

Synthesis of Corn starch based Bioplastic using Chitosan-Sorbitol-Glycerol blend Additives

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Abstract: Petroleum based plastics are used in packaging, domestic, industrial, medical and biotechnological applications are non-biodegradability, unfriendly to the environment, hazardous and toxic when burnt. This has made bioplastics from starch base materials suitable alternatives because of their ease of use, biodegradability and low cost. This research work synthesized bioplastic from corn starch using sorbitol/glycerol as plasticizers with chitosan to improve on the elongation, flexibility, rigidity and tensile strength of the plastic. The result showed that bioplastic synthesized using sorbitol/glycerol/chitosan/corn starch blend was transparent, flexible, rigid with tensile strength (16.75 MPa) and Young modulus (356 MPa) followed by sorbitol/chitosan/corn starch blend bioplastic with tensile strength (13.12 MPa) and Young Modulus (257 MPa) and the least properties from bioplastic synthesized with glycerol/chitosan/corn starch blend. These improved properties in sorbitol/glycerol/chitosan/corn starch bioplastic are attributed to the synergy between the sorbitol/glycerol blend which penetrated the starch/chitosan structure forming bonds that improved the rigidity and tensile strength of the bioplastic. SEM images corroborated this result and showed no fractures in the bioplastic with minimal rough surfaces attributed to starch not completely homogeneous. Bioplastic from glycerol/chitosan/corn starch had cracks due to the inability of glycerol to bond effectively chitosan/starch mixture at 20% concentration. Bioplastic from sorbitol/chitosan/corn starch blend had no cracks with smooth surface which is attributed to the ability of sorbitol to penetrate chitosan/starch structures effectively. FTIR analysis showed the bioplastics had the same type of functional groups with similar identical characteristics. Hydroxyl functional group (OH) was found at high absorption peaks of 3272.6 cm^{-1} , 3276.3 cm^{-1} and 3272.6 cm^{-1} for the respective bioplastics. The widening of the OH groups indicate hydrogen bond formed between the blends Also peaks at 1636.3 cm^{-1} , 1636.3 cm^{-1} , 1640.0 cm^{-1} respectively indicated the presence of N-H bond from chitosan in the blends.

Keywords—Bioplastic; Corn starch; Chitosan; Sorbitol; Glycerol; Fourier transform infrared spectrophotometry (FTIR); Scanning electron microscopy (SEM).

1. INTRODUCTION

Increase in population and industrial development around the world has given rise to the wide spread use of petroleum-based plastics in homes, industries, medical, cosmetics etc. due to their ease-of-use, affordability and available. This wide application of petroleum-based plastics has in turn resulted to serious hazards and environmental pollution affecting humans, plants and aquatic lives due to the non-biodegradability of the plastics and the emission of poisonous gases from the plastics when burnt [1-2]. This has made researchers to look for alternative replacement for petroleum-based plastic such as bioplastics which are biodegradable, environmentally friendly and cheap.

Bioplastics are plastic derived from starchy or polysaccharide materials such as yam, cassava, corn, rice, potato, sorghum, wheat, cellulose etc. which are renewable resources and are biodegradable. Research have shown that bioplastics and biofoams from starch-based materials have limitations due to starch low shear resistance, hydrophobicity, thermal decomposition, thermal resistance, and high starch retrogradation tendencies which in turn limits its wide applications [3]. Starch based bioplastics are known to be rigid, brittle and fragile [4] which has led to their modification

to improve on their properties and mechanical strength so as to reduce the dependance on petroleum-based plastics.

To enhance the performance of bioplastics, researchers have explored the incorporation of various additives. Additives such as biodegradable polymer/starch combination, sorbitol/starch, glycerol/starch combinations, fiber/starch have been incorporated in the synthesis of bioplastics with different properties [5-7], [4], [8]. This research paper looks at the synthesis of bioplastic using corn starch and blend of chitosan, sorbitol, and glycerol as additives to enhance the flexibility mechanical strength, and water resistance of the corn starch-based bioplastics.

