Mechanical properties of bioplastics of various starch to eggshell reinforcement ratios

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Abstract

Bioplastics are biodegradable polymers derived from the starch of natural and renewable sources such as tuber crops. While it is possible to create bioplastic with cassava starch, the resulting product has high moisture content and poor mechanical properties. In addition, the effects of varying the ratios of eggshell reinforcements on the mechanical properties of cassava-starch-based bioplastics have yet to be studied. The purpose of this study is to determine the optimal ratio of *Manihot esculenta* starch to eggshell reinforcement through comparison treatments and control groups. Unsuitable drying methods, improper storage, and handling caused multiple failed samples. This included the development of molds, samples not drying, and the inability to peel samples from the mold. Further development of better conditions in formulating plastic from cassava starch along with assessment of other properties should be investigated.

Introduction. - Bioplastics include all plastics that are derived from biodegradable resources. The importance of bioplastics lies in their biodegradability and source due to them being mainly composed of biological wastes. The study on bioplastics also has advantages for the environment due to their low carbon footprint and low energy cost in manufacturing [1]. While it is possible to create bioplastic with cassava starch, its unique chemical structure and processing behavior results in a product that has high moisture content and poor mechanical properties as stated by Xie (2013). [2]

Existing research utilized cassava starch in bioplastic development with additional reinforcements to strengthen the mechanical properties of their plastics [3,4,5]. These reinforcements increased the tensile strength as well as the biodegradability of their bioplastics based on their results. Furthermore, other studies utilized eggshells for reinforcing their bioplastics from cornstarch and potato starch [6,7]. Results showed that reinforcing bioplastics with eggshells decreased the water absorption and increased tensile strength of the bioplastic. However, the cited studies only used a singular specific ratio during the conduct of comparative analysis between samples, the variation of the ratio of reinforcements and starch composition and the effect of these changes on the mechanical properties of cassava-starch-based bioplastics is yet to be investigated. Based on Xie's (2013) study, the creation of a starch-based bioplastic with the integration of a viable plasticizer and reinforcement ratio is necessary. Calcium carbonate or $CaCO_3$ reinforcements have properties that are hydrophobic, this in turn causing the bioplastic sample to repel the water [4]. Eggshells contain approximately 95% calcium carbonate and 5% organic materials [19]. Therefore, the presence of $CaCO_3$ can increase the strength of the mechanical properties of the bioplastic. With the addition of reinforcements, the mechanical properties of the plastic would improve. Studies have stated that the integration of plasticizer and reinforcement is necessary; however, the amount used for these components in respect to the amount of cassava starch may negatively affect its tensile strength and water absorption. Thus, varying the ratios of reinforcements to the matrix is essential to determine how they would change the tensile strength and water absorption of the plastic.

The aim of the study was to determine the optimal ratio of *Manihot esculenta* (cassava) starch to eggshell reinforcement by comparing the water absorption and tensile strength. With this, the objectives of the study were:

(i) To evaluate the tensile strength of the bioplastic treatment groups containing 10%, 15%, and 30% eggshell reinforcements in comparison to the control group (0% reinforcement);

(ii) To evaluate the rate of water absorption among the bioplastic treatment groups, 10%, 15%, and 30% reinforcements;

(iii) To evaluate the tensile strength and water absorption of the various treatment groups and analyze the data using ANOVA or Kruskal-Wallis test if the distribution of the data is not normal; and

(iv) To identify the functional groups present in the various ratios of bioplastic using Fourier-Transform Infrared Spectroscopy (FTIR) spectrometer and compare their spectra.

Methods. - The methods of the study were done in

seven steps. These steps comprised of: preparation of materials, formulation of the samples, casting and drying, tensile strength test, water absorption test, and Fourier-transform infrared spectroscopy. The methodology of the study included several changes during the different trials in the formulation of the plastics. All the methods and changes were stated in each step.

Preparation of materials. Medium sized (21 oz.) chicken eggs were utilized as the source for 120 grams of eggshells. The shells were thoroughly washed with distilled water and then dried in a preheated forced-air oven at 60°C for 10 minutes. Once no excess water was observed in the eggshells, these were powderized inside an industrial blender (2.0L Drink Machine; 220 V) for 3 minutes.. Subsequently, the resulting eggshell powder was initially sieved using a mesh size 60 sieve (<0.250 mm), followed by a 30 µm sieve to ensure a uniform and fine particle size.

