

EFFECT OF STARCH CONTENTS ON THE CREEP PROPERTIES AND BIO-DEGRADATION BEHAVIOURS OF POLYPROPYLENE

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Abstract

The fact that polymers do not decay or degrade after disposal is a serious environmental problem, which need to be looked into. The idea of blending polymer with starch has been making the day in many societies to reduce the menace of produced by polymers waste in the society. 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 Creep tests, Microscopic examinations and Degradation behaviours. The results show that the creep properties of the samples at 35°C revealed that the hardener has paramount impact on the polymer creep resistance. Such that for samples with 0% starch content, the sample without hardener has strain level of 180 at 120 minutes when it failed, where the sample with hardener, which has strain level of 150 at 160 minutes to failed. and with 10% starch content is the samples without hardener failed within 78 strain level at 110 minutes against 75 at 130 minutes for the one with hardener. Considering the creep properties of the samples at 70°C, it will be observed that the hardener has positive influence on the polymer creep resistance. comparing the samples with 0% starch content it will be observed that the sample without hardener has strain level of 200 at 80 minutes when it failed as against the sample with hardener, which has strain level of 280 at 120 minutes to failed. and 10% is 80 at 80 minutes for sample without hardener against 90 at 120 minutes. 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 observed 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.

KEYWORDS: *Polymer, Polypropylene, Starch, Cassava, Creep, Degradation*

INTRODUCTION

Averous, Moro, Dole and Fringant, (2000), has stated that polymers have undergone numerous modifications and improvements to the 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 (2006) and Shogren (2009), 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.

Starch is a versatile biopolymer obtained from renewable plant resources such as maize, wheat and potato harvests. Starch consists of two component polymers, amylose (AM) and amylopectin (AP). Amylose is the linear polysaccharide, poly(α -1,4-glucopyranosyl). Amylopectin is poly(α -1,4-glucopyranosyl) with many a -1,6-glucopyranosyl branches. The molar mass of AM is large, >106 g/mol, while AP is >107 g/mol. There are various crystal forms of starch, due to double helix formation of linear regions of AP. The crystalline and amorphous regions assemble in layered formations to ultimately constitute the starch granules. Starch is economically competitive with polymers derived from petroleum for manufacture of packaging materials. Starch based materials are biodegradable (Arroyo, Huneault, Favis and Bereau, 2010).

Polpropylene or polythene is a thermoplastic polymer used extensively in a wide variety of applications (Geyer, Jambeck and Law, 2017). 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 (Geyer *et al.*, 2017 and Royer, Ferron, Wilson and Karl, 2018). Kenneth, Whiteler, Geoffrey, Hartmut, Ralph and Wolfgang, (2005), 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. (Morris, 2005). 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) (Kurtz, 2015).

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 (Yang, Yang, Wu, Zhao and Jiang, 2014). 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 (Hadad, Geresh and Sivan, 2005). *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 (Yang *et al.*, 2014). 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% (Kurtz, 2015). In 2017, researchers reported that the caterpillar of *Galleria mellonella* eats plastic garbage such as polyethylene (Royer *et al.*, 2018).

Applications of Polypropylene

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 (Intratec, 2012 Nuyken, Sebastian, Koltzenburg and Maskos, 2013):

- **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 not decay 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 carry out creep test on 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 the property modification of the addition of cassava flour into polypropylene polymer as an additive to introduce degradability into the product. This will go a long 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°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.

Results and Discussions

The results and the discussions on the experimental tests on the various polymers produced are presented below.