Chitosan is a biopolymer derived from chitin and is known for its excellent film-forming properties and has been widely used as a non-toxic, biodegradable and biocompatible material [9-10]. It possesses antimicrobial and antioxidant properties, which can help enhance the shelf life of products packaged with bioplastics [11].

Sorbitol and glycerol are both sugar alcohols called polyols and are often used to enhance the flexibility and reduce the brittleness of bioplastics as plasticizers because of the presences of hydroxyl groups in their structures, and plasticizers generally in starch-based blend bioplastics are known to weaken the film thickness of the blend [4]. These additives can also enhance the moisture barrier properties of

the material. By combining these additive blends in specific ratios with corn starch, can optimize the properties of corn starch-based bioplastics.

2. MATERIALS AND EQUIPMENT

The following materials and equipment were used for this research; De-acetylated Chitosan, Sorbitol, Glycerol, Acetic Acid, Distilled Water, Corn starch, Electric heater, Mass balance, oven, Tensile tester machine, Scanning Electron Microscopy, Fourier transform infrared spectrophotometry, Hot Plate, Beaker, Stirrer, Petri dish, and Grinder.

2.1 Extraction of corn starch

Corn kernels were taken from fresh corn cobs, washed with clear water and was soaked in water for 1-2 hours until soft. The soaked Corn were removed from the water and put into a grinder for grinding. The corn was grounded with equal proportion of water in batches to produce more starch. The grounded corn mixture was then sieved into a bowl twice to obtain fine corn particles.

The particle was then place in a water and the starch/water solution allowed to rest for 1-2 hours to let the starch separate from the water after which the water was decanted leaving thick starch at the bottom of the bowl. Starch sediment obtained was spread on broad Petri dish thinly and allowed to dry using oven. The dried starch was then grounded using a mix grinder to get fine powdered corn starch.

2.2 Synthesis of the bioplastic

The bioplastic was prepared by following similar procedure adopted by Utami and co-researchers [5] with modification. Starch was measured (60 grams) and dissolved in distilled water (50 ml) while stirring vigorously with heat for the starch to dissolve. 40 grams of chitosan was dissolved in 1 % acetic acid (5ml) and transferred to the starch solution. The starch/chitosan solution was mixed thoroughly followed by the addition of 20% sorbitol and 20% glycerol solution and the total mixture volume made up to 100 ml by the addition of distilled water in a ratio. The 20% sorbitol and 20% glycerol solution were prepared by dissolving 20 grams sorbitol in 5 ml distilled water and mixing it with 20 ml glycerol solution and stirred thoroughly before transferring to starch chitosan mixture and the total mixture volume increased to 100 ml. The mixture was heated on a hot plate at 75°C for 30 minutes until gelatinization while stirring vigorously. After heating, the mixture was poured on a plate and allowed to cool before drying in an oven at 70°C before storing the synthesized bioplastic in a dry place.

This process was repeated with only sorbitol as the plasticizer (20% sorbitol, 60% corn starch and 40% chitosan blend) and also repeated for glycerol as plasticizer (20% glycerol, 60% corn starch and 40% chitosan blend) respectively.

3. RESULT AND DISCUSSION

Fig. 1a, 1b and 1c shows the bioplastics synthesized from chitosan/glycerol/corn starch, chitosan/sorbitol/corn starch, and chitosan/sorbitol/glycerol/corn starch blends respectively. They are colourless, transparent, odourless and tasteless which corresponds to the physical characteristic of starch-based bioplastics. Fig. 1a showed that the bioplastic synthesized using glycerol as plasticizer in the chitosan/glycerol/corn starch blend, showed that the bioplastic is brittle, fragile with the presence of granules and bubbles. The granules and bubbles maybe as a result of the starch not completely gelatinized during synthesis and the brittle nature and fragility of the bioplastic is as a result of the inability of 20 % glycerol to act as a good plasticizer in the glycerol/chitosan/starch blend. This in turn results to the poor elongation and elasticity of the bioplastic as shown by the tearing of the bioplastic when stretched.