For the preparation of the cassava starch, the starch was initially sieved using a mesh size 60 sieve sieve before oven drying. The starch was oven-dried for 30 minutes at 60°C using a Biobase BOV-V65F oven of the PSHS-WVC laboratory before it was used for the formulation of the samples.

Formulation of the bioplastic. The conduct of the study involved the following treatment groups:

Treatment Groups in the Creation Process
Control Group - 100:0 with 5 g starch and 0 g of eggshell reinforcement
Treatment 1 - 90:10 with 4.5 g starch and 0.5 g eggshell reinforcements
Treatment 2 - 85:15 with 4.25 g starch and 0.75 g eggshell reinforcements
Treatment 3 - 70:30 with 3.5 g starch and 1.5 g eggshell reinforcements

Starch and eggshell reinforcement were mixed with 70 mL of distilled water. The mixture was then stirred starting from 350 RPM for 2 to 3 minutes until the starch had been dissolved by the water. Five ((5)) mL of glycerol and 1.5 mL of 0.1 M acetic acid were then added to the same mixture. In a separate beaker, 1.25 g of polyvinyl alcohol (PVA) was placed in a separate beaker and dissolved with distilled water in a 1:24 mass-to-volume ratio. The PVA-water solution was stirred with a magnetic stirrer at 350 RPM until the polyvinyl alcohol was visually observed to be visually observed to be dissolved in water. The contents of the two separate beakers were then combined in a singular 400 mL beaker. The mixture was then heated on a hot plate at an internal temperature range of 60 to 70°C. The content after all the components have been added was stirred gradually with a magnetic stirrer for 30 minutes. The formulation involving the diluted PVA solution was only used for trials 1 to 4. The rest of the trials followed the same formulation without the polyvinyl alcohol. The solutions formulated during trials 4 to 9 were also subjected to degassing using a Bransonic ultrasonic bath.

Casting and drying of samples. After the mixture was stirred and heated, the mixture was poured into a 15 cm x 8 cm aluminum pan. The initial trial followed this procedure however, further development prompted the researchers to change the container to a glass Petri dish with a diameter of 9 cm. This method was followed for trials 2 and 3. For the succeeding trials, 4 to 9, a plastic petri dish with similar dimensions was utilized in the casting of the bioplastic mixture. Once the mixture was casted into the Petri dish, the samples were subjected to oven drying for 30 minutes at 60°C. After the oven-drying process, the Petri dishes were transferred to a fume hood to be air-dried for a period of 48 hours. Trials 4 to 9 were also sprayed with 99% ethanol to eliminate surface bubbles.

Tensile strength test. After the bioplastic samples had fully dried in their respective molds, a minimum of 100 mm length of sample was required to be tested using the Ametek Brookfield Texture Analyzer for food-grade and low-density samples. It was then cut and peeled from the casting molds. The samples were contained and sealed in a container which was transported to the University of the Philippines Visayas Regional Research Center Food Laboratory for further testing.

Water absorption test. ASTM-D570 was used to measure the percent of water absorption [4]. Samples with dimensions of 1 cm x 3 cm were cut from the bioplastic sheets peeled from the casting mold (i.e., petri dish). These samples were created using a centimeter ruler and were cut from the bioplastic sheet using a scalpel from a dissecting kit. The initial weight of the sample was measured using an analytical balance (KERN ABJ-NM). Then, it was placed inside a 250 mL beaker containing 100 mL of distilled water for 24 hours. Once the immersion period had ended, the sample was cloth-dried until no water could be retrieved from its outer surface. The final weight was recorded using an analytical balance. Similarly, the percentage of water absorption was solved through this formula,

$$\text{WA } (\%) = \frac{(FW - IW)}{IW} x\ 100.$$

Equation 1. Formula for the Water Absorption Rate

Where:

WA = Water Absorption

FW = Final Weight of the Sample Post-Immersion

IW = Initial Weight of the Sample Pre-Immersion

FT-IR Spectroscopy. The samples were subjected to FT-IR analysis to determine the presence of bonds and functional groups present. A 1 cm x 1 cm sample was cut from the prepared bioplastic sheets for testing. A Shimadzu IRAffinity-1S FTIR equipped with a QATR 10 was used to scan the samples.

