Influence of Glycerol Contents on The Morphological (SEM) and Functional (FTIR) Properties of Corn-based Bioplastic

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Abstract. Plastic that made form starch has gain a lot of attraction in research to replace traditional plastic. Starch offers a great deal which is hard to resist such as renewable resource, inexpensive and eco-friendly raw material. However, due to unfavorable properties such as brittleness, poor mechanical properties, and lack water barrier, starch-based bioplastic have a limited range of applications. To produce better corn-based bioplastic properties, concentration of glycerol needs to be optimized. This work focuses on the effect of different concentration of glycerol (20%, 30%, 40% w/v of corn starch) on the morphological (SEM) and functional (FTIR) properties of corn-based bioplastic film prepared by solvent casting method were investigated. Interactions between corn starch and glycerol occur between C–O and OH groups, indicating the presence of mainly hydrogen bonds. Morphology properties for all film sample presented a smooth surface without pores and cracks with compact structures. This work shows that glycerol can affect the morphological and functional properties of corn-based bioplastics.

Keywords: Corn, Bioplastic, Glycerol, SEM, FTIR

I. INTRODUCTION

In recent years, there has been a lot of focus on the development of biodegradable polymers made from renewable resources, especially for packaging and disposable applications, in order to maintain the long-term development of economically and environmentally appealing technology that leads to a greener environment. Starch is one of the most promising biopolymers because of its wide availability, low cost, renewable resources, and biodegradability [1].

Polysaccharide is mostly obtained from native starch in plants. Many studies have previously focused on corn, wheat, and potato starches. According to [2], corn starch has also been employed as a source of environmentally friendly and sustainable raw material. Compared to potato-based bioplastic and rice-based bioplastic, corn-based bioplastic expected to have a better film property [3], [4]. This is because films with a higher amylose content often have better film properties such as tensile strength, elongation at break, and gas barrier properties. Corn starch typically contains 24.8 % of amylose, meanwhile the potato and rice starch both contain 20.5 % and 16.9 % of amylose respectively. On the other hand, unmodified starch-based bioplastic has poor mechanical and barrier properties.

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Plasticizers must be added to the film matrix to prevent film pore and crack formation, which causes brittleness. Films without plasticizer possess high tensile strength and low flexibility [5]. The most commonly used secondary plasticizer agent is glycerol. However, to produce corn-based bioplastic with adequate properties, the concentration of glycerol needs to be optimized.

This work focuses on the effect of different concentration of glycerol (20%, 30%, 40% w/v of corn starch) on the morphological (SEM) and functional (FTIR) properties of corn-based bioplastic film.

II. MATERIAL & METHOD

Materials used in this work were corn starch, glycerol as a plasticizer, acetic acid with 5% acidity and distilled water. Glycerol supplied by the HmbG chemicals with 99.9 % of purity.

Preparation of Corn-based Bioplastic Films

The film (corn-based bioplastic) solution was prepared by mixing 100 ml of distilled water and (10% of distilled water) corn starch. Then, the glycerol (20%, 30% and 40% w/v of starch) was added as a plasticizer and lastly, 5ml of acetic acid (5% w/w) was poured into the solution. The film solution was heated to 75℃ under constant stirring using a magnetic stirrer to obtain starch gelatinization and continue to stir manually until the solution becomes viscous and transparent. After that, the solution was poured into the petri dish, which acts as a casting plate and dried in the air-conditioned room (25±1℃) for 72 hours on the flat surface (to ensure the film thickness was consistent). The drying process was using a solvent casting method. After the film sample dried, the film was stored in desiccator prior to analysis. FIGURE 1 show the illustration process of making the corn-based bioplastic film.