Creep Test Results

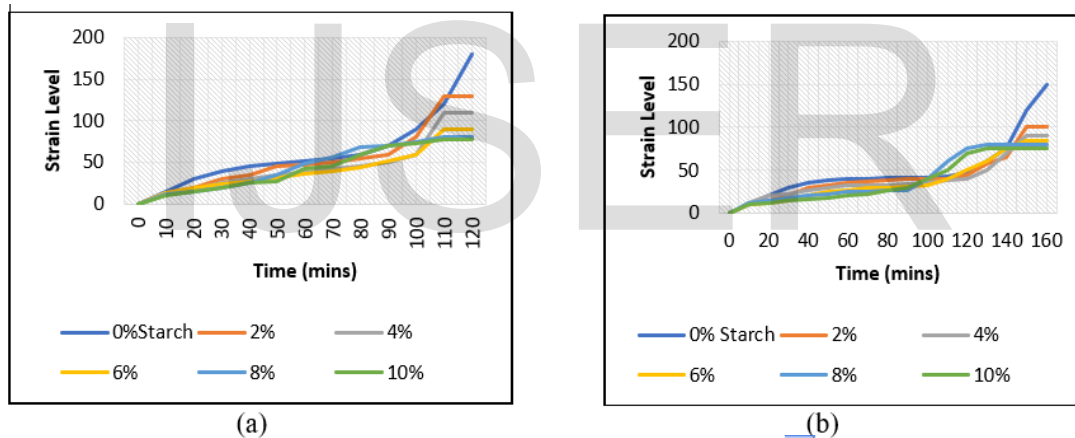


Fig. 1: Creep Behaviours at 35°C Temperature for various Samples: (a) Samples without Hardener and (b) Samples with 20% Hardener

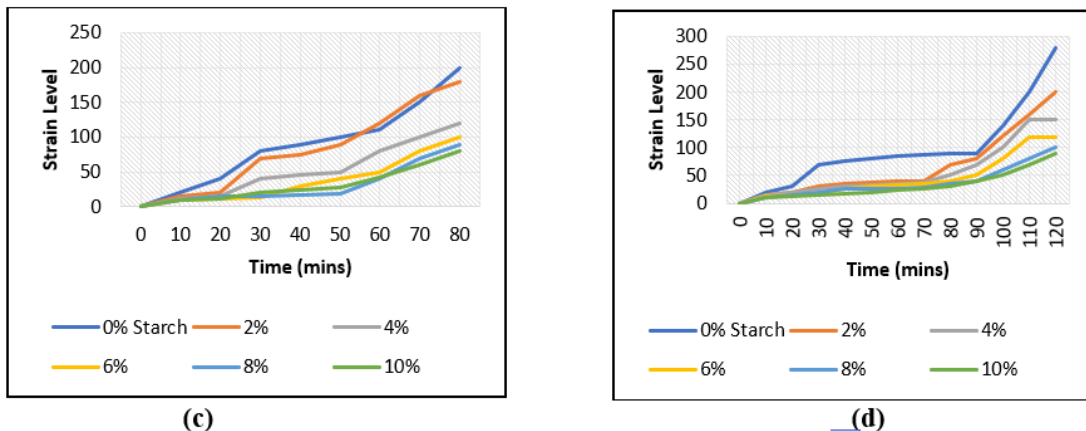


Fig. 2: Creep Behaviours of Samples at a Temperature of 70°C: (c) Samples without Hardener and (d) Samples with 20% Hardener

From the figure 1 above, two separate graphs can be observed. (a) is the one for samples without hardener and (b) is for samples with 20% hardener. Observing the two graphs, it can be seen that for (a), the sample with 0% starch content has rapid strain from the beginning up to 30 minutes and then the flow reduced and grow gradually up to 70 minutes, then it flows again rapidly up to 120 minutes and then failed at a strain level of 180. The sample with 20% starch follows similar pattern, but at lower strain level and failed at 110 minutes with a strain level of 130. Sample with 40% failed at 110 minutes with strain level of 110, 6% sample failed at 110 minutes with strain level of 90. While, sample with 8% has a strain level of 80 at 110 minutes before breaking and sample with 10% has 78 strain level at 110 minutes to break.

On the other hand, the (b) graph is for samples with 20% hardeners. The one with 0% starch content has rapid strain up to 30 minutes before it reduced the flow and from 120 minutes to 160 minutes the flow changed to rapid strain again and failed at 150 strain level at 160 minutes. The sample with 2% starch content has 100 strain level at 150 minutes, 4% has 90 at 150 minutes, 6% has 85 at 150 minutes, while 8% has 80 at 130 minutes and 10% has 75 at 130 minutes.

If the two graphs are compared, it will be revealed that the hardener has paramount impact on the polymer creep resistance. If we look at the samples with 0% starch content it will be clear that the sample without hardener has strain level of 180 at 120 minutes when it failed as against the sample with hardener, which has strain level of 150 at 160 to failed. For 2% the strain levels are 130 at 110, against 100 at 150 minutes, 4% is 110 at 110 minutes against 90 at 150 minutes, 6% is 90 at 110 minutes against 85 at 150 minutes, 8% is 80 at 110 minutes against 80 at 130 minutes, and 10% is 78 at 110 minutes against 75 at 130 minutes.