Disposal and safety procedures. Wearing of laboratory personal protective equipment (PPE) was observed during the handling of glassware, equipment, reagents, and samples. Used gloves, unused eggshells, and disposable containers were properly disposed into designated disposal bins inside the chemistry laboratory of PSHS-WVC.

Results and Discussion. - The aim of the study is to determine the optimal ratio of eggshell reinforcement to *Manihot esculenta* (cassava) starch. This section includes the results and key findings from the following tests: tensile strength, water absorption, and FTIR analysis.

Tensile Strength. A total of nine (9) trials of bioplastic samples were created and subjected to a feasibility test for the tensile strength test. The feasibility test has three criteria which need to be met. The samples must: (1) have the prescribed minimum operating length of 100 mm as required by the Ametek Brookfield Texture Analyzer; (2) have an even surface area [8]; and (3) be dry after the conduct of the following drying methods: (i) air-drying - the sample is dry at room temperature (30˚C) after 48 hours. (ii) oven-drying - the sample is dry after 30 minutes at a temperature of 60˚C inside a biobase forced air oven.

In the evaluation of the tensile strength of the produced samples, none of the samples were subjected to the procedure due to the failure to produce a viable material for testing.

The key finding which affected the viability of samples is the occurrence of clumping. The clumping of polyvinyl alcohol granules was observed in the circumference and center of the petri-dish containing samples sourced from trials 2, 3, and 4 of all the prepared reinforced samples. Clumping resulted in the strong adhesion of the samples to the casting mold and the uneven distribution of the polymer throughout the mixture. This defect can be further attributed to the undissolved PVA present in the casting slurry. Studies point out that for the PVA to be dissolved it must be within a temperature range of 60˚C to 70˚C to avoid hydrolysis and must be at a stirring speed of 200 RPM to minimize bubbling at the surface [9,10]. The clumping of the polymer matrix in the samples can be explained by the uneven distribution of components in the mixing and casting process of the bioplastic [11]. Therefore, factors such as the RPM rate of the magnetic stirrer and the temperature range of polyvinyl substances must be monitored to ensure that it can be incorporated into the mixture into a dissolved form. Failure to take note of these components had led to uneven dissolution of granules. Without samples meeting the aforementioned criteria, the conduct of the tensile strength test was no longer feasible

Water Absorption. The water absorption test involves the use of ASTM-D570 in order to determine the percent of water absorption. The procedure is used to assess the hydrophobic properties brought about by the eggshell reinforcement [4]. The data analysis process consists of the Shapiro-Wilk normality test followed by the Analysis of Variance with 5% confidence level or the Kruskal-Wallis test depending on the normality of the distribution.

The replicates of the reinforced samples were subjected to the water absorption feasibility test. As adapted from previous studies, the following criteria must be met by the samples prior to the test. The samples must: (1) have a size of 1 cm x 3 cm [4]; and (2) not contain signs of fungal growth as it would affect the water absorption of the samples [12].

A key finding observed during the post-casting phase is the occurrence of glycerol leaching which prevented the drying of the samples within the prescribed time period. The humidity of the storage area of the sample undergoing air-drying is also a factor that contributed to the inability of the samples to dry within the prescribed time. Previous studies such as that of Jones et al. (2013) have expressed that glycerol leeching would render samples unsuitable for usage and testing [13]. This phenomena negatively affects the viscoelastic properties of the bioplastic and weakens the hydrogen bonds within the product. While the water absorption test does not depend on the weight of the sample to be utilized but rather the percent increase of the sample under water immersion, the failure to extract suitable samples is a hindrance to perform the test on the prescribed amounts of samples. The conduct of the procedure was limited by the presence of moisture which caused the wetness of the sample, which consequently could not be subjected to the test. Additionally, fungal growth in the sample is another factor that prevented the conduct of the procedure.