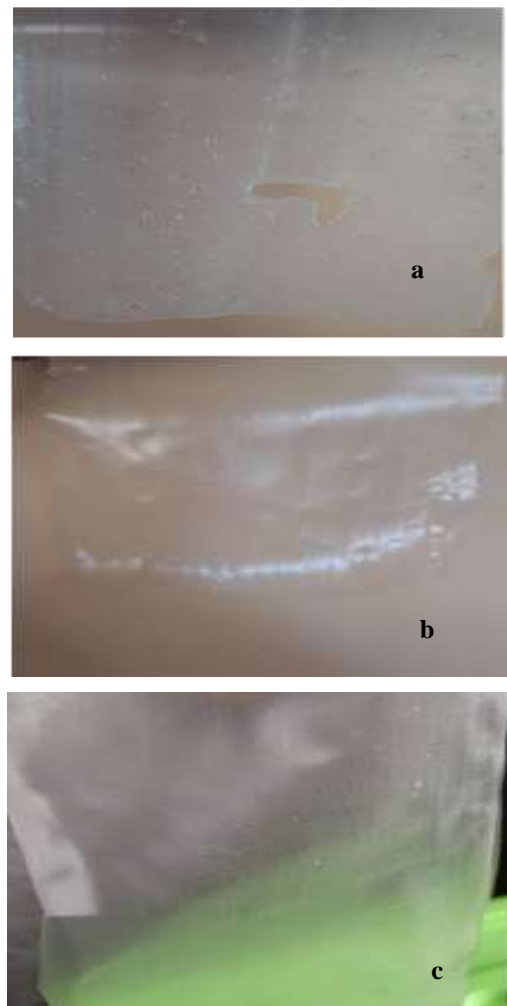


Fig. 1. Chitosan/glycerol/cornstarch blend bioplastic (a), Chitosan/sorbitol/cornstarch blend bioplastic (b) and Chitosan/sorbitol/glycerol/cornstarch blend bioplastic (c)

Fig. 1b showed the bioplastic formed from the blend of chitosan/sorbitol/cornstarch. From the figure, it can be seen

that the bioplastic is flexible, transparent with no granules. This showed that sorbitol was able to penetrate the starch intramolecular and intermolecular space with chitosan due to the presence of six hydroxyl bond in its structure. This in turn improve the bioplastic properties compared to Fig. 1a with glycerol which had three hydroxyl groups in its structure [8], [12]. Research have shown that the transparency of the sorbitol treated bioplastic increases as the concentration of sorbitol increases [4].

Fig. 1c shows the bioplastic synthesized using chitosan/sorbitol/glycerol/cornstarch blend. The figure shows that the bioplastic is flexible, transparent, more rigid with good tensile strength compared to Fig. 1a and 1b. Chitosan in the bioplastic formation is known to reduce the elongation and elasticity of the bioplastic but improves the rigidity and tensile strength [6]. Thus, the addition of sorbitol and glycerol mixture as plasticizers, is to improve on the elongation and elasticity of the bioplastic in the presence of chitosan. Fig. 1c showed that the combination of sorbitol and glycerol greatly improved the transparency, elasticity and elongation of the bioplastic. These results are corroborated with SEM images shown in Fig. 2.