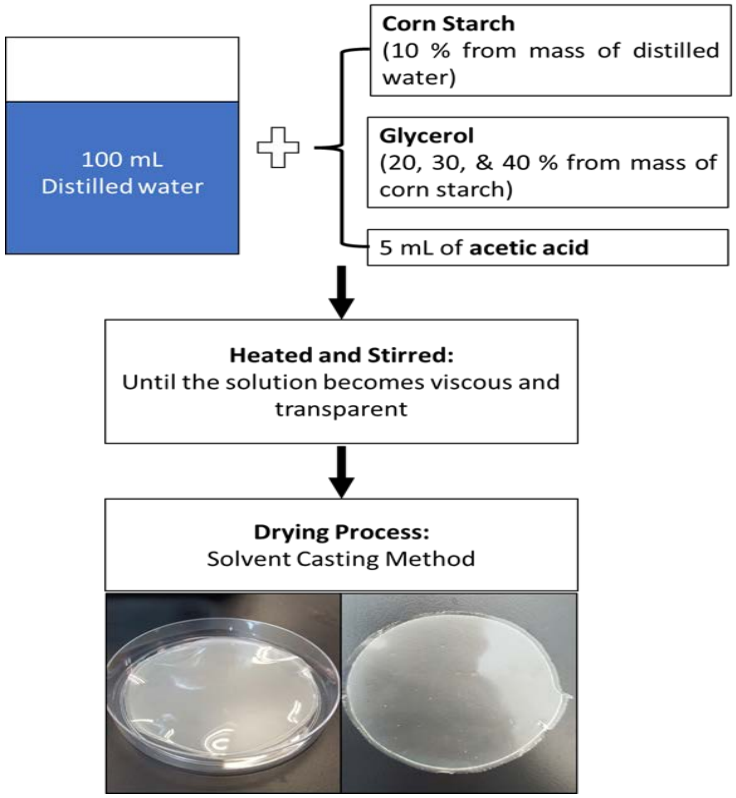

FIGURE 1. Process of making the corn-based bioplastic film.

Analysis: Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR test was performed by an infrared spectrometer (Bruker vector 22). The spectral frequency range was set between 4000 and 400 cm^{-1} over a spectral resolution of 4 cm^{-1}.

Analysis: Scanning Electron Microscopy (SEM)

An instrument type COXEM EM-30AX was used to investigate the surface morphological structure of samples. High-resolution images at different magnification factors resulted from this test.

III. RESULT & DISCUSSION

Fourier Transform Infrared Spectroscopy (FT-IR)

All films spectra show a peak at 3272-3283 cm^{-1} (O-H stretching), 2929-2935 cm^{-1} (C-H stretch), 1644 cm-1 (O-H bending from water), 1104-1106 cm^{-1} (C-H belong to glycerol), 1078-1076 cm^{-1} (C-O bond stretching) and 1000-1018 cm^{-1} (C-O stretch). When the concentration of glycerol was increased, the OH stretch peak were shifted to higher wavenumber (3272>3273>3283) indicating the weakening of hydrogen bonds between starch molecules due to the formation of hydrogen bond between some of starch molecules with glycerol. A lower wavenumber resulted a stronger interaction of hydrogen bond. The peak 1078 cm^{-1} (20% and 30% of glycerol) was shifted to 1076 cm^{-1} (40% of glycerol) which means that there was hydrogen bond formation involved due to the OH group of starch. The C-O stretch peaks were shifted from 1016 cm^{-1} to 1000 cm^{-1} show that glycerol could from a more stable hydrogen bond. These results have previously been observed by Zuraida et al. [6] and Ewelina et. al [7]. When the concentration of glycerol was increased, the intensity of spectrum decreased. This observation also indicated that the mobility of the proton in starch chain was progressively restricted. This due to hydrogen bonding interactions occurring between corn starch-glycerol films. Akbar et al. observed the same tendency, the shift in peak intensity was linked to changes in conformations such as crystallinity and long-range ordering, which resulted in polymer disordering and an increase in the number of conformations [8].

The hydrogen bond is the most critical intermolecular interaction that determines the characteristics of starch-based films [9]. Compared to the control films (without glycerol), when glycerol was added to the films, the O–H stretching peak decreased from 3294 cm^{-1} to 3272 cm^{-1}. This is due to the formation of more strong and stable hydrogen bonds between glycerol and corn starch, compared to the intramolecular and intermolecular of hydrogen bonds in starch films that just contain water as plasticizer [6]. FTIR analysis further demonstrated that adding glycerol to films has no substantial impact on the chemical structure of corn-based bioplastic films. This showed that the molecular frames of the resulting corn-based films were totally stable, with no significant chemical changes occurring as a result of the addition of the glycerol.

