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The Effects of Glycerol Addition on Mechanical Properties of Thermoplastic Films Based on Mango Seed Starch

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Abstract:

The aimed of the present work is to examine the effects of glycerol as plasticizer incorporated with mango seed starch. The fabrication of films involved mixing between the fixed amount of mango seed starch (3 wt. %) with various amount of glycerol ranges from 5 to 30 wt. % through solution casting method. From the analysis, the tensile strength of films decreases with increasing glycerol content from 5 to 30 wt. %. This can be correlated to the presence of free volume or voids in the films as indicated by scanning electron microscope. Contrarily, the films' elongation at break increases with increasing glycerol content from 5 to 25 wt. %. The findings are corroborated with the Fourier transform infrared spectra, in which the hydrogen bond formation was observed. However, the elongation of film is significantly reduced when glycerol content increased from 25 to 30 wt. % due to the anti-plasticization phenomenon by highly plasticized starch. Therefore, the variance of glycerol content in mango seed starch demonstrates a significant effect on the mechanical properties of fabricated films.

Keywords: *Mango seeds, thermoplastic starch, films*

I. INTRODUCTION

The development of thermoplastic films based on natural resources like polysaccharide (e.g. starch) has been extensively grab the attention of many researchers during the past years [1]. This is mainly due to the properties of these developed films which are environmentally friendly and a promising alternative for biodegradable plastic packaging in wide applications such as food and pharmaceuticals [2], [3]. Currently, approaches on utilizing starch such as corn, rice, potato, and wheat to develop the thermoplastic films has been attempted [4]. Interestingly, starch from waste like fruit seeds also can be utilized as raw material to develop the film [5], [6]. Therefore, this study utilized the mango *(Mangifera indica)* seeds as source of starch to develop the film.

Generally, mango fruits are grown all over tropical and sub-tropical regions of the world including Malaysia, India, and Thailand. Normally, in Malaysia, the mango seeds are wastes after the fruits are eaten or being processed to juice etc. In fact, this type of agricultural waste could be exploited as value-added products due to the availability and be a reliable source of starch. According to Shahrim et al. [7], these seeds have a high starch content (74% – 91%), hence, a promising alternative source of starch. However, this starch is in form of a native starch, thus, cannot form the thermoplastic film [8]. Thus, incorporating starch with plasticizer like glycerol via gelatinization process is expected to develop film that exhibits good mechanical properties comparable to the conventional plastic [9]. Having said that, this study specified the utilization of inner part of mango seeds, since, different parts would result in different properties compare to the one reported by Nawab et al. [10]. For that reason, the present work aims to fabricate glycerol-plasticized mango seed starch (GTPS) film through solution casting method and to evaluate the effect of glycerol content on the mechanical, morphological, and functional properties of mango seed starch film.

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II. MATERIALS & METHODS

Mango seeds were prepared and extracted to starch via distillation method as described by Shahrim et al. [7]. The fabrication of GTPS was done via solution casting method as reported by Shahrim et al. [6] with a slight modification. The total mass of the system is 100 g, consists of fixed starch content at 3 wt.% and varied glycerol content from 5 to 30 wt.%. The materials' abbreviations and corresponding sample compositions are listed in Table 1. The starch, glycerol and distilled water were mixed and heated up to 85 ± 5 °C on a hot plate and held at that temperature for 20 minutes. At the same time, the solution was stirred continuously at 250 rpm. Then, the solution was cooled to 65 °C, casted on acrylic plates and dried for 24 hours in the oven. Afterward, the fabricated film was peeled from the plates and stored in the desiccator maintained at 23 °C and 30% relative humidity preceding to characterization.