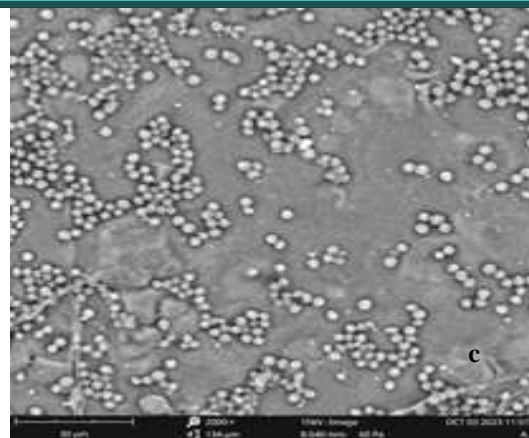
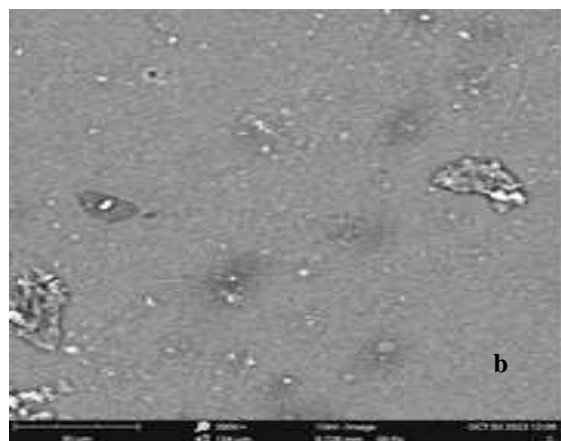
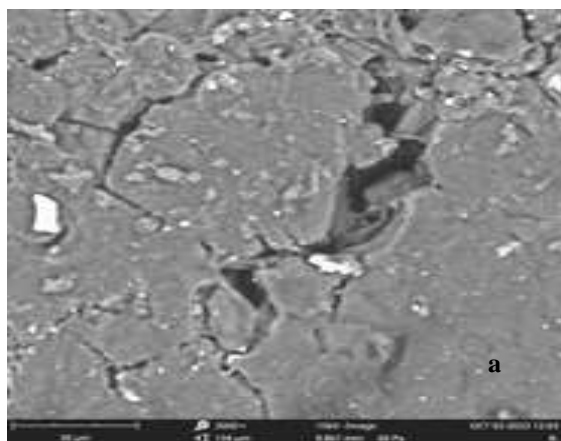


Fig. 2 SEM image of Corn starch bioplastic with (a) glycerol and chitosan (b) sorbitol and chitosan(c) glycerol, sorbitol and chitosan blend

Fig. 2a shows SEM image of the bioplastic synthesized from chitosan-glycerol-cornstarch blend. In the figure it can be seen that there are cracks in the surface morphology of the bioplastic. The cracks in the bioplastic are due to the presence of chitosan which makes the bioplastics less elastic when exposed to excessive pressure or friction from outside and the inability of the glycerol to completely solubilize the starch granules.

Fig. 2b shows the SEM of bioplastics synthesized using chitosan-sorbitol-cornstarch blend. The figure showed that the surface of the bioplastic is smooth with no cracks. This is due to the ability of sorbitol to increase the film elongation in the blend with low tensile strength thus minimizing the less elastic effect of chitosan in the blend. Sorbitol in the figure 2b also bonded very well with the starch due to the presence of its six hydroxyl groups that easily penetrates cell membrane compared to glycerol with three hydroxyl group in Fig. 2 a. The presence of few lumps in the SEM images might be attributed to starch in the sample not completely homogeneous.

Fig. 2 c shows the surface morphology of chitosan-sorbitol-glycerol-cornstarch blend synthesized bioplastic. The figure showed starch granules on the surface of the plastic, indicating incomplete starch gelatinization during the formation process. Researchers have reported that this is as a result of insoluble starch remnants due to the swelling of starch granule [13]. There are no fractures in the bioplastic formed in Fig. 2c which showed that the combination of glycerol and sorbitol bonded the starch chitosan structure in the bioplastic very well. Although there are some rough surfaces on the bioplastic which might be attributed to starch in the sample not completely homogeneous.