Similarly, from the figure 14 above, two separate graphs can be observed. (c) is the one for samples without hardener and (d) is for samples with 20% hardener. Observing the two graphs, it can be seen that for (c), the sample with 0% starch content has gradual strain from the beginning up to 20 minutes and then the flow increased up for a second and grow gradually again up to 60 minutes, then it flows again rapidly up to 80 minutes and then failed at a strain level of 200. The sample with 20% starch follows similar pattern, but at lower strain level and failed at 80 minutes with a strain level of 180. Sample with 40% failed at 80 minutes with strain level of 120, 6% sample failed at 80 minutes with strain level of 100. While, sample with 8% has a strain level of 90 at 80 minutes before breaking and sample with 10% has 80 strain level at 80 minutes to break.

On the other hand, from the (d) graph, the sample with 0% starch content has moderately rapid strain up to 20 minutes before it reduced the flow till 80 seconds and from then to 120 minutes the flow changed to rapid strain again and failed at 280 strain level at 120 minutes. The sample with 2% starch content has 200 strain level at 120 minutes, 4% has 150 at 120 minutes, 6% has 120 at 120 minutes, while 8% has 100 at 120 minutes and 10% has 90 at 120 minutes.

If the two graphs (c and d) are compared, it will be revealed, as well, that the hardener has positive influence on the polymer creep resistance. comparing the samples with 0% starch content it will be observed that the sample without hardener has strain level of 200 at 80 minutes when it failed as against the sample with hardener, which has strain level of 280 at 120 minutes to failed. For 2% the strain levels are 180 at 80 minutes, against 200 at 120 minutes, 4% is 120 at 80 minutes against 150 at 120 minutes, 6% is 100 at 80 minutes against 120 at 120 minutes, 8% is 90 at 80 minutes against 100 at 120 minutes, and 10% is 80 at 80 minutes against 90 at 120 minutes. The Bar charts below will give clear picture of the information.

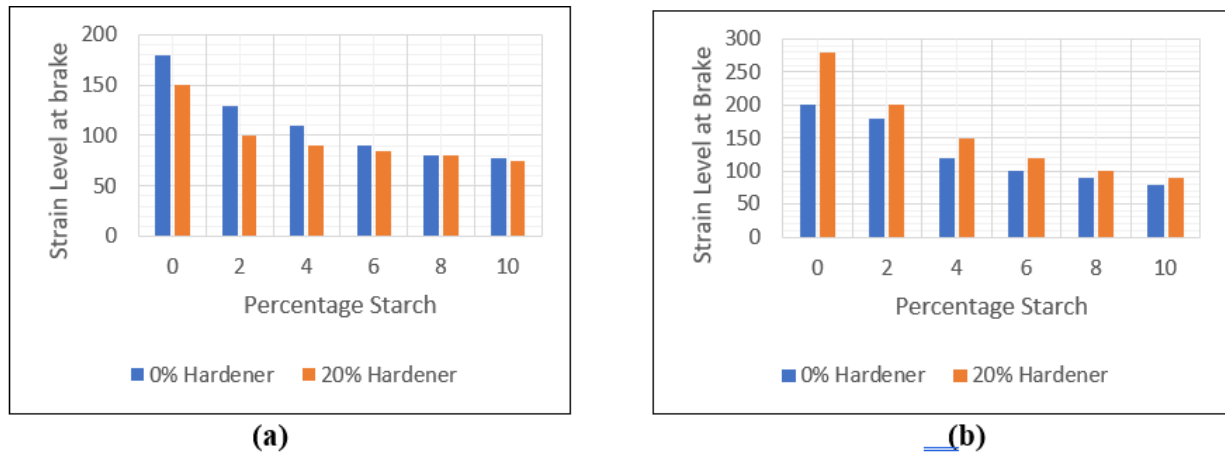


Fig. 3: Bar Charts showing the Strain Level of the Various Samples at Brake

The (a) is for samples that were crept at a temperature of 35°C and (b) is for the samples that were crept at 70°C temperature. As it can be seen, the starch has more negative effects on the samples with 20% Hardener crept at a temperature of 35°C compared to those crept at a temperature of 70°C, where the effects are seen on the samples that do contain hardener. Which show that at lower temperature, the flowability of the starch is more polymer without hardener than those with hardener. Whereas at higher temperature the flowability is more on polymer with hardener. In conclusion, polymers with hardener has more time to creep compared to those without hardener.