Table I. Used symbols and corresponding compositions of each sample

Materials	Abbreviations	Samples (weight proportions, gram)		
		Starch	Glycerol	Distilled Water
GTPS1	G5	3.0	0.5	96.5
GTPS2	G10	3.0	1.0	96.0
GTPS3	G15	3.0	1.5	95.5
GTPS4	G20	3.0	2.0	95.0
GTPS5	G25	3.0	2.5	94.5
GTPS6	G30	3.0	3.0	94.0

The mechanical properties of the films were measured according to ASTM standard D882-02 with a MTS tensile tester (Shimadzu; Material Testing System). Five samples with a dimension of 70 mm x 10 mm were prepared according to standard ISO–527. The tensile test was carried out with 5 kN of load and 20 mm/min of speed. Furthermore, the morphological properties of the films' surfaces measured at 10 mm × 10 mm were observed on the Scanning Electron Microscope (JEOL, JSM-IT 100; Japan) operated at an acceleration voltage of 10 kV with 500X magnification. Moreover, the functional properties of the thermoplastic starch films were analyzed in Fourier-Transformed Infrared spectroscopy (Spectrum 100, Perkin Elmer; USA). The analysis was done in the range of 4000 cm^{-1} – 600 cm^{-1} with a resolution of 8 cm^{-1} and a scanning frequency of 32 per sample.

III. RESULTS & DISCUSSION

The glycerol addition in the mango seed starch has substantial effect on the tensile strength (TS) and elongation at break (E%) of the films as can be seen in Fig. 1 and Fig. 2.

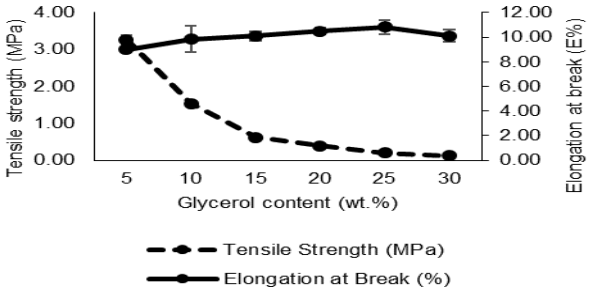

Fig. 1. Effect of increasing glycerol content on the tensile properties of starch films

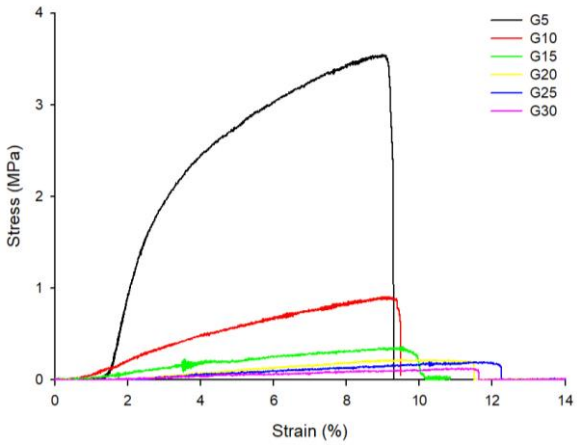

Fig. 2. Effect of increasing the glycerol content on stress-strain curve of starch films

It is noted that, below 5 wt. % glycerol content, the starch film was found to be brittle, thus, it was ignored. The incorporation of 5 wt. % glycerol content in mango seed starch films demonstrate the highest tensile strength value of 3.26 MPa. This could be explained by the formation of stronger hydrogen bonds between starch–starch intermolecular interaction compare to starch–plasticizer attraction [11]. Further addition of glycerol content from 10 wt. % to 30 wt. % significantly decreased the tensile strength of the films from 1.53 to 0.12 MPa. The decrement of tensile strength at higher glycerol content might be correlated to the presence of free volume or voids in the films [12], as evidenced under SEM (Fig. 3). However, the highest tensile strength values obtained in this study were found to be lower than jackfruit seed starch with glycerol (4.40 MPa) [6], durian seed starch with glycerol (2.94 MPa) [13], and mango

