sample with hardener has higher breaking stress ($35 \times 10^3 N/cm^2$) and elongation compared to the sample without hardener ($25 \times 10^3 N/cm^2$). (d), with 6% starch has sample with hardener with higher breaking stress ($35 \times 10^3 N/cm^2$) and elongation as compared with the one without hardener ($20 \times 10^3 N/cm^2$). Looking at (e), it can be seen that sample with hardener has breaking stress of ($30 \times 10^3 N/cm^2$) at a higher elongation compared with the samples without hardener with breaking stress of ($20 \times 10^3 N/cm^2$) and lastly, for (f) it can be observed that the sample with hardener failed at a stress of ($25 \times 10^3 N/cm^2$), with higher elongation than the sample without hardener with a stress of ($20 \times 10^3 N/cm^2$). The graph on figure 2 below give more information about the different failure levels of the various polymers.
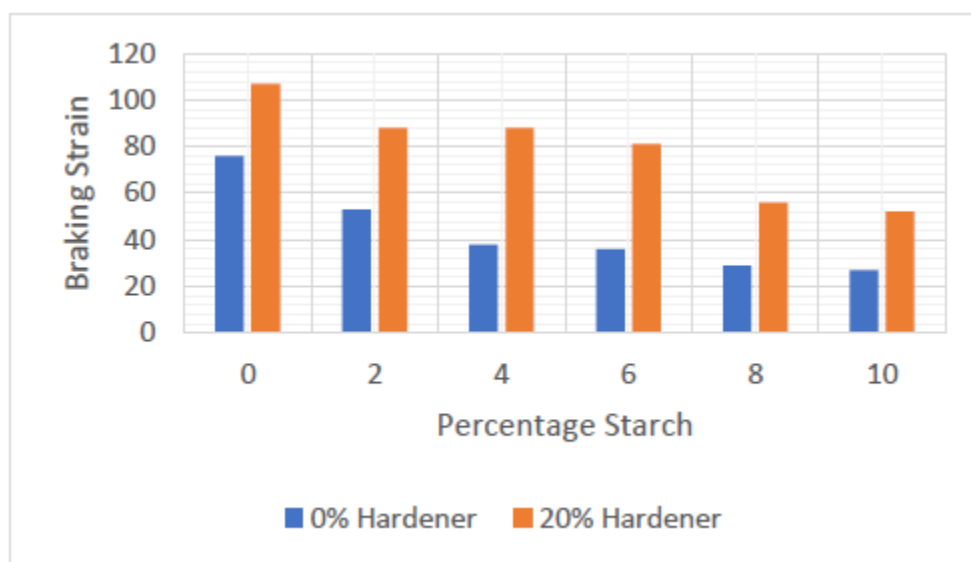

Figure 2: Comparative Bar Chart of Braking Strain of Samples with 20% Hardener and Samples without Hardener

From figure 2 above, it can be seen that the samples with 20% hardener have higher braking strain than those without hardener. This indicate that hardener induce rigorous strength to the polymers. Such polymer for every day application must be hardened by the introduction of hardener into the melt before cast. While starch content has adverse effect on the strength of the polymer, such that increase in the amount of starch further reduce the strength of the polymer.

Microstructures of the Samples

This shows the microscopic appearances of the samples as observed under the microscope. In the case of the optical microscope was used for the examination. The results are displayed below.
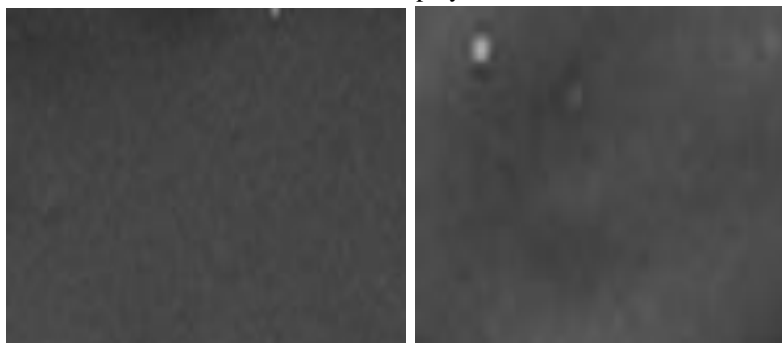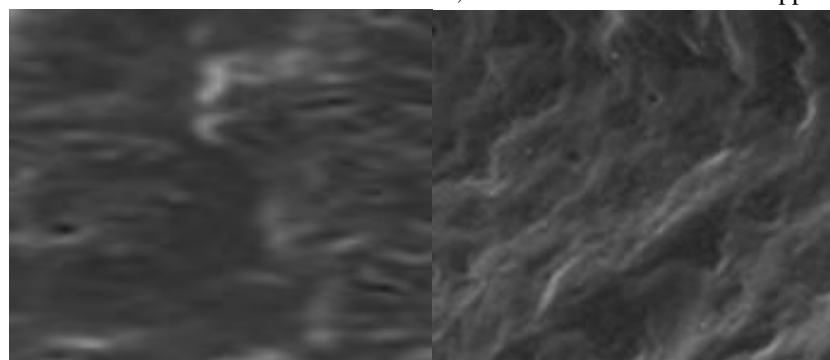