Degradation Behaviour of the Samples

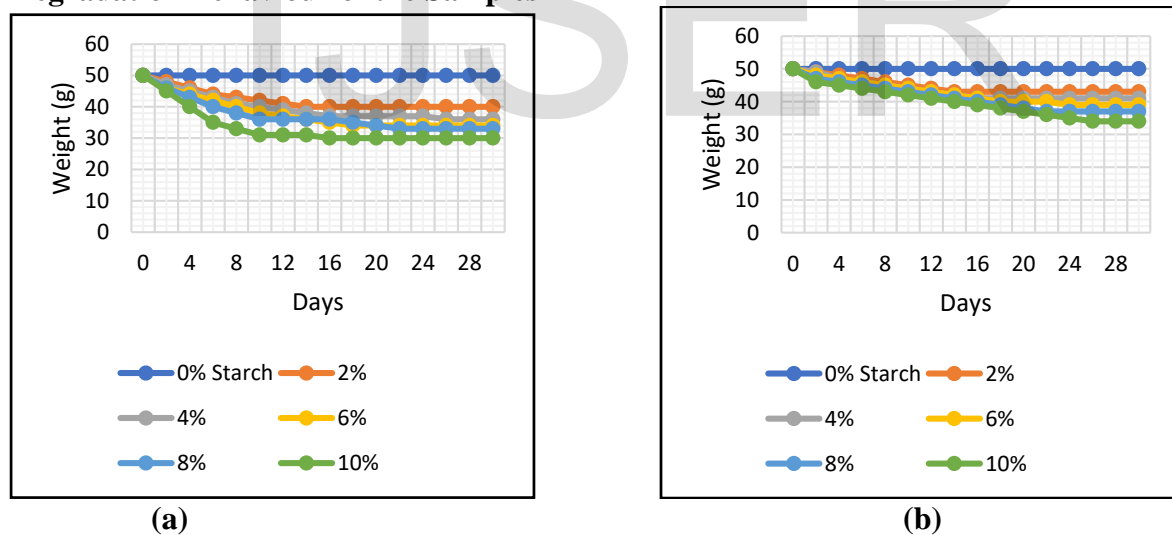


Fig. 4: Decay Curves of the Samples for the period of 30 Days: (a) Samples without Hardener, (b) Samples with Hardener

From Figure 4(a) 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 4(b), is the decay curves for samples with 20% hardner content. It can be observed that the hardner has serious effect on the degradation of the polymer. Even though the decay rate followed the same pattern as in figure 4(a), 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 Creep test of the sample without hardener, the sample with 0% starch content has the highest strain level, as it failed at a strain level of 180 in 70 minutes, while the sample with 10% has 78 strain level at 110 minutes to break. On the other hand, for samples with 20% hardeners, the one with 0% starch content failed at 150 strain level at 160 minutes and 10% has 75 at 130 minutes.

The hardener has paramount impact on the polymer creep resistance. For instance, the samples with 0% starch content shows that the sample without hardener has strain level of 180 at 120 minutes when it failed as against the sample with hardener, which has strain level of 150 at 160 minutes to failed. For 2% the strain levels are 130 at 110, against 100 at 150 minutes, 4% is 110 at 110 minutes against 90 at 150 minutes, 6% is 90 at 110 minutes against 85 at 150 minutes, 8% is 80 at 110 minutes against 80 at 130 minutes, and 10% is 78 at 110 minutes against 75 at 130 minutes.

If the two graphs (c and d) are compared, it will be revealed, as well, that the hardener has positive influence on the polymer creep resistance. comparing the samples with 0% starch content it will be observed that the sample without hardener has strain level of 200 at 80 minutes when it failed as against the sample with hardener, which has strain level of 280 at 120 minutes to failed. For 2% the strain levels are 180 at 80 minutes, against 200 at 120 minutes, 4% is 120 at 80 minutes against 150 at 120 minutes, 6% is 100 at 80 minutes against 120 at 120 minutes, 8% is 90 at 80 minutes against 100 at 120 minutes, and 10% is 80 at 80 minutes against 90 at 120 minutes.

The starch has more negative effects on the samples with 20% Hardener creped at a temperature of 35°C compared to those creped at a temperature of 70°C, where the effects are seen on the samples that do contain hardener. Which show that at lower temperature, the flowability of the starch is more in polymer without hardener than those with hardener. Whereas at higher temperature the flowability is more on polymer with hardener. In conclusion, polymers with hardener has more time to creep compared to those without hardener.

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 observed 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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