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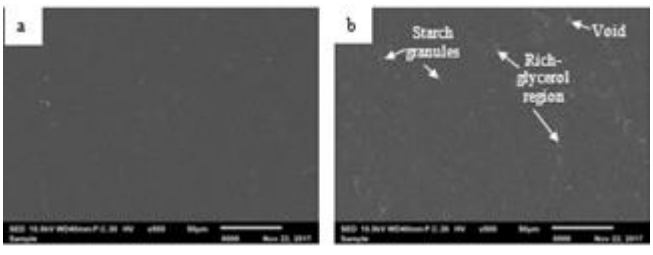
kernel starch with glycerol (3.57 MPa) [10], but higher than cassava starch with glycerol (1.07 MPa) [14]. The difference in tensile strength of starch films could be associated to the structure of extracted starch, which the starch chains are arranged in a specific pattern and attractive forces between the chains provide the cohesiveness that affect the strength of polymer [10].

In contrast, the elongation at break (E%) of the films showed an inverse behavior compared to their corresponding TS. As predicted, the increase of glycerol content from 5 wt. % to 25 wt. % conveyed significant improvement in mango seed starch film elongation: 8.99% – 10.82%. The increment in film elongation is because the boost in mobility of starch molecular chains with increasing glycerol content by assisting the slipping of molecules between the chains, decreases the rigidity of film, thus promotes the flexibility of films [15]. In fact, flexibility and elasticity of the films are vital factors that are contemplated during the application of the polymeric films, especially for packaging [16]. The FT-IR spectra further justified the formation of hydrogen bonds between plasticizer and starch molecules in the starch films, deteriorated the strong interaction of starch intermolecular and intramolecular hydrogen bonds, consequently made the starch film flexible. Similar tensile strength and elongation behavior of the film has been testified by previous researchers [9,10,14,15]. However, the elongation of film is significantly reduced from 10.82% to 10.12% when glycerol content increased from the 25 wt. % to 30 wt. %. This could be described by the anti-plasticization phenomenon in highly plasticized starch. During this phenomenon, the plasticizer concentration exceeds its compatibility limits, hence, the phase separation of starch films occurs. This is associated to the formation of starch-rich and glycerol-rich regions caused by the glycerol movement from starch matrix, facilitates the intermolecular interaction between starch molecules once more, thus decrease the elongation of the films [11].

Furthermore, the tensile failure stress-strain curves in Fig. 2 illustrates the improvement of films' ductility with increasing glycerol content. This was exhibited by the reduced tensile strength and enhanced flexibility by means of increase in glycerol content from 5% to 25%. G5 showed high stress with low strain, hence, was contemplated brittle. Further addition of glycerol content improved the ductility of G25 film, which is shown by its substantial deformation before fracture. Similar to the Fig. 1, the stress-strain curve in Fig. 2 for G30 film showed reduction of the flexibility by the low strain compared to G25. Overall, the tensile strength value obtained by mango seed starch films is in the range of typical strength of casted starch films (<5 MPa) [18], thus, the mango seed starch could be utilized in developing a thermoplastic film.

The surface morphologies effects of glycerol incorporated in mango seed starch films are depicted in SEM micrographs (Fig. 3). Micrograph of film surfaces revealed significant difference among glycerol-plasticized mango seed starch films. Fig. 3(a) revealed the surface of film with 5 wt. % glycerol content is clear and smooth without gross defects. This denoted that, the starch molecules are well-dispersed since not many granules were exposed in low glycerol content. Thus, the result indicates the structural integrity of the observed film. This result is consistent with Dai [19] who observed the smoothness of film surface improved with the addition of glycerol in corn starch films. Further addition of more than 5 wt. % glycerol content revealed rougher surface and phase separation between starch and glycerol in the films were clearly spotted as depicted in Fig. 3(b) – 3(f). Traces of oval or cuboidal like shapes of mango seed starch granules were still noticeable in the SEM, showed by arrows in the micrographs. Similar observations have been reported by Coniwanti et al. [20] on corn starch with glycerol films, in which the hydrophilicity nature of glycerol contributed to the occurrence of glycerol-rich regions on surface films with increasing glycerol concentration. Hence, the film with 5 wt. % glycerol had higher strength and lower elongation compared to the blend with 30 wt. % glycerol justified the disappearance of voids and cracks. In fact, the SEM observations are fully corroborated with the mechanical properties finding based on tensile test.