(a) No Hardener   *(b) 20% Hardener*

Figure 3: SEM Picture of Samples with 0% Starch Content

From figure 3 above, the difference can be seen between (a) and (b), owing to the fact that the hardner content has made the appearance of (b) look fearer than that of (a). On the top left a white spot is observed in (b), which is the undissolved hardner that is segggregated.
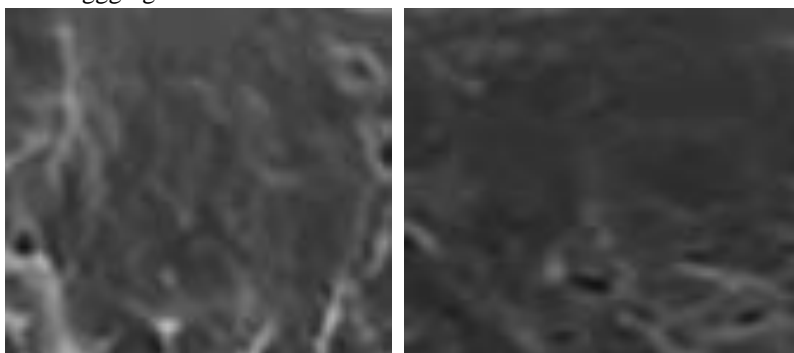
(c) No Hardener   *(d) 20% Hardener*

Figure 4: SEM Pictures of Samples with 2% Starch Content

Form figure 4, it can be observed that (c), which does not contain hardner looks fearer than the (d) in this case. This may be due to the reaction between the starch and the hardner, which darken the structural appearance.
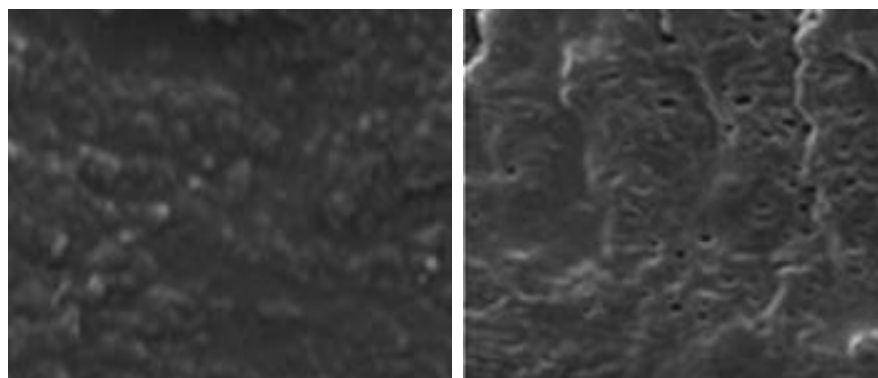

(e) No Hardener   *(f) 20% Hardener*

Figure 5: SEM Picture of Samples with 4% Starch Content

Figure 5 shows the microstructure of (e), the sample with starch but no hardner and (f), the sample with starch and hardner. The sample without hardner still look lighted in appearance compared to (f), this could be as a result of the reaction between the hardner and the starch as discussed above.
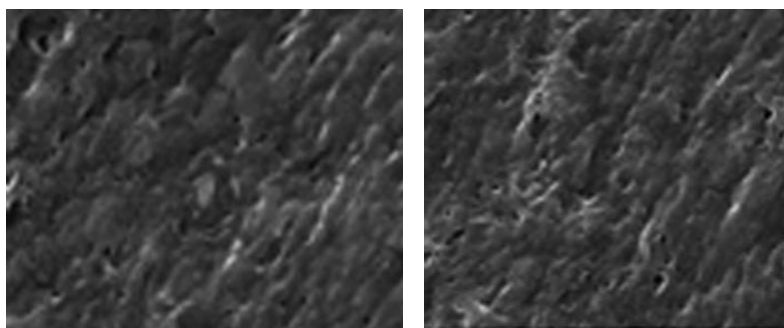

| *(g) No Hardener* | *(h) 20% Hardener* |

Figure 6: SEM Picture of Samples with 6% Starch Contents

As the starch content increases, both the sample without and with hardner look more darker and coarse, according to the microstructure shown in figure 6, above. (h) looks more coarse than (g), which has a strong link to the starch hardner reaction.
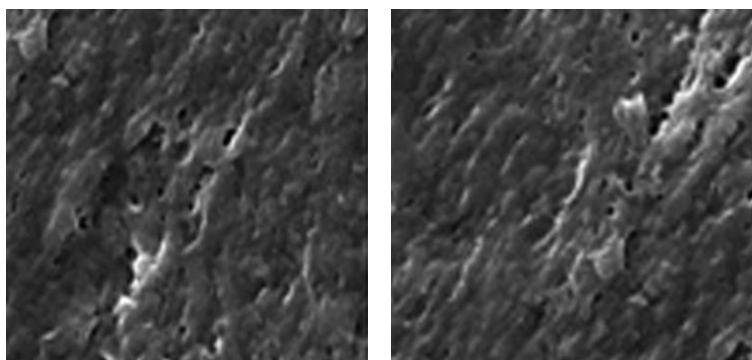

| *(i) No Hardener* | *(j) 20% Hardener* |

Figure 7: SEM Pictures of Samples with 8% Starch Contents

From figure 7, (i) and (j) look almost similar in appearance, but (i) look darker by the left side of the micrograph. May be due to accumulation of starch on the side.