Fig. 3, 4 and 5 shows the FTIR spectrum for the synthesized bioplastics using chitosan-sorbitol-glycerol-cornstarch, chitosan-glycerol-cornstarch, and chitosan-sorbitol-cornstarch blends respectively. The FTIR spectrum in Fig. 3, 4 and 5 showed similar identical characteristics which

indicates that the process for the bioplastic production was well carried out and they had the same type of function group. In Fig. 3, 4 and 5, hydroxyl functional group (OH) was found at high absorption peaks of 3272.6 cm^{-1} , 3276.3 cm^{-1} and 3272.6 cm^{-1} respectively. The widening of the OH groups indicates that hydrogen bond was formed between starch,

sorbitol, glycerol and chitosan in Fig. 3, chitosan-glycerol-cornstarch in Fig. 4 and chitosan-sorbitol-cornstarch in Fig. 5 respectively. The OH group also indicates the presence of sorbitol and glycerol which are both polyol with hydroxyl groups in their chain in the respective bioplastic formed [8], [12].

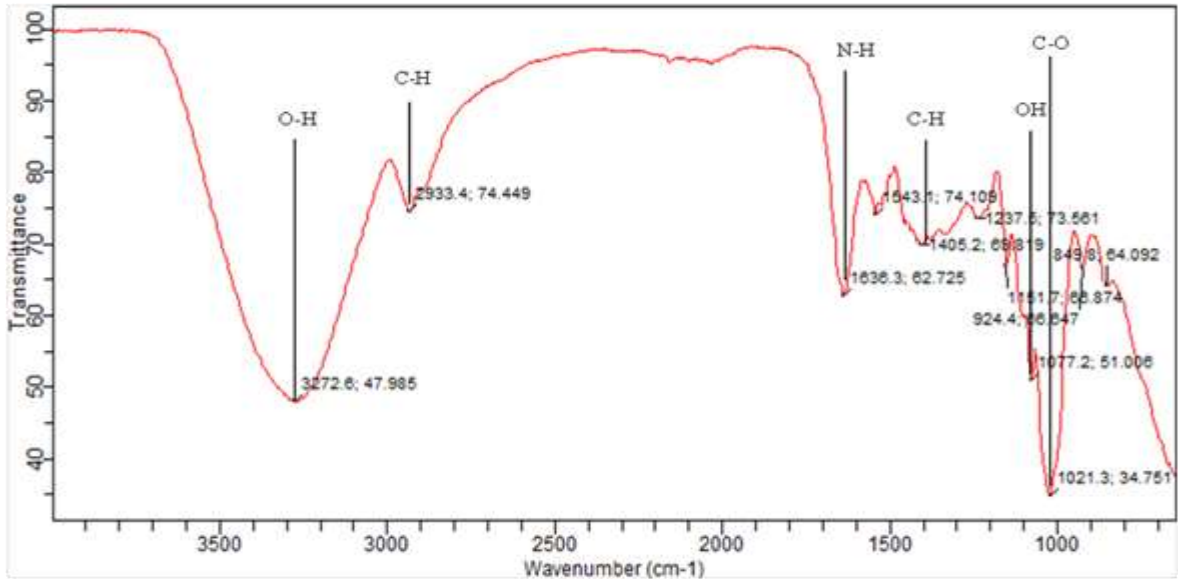


Fig. 3. FTIR spectrum for chitosan-sorbitol-glycerol-cornstarch bioplastic

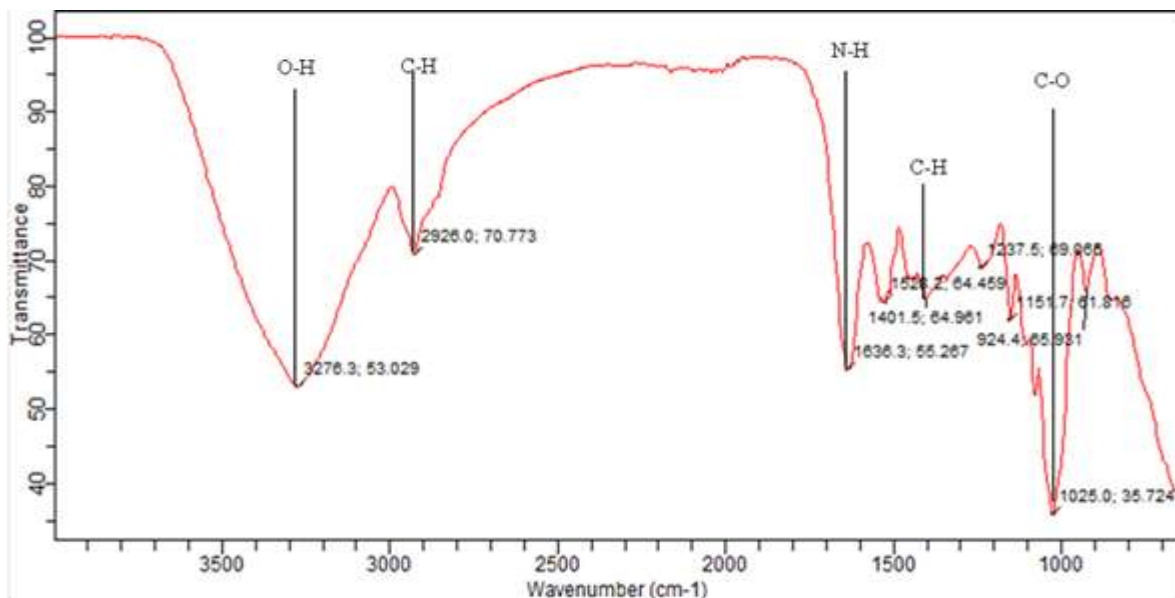


Fig. 4. FTIR spectrum for chitosan-glycerol-cornstarch bioplastic

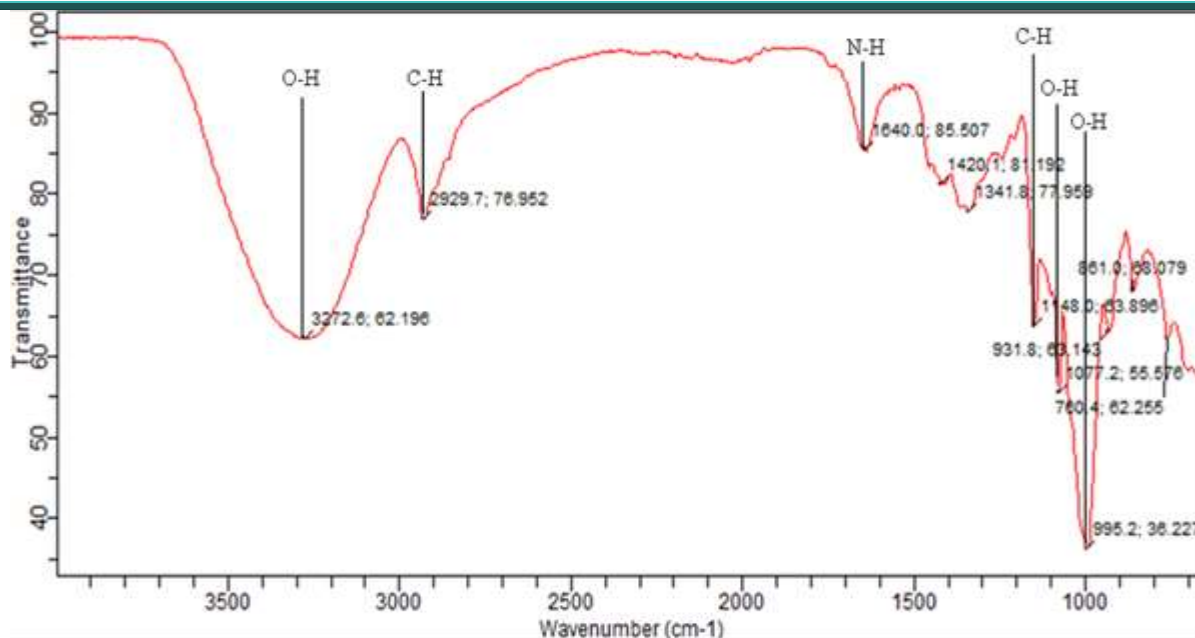


Fig. 5. FTIR spectrum for chitosan-sorbitol-cornstarch bioplastic

The peak at 1636.3 cm^{-1} in Fig. 3, 1636.3 cm^{-1} in Fig. 4 and 1640.0 cm^{-1} in Fig. 5 indicates the presence of primary amine group (N-H group) from chitosan. The peak at 2926.0 cm^{-1} in Fig. 3, same wave band in Fig. 4 and 2929.7 cm^{-1} in Fig. 5, showed the stretching of C-H carbon