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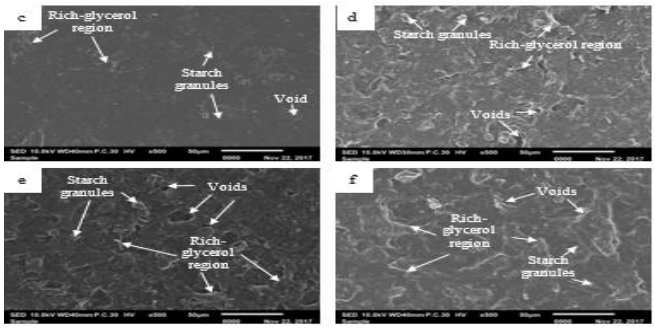

Fig. 3. SEM micrographs at 500× magnification for plasticized mango seed starch films with various glycerol concentrations (a) 5, (b) 10, (c) 15, (d) 20, (e) 25, and (f) 30 wt. %

The FT-IR spectra of the glycerol-plasticized mango seed starch films are shown in Fig. 4. All spectra in Figure 4.24 presented the following characteristic bands: 3270 – 3282 cm^{-1} relates to the stretching of O-H group belonging to starch, glycerol and water, 2924 – 2933 cm^{-1} relates to the C-H stretching because of intermolecular and intramolecular bonds formation between starch and glycerol hydroxyl groups, 1703 – 1705 cm^{-1} relates to the C=O stretching (aldehydes) due to the breaking of glycoside chains on starch, 1611 – 1642 cm^{-1} relates to the bound water related absorbance, and 1150 – 998 cm^{-1} relates to the C-O stretching in starch films. The addition of glycerol more than 5 wt. % to mango seed starch films resulted in displacement of peaks 999.06 cm^{-1}, 1000.30 cm^{-1}, 1021.53 cm^{-1}, 1025.25 cm^{-1} and 1024.90 cm^{-1} for C-O in C-O-C bond, which suggests the oxygen molecules of C-O-C group in starch chain partook in the hydrogen bond with glycerol [21]. These results are corroborated with the flexibility of starch films, as discussed earlier. These observed peaks were similar to the peaks appearance of thermoplastic tapioca starch Kahar et al. [22].

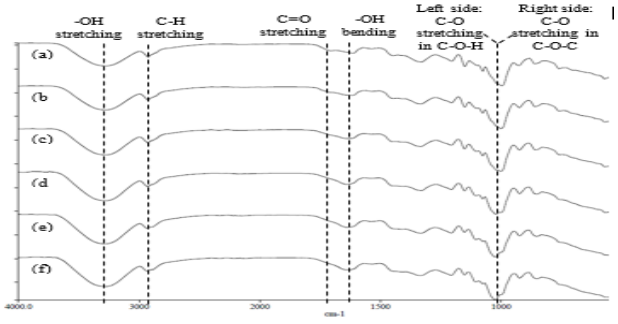

Fig. 4. FT-IR spectra for mango seed starch film with various glycerol content (a) 5, (b) 10, (c) 15, (d) 20, (e) 25 and (f) 30 wt. %

IV. CONCLUSION

In conclusion, significant effects on the mechanical properties of developed glycerol-plasticized mango seed starch films were exhibited when various glycerol concentration was incorporated in starch. The flexibility of films was enhanced when adding more than 5 wt.% glycerol in starch, but consequently reduced the strength. The highest strength, 3.26 MPa, has been achieved with starch film plasticized with 5 wt.% glycerol. Moreover, the film revealed homogeneous structure and formation of hydrogen bond interactions between the starch and glycerol.

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