| *(k) No Hardener* | *(l) 20% Hardener* |

Figure 8: SEM Pictures of Samples with 10% Starch Content

From figure 8, (k) and (l) look similar as well, but there are more pronounced white patches on (l) than in (k). This could be attributed to excess starch which could not go into solution or reaction.

Degradation Behaviour of the Samples

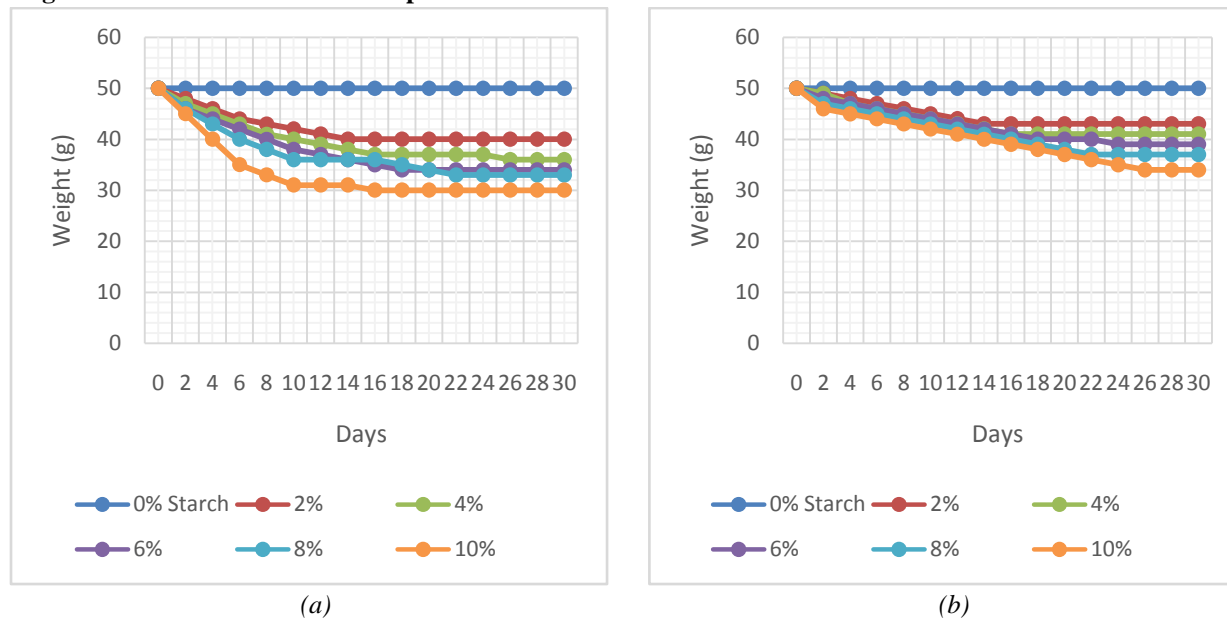(a)   (b)

Figure 9: Decay Curves of the Samples for the period of 30 Days. (a) is without hardener, while (b) is with hardener

From Figure 9 above, it can be observed that the rate of decay increases with increase in starch content. Such that the sample with zero starch had no degradation at all, the weight still remained 50g at the end of the period of 30days. The sample with the highest decay rate is the sample with 10% starch, which is the highest starch content for the research, which reduced to 30g at the end of the 30 days period.

Figure 23, is the decay curves for samples with 20% hardner content. It can be obseved that the hardner has serious effect on the degradation of the polymer. Even though the decay rate followed the same pattern as in figure 22, but the pattern shows slower decay rate. The sample with the highest starch content (10%) reduced to 34g at the end of the 30 days period.

Conclusions

For the samples without 0% starch content, the sample with 20% hardener is more ductile than the sample without hardener, as it failed at higher stress (45×10^3N/cm^2) and much more percentage elongation compared to the sample without hardener (30×10^3N/cm^2). The least is the sample with 10% starch content, where the one with hardener failed at a stress of (25×10^3N/cm^2), with higher elongation than the sample without hardener with a stress of (20×10^3N/cm^2).

The rate of decay increases with increase in starch content. Such that the sample with zero starch had no degradation at all, the weight still remained 50g at the end of the period of 30days. The sample with the highest decay rate is the sample with 10% starch, which is the highest starch content for the research, which reduced to 30g at the end of the 30 days period.For samples with 20% hardner content. It can be obseved that the hardner has serious effect on the degradation of the polymer. Even though the decay rate followed the same pattern with the samples without hardener, but the pattern shows slower decay rate. The sample with the highest starch content (10%) reduced to 34g at the end of the 30 days period.

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