chain group indicating glycosidic bond in starch that joins two carbohydrate bonds. And the sharp absorption at wave band 1025.0 cm^{-1} indicates the C-O vibration in glycerol [9]. In Fig. 5, the wave band at 995.2 cm^{-1} and 1077.2 cm^{-1} correspond to sorbitol OH bonds.

The tensile strength (σ) of the bioplastics were measured using a tensile tester machine where bioplastic film of dimension 7 cm by 2cm was cut, attached and stretched to break off point with the corresponding applied force shown on the machine screen. The result showed that bioplastic film synthesized with Corn starch/chitosan/sorbitol/glycerol blend had tensile strength (16.75 MPa) and Young Modulus (E) (356 MPa) followed by Corn starch/chitosan/sorbitol blend with tensile strength (13.12 MPa) and young modulus (257 MPa). The increase in tensile strength of the Corn starch/chitosan/sorbitol/glycerol blend bioplastic is due to the synergy of the sorbitol/glycerol mixture with chitosan. Sorbitol is known for its larger and higher molecular length and molecular weight respectively and create more entanglement with starch/chitosan chains with glycerol, resulting in the increase in Young modulus and tensile strength of Corn starch/chitosan/sorbitol/glycerol blend and Corn starch/chitosan/sorbitol/blend compared to the reduced tensile strength of 10.68 MPa recorded for Corn starch/chitosan/glycerol blend bioplastic. This reduced tensile value can be attributed to poor plasticizing ability of glycerol (20%) and the smaller and lower molecular length and molecular weight of glycerol compared to sorbitol. The tensile