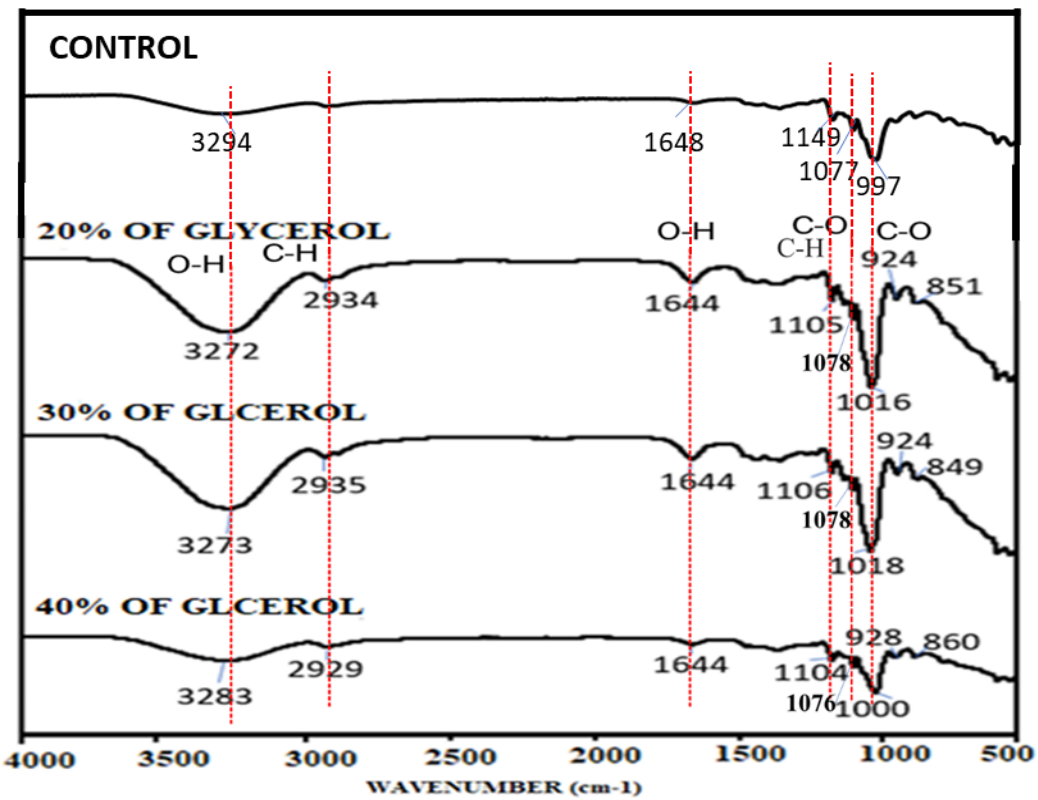

FIGURE 2. FTIR spectra for all film sample.

Scanning Electron Microscopy (SEM)

As can be seen, the more glycerol in the corn-based bioplastic mixture, the smoother the films were. For 30% & 40% of glycerol films showed smooth surfaces without pores or crack, meanwhile for 20% of glycerol films surface were quite coarse due to domination of corn starch, in interaction of starch-glycerol in the matrix. The homogeneous structure of films was a good indicator of structural and mechanical properties [7]. Similar result obtained by Ewelina et. al, at higher concentration of plasticizer (33% and 50% glycerol), the wheat-based film surfaces become smoother [7]. Based on Basiak et al., when the concentration of glycerol increases resulting film with more homogenous surface because of a higher interfacial adhesion between the starch and glycerol [9]. When glycerol is added to a film, the microstructural arrangement of starch chains changes, and the film becomes less dense. However, according to Xie et al., a higher glycerol concentration (70%) could result in a more visible granular morphology in maize films [10].

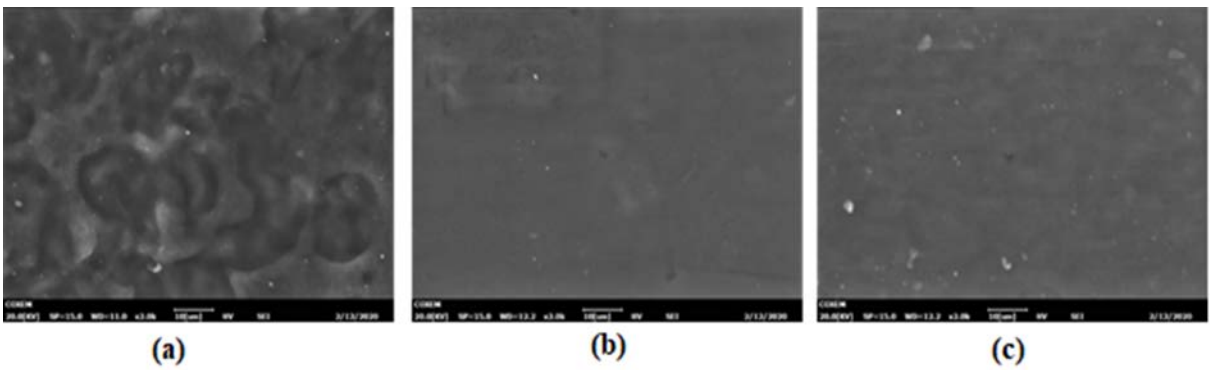

FIGURE 3. SEM: (a) film with 20% of glycerol (b) film with 30% of glycerol and (c) film with 40% of glycerol.

IV. CONCLUSION

The effect of glycerol contents on the morphological and functional properties of corn-based bioplastic films was studied. When the concentration of glycerol increases, the corn-based bioplastic film inhibits a smoother surface. Meanwhile for FTIR result, when the concentration of glycerol was increased, the intensity of FTIR spectrum were decreased and the peak were shifted to higher wavenumber indicating the weakening of hydrogen bonds between starch molecules due to the formation of hydrogen bond between some of starch molecules with glycerol. In conclusion, properties of corn-based bioplastic are depending on concentration of glycerol. Altering the glycerol content allows an increase or reduction of morphological and functional parameters. This work shows how glycerol can affect the morphological & functional properties of corn-based bioplastic films.

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