Statistical Analysis. With the failure to conduct the tensile strength test and water absorption tests, statistical analysis was not conducted. The two aforementioned tests failed to provide any numerical data because of the insufficient number of samples that could be extracted while meeting the prescribed criteria for each test. As previously mentioned, samples that could meet the required size for the conduct of the tensile strength test were not possible. Additionally, a significant number of samples (i.e., samplessamples 1, 2, 5, 6, 7, 8, and 9) presented mold growth and presence of surface moisture which hindered the conduct of the water absorption test. Crops producing tubers or roots have specific requirements for storage because of their high moisture content (60 to 80%) [14]. Flour with high moisture content will be more vulnerable to mold growth [15]. In line with this, proper storage and drying of the cassava starch must be done in order to prevent mold growth during the formulation and drying of samples. Additionally, ensuring that the samples are fully dry is essential for the tests to be conducted.

FTIR Results. FT-IR spectroscopy was only conducted on the samples containing 10% and 15% eggshell reinforcements and the control group. The results of the various treatments were compared with each other in regard to the identification of functional groups present. The analysis of the spectra was limited to the wavelength of the functional group region. Moreover, FTIR analysis through the identification of the functional groups presence confirmed that the dried product is defined as a bioplastic [11]. The presence of C-H bonds and O-H bonds is brought about by the polymerization of starch and water. The two components undergo polymerization with the

addition of heat. This reaction results in the presence of C-H, O-H (carboxylic acid) and O-H (alcohol) functional groups, thus forming polymer chains. The common functional groups reflected by the extracted samples with respective starch-to-reinforcement ratios of 0% (control group), 10%, and 15% reinforcement content indicate the presence of the following bonds: C-H, O-H (carboxylic acid) and O-H (alcohol). The analysis of the spectra was restricted to the region to the left of 1400 cm^{-1} which is defined as the "functional group region". Meanwhile, the range between 600 and 1400 cm^{-1} is defined as the "fingerprint region". The interpretation of the results was focused on the "functional group region" as it is where most stretching frequencies occur and the "fingerprint region" was not integrated into the findings since the overlapping of bonds is prone to unreliable interpretation. All functional groups that are relevant to the creation of bioplastic are present within the spectra and peaks have also been observed within the prescribed range.

Recommendations. In order to obtain bioplastic that has better characteristics, the researchers highly recommend to:

a. Use a desiccator for sample storage to prevent excess moisture and prevent possible mold growth.

b. Explore the effects of other starch to reinforcement ratios in the creation of bioplastic. Further modification of the proportion of reagents such as acetic acid to the volume of the mixture should also be taken into consideration to provide a broader range of options in the optimization of the mechanical properties of the product.

c. Refine the air-drying method through storing the samples in an area which prevents the build-up of moisture while simultaneously protecting the contents of the casting mold from contamination.

d. Consider factors such as temperature and relative humidity of the working and drying area of the samples inside the laboratory.

e. Perform FTIR analysis for samples from various trials to discover trends and the consistency of the data procured; it is also advised to explore other data sets of wavelengths that could be made to determine the presence of other functional groups.

f. Compare FTIR graphs of glycerol and the dried casted mixture to confirm that glycerol leeching has occurred in selected samples that feature branch-like patterns on the surface.

Limitations. The bioplastic samples had high moisture content attributed to poor drying conditions and a lack of appropriate facilities. With this, the samples were not extracted and were not viable to be subjected to the tensile strength testing. In addition, the presence of molds contributed to the reason why the samples were not viable to be subjected to the water absorption test. The data analysis through ANOVA or Kruskal-Wallis test was not conducted due to the absence of quantitative data that had to be collected from the tests. With regard to the FTIR analysis, the data set of the wavelength was limited to the functional group region. From a chemical standpoint, it is limited to the enumeration of functional groups within the said region found during analysis. This is defined as the region to the left of 1400 cm^{-1} in the spectra and is where most stretching frequencies occur. As such, peaks in the fingerprint region were not noted in the presentation of the findings. The absence of a confirmatory test for bioplastics hindered the classification of the produced material to a specific type of bioplastic. This limited the researchers to the evaluation of present functional groups based on the necessary functional groups prescribed for the polymerization and formation of bioplastic [15]. The basis for the functional groups evaluation was the library database of the LabSolutions IR software.

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