strength and Young Modulus are calculated using equation 1 and 2 respectively.

$$\sigma = \frac{F}{A} \quad 1$$

$$E = \frac{\sigma}{\epsilon} \quad 2$$

Where F, represent applied force, A, is the area of the bioplastic film, and ϵ , the film elongation.

4. CONCLUSION

In conclusion, the use of sorbitol and glycerin blend as plasticizers with chitosan in the synthesis of bioplastic from corn starch (Chitosan/sorbitol/glycerol/cornstarch) improved, flexibility, elongation, tensile strength, and rigidity of the bioplastic compared to using sorbitol or glycerol separately as plasticizers. This is due to the synergy of the six-hydroxyl group in sorbitol combined with the three-hydroxyl group in glycerin that penetrated effectively the chitosan/corn starch mixture to form bonds that improved the bioplastic properties. Sorbitol as plasticizer alone with chitosan and corn starch (Chitosan/sorbitol/cornstarch) produced bioplastic that is transparent, flexible, less rigid with less tensile strength but higher compared to using only glycerol as plasticizer. The SEM images and FTIR spectrum corroborated these findings. The SEM images showed smooth surfaces with no cracks with few ungelatinized starch granules on the surfaces of chitosan/sorbitol/glycerol/cornstarch blend bioplastic, smooth surfaces on chitosan/sorbitol/cornstarch blend bioplastics and cracked surfaces on chitosan/glycerol/cornstarch blend

bioplastic. The FTIR spectrum showed similar functional groups in the bioplastics formed.

5. REFERENCES

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