BIOFILM DERIVE FROM PLANTAIN PEEL: EFFECT OF MECHANICAL PROPERTIES

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ABSTRACT
The effect of modified and non-modified starch as a filler was investigated in this study. The blend of Polyvinyl Alcohol (PVA) and starch was prepared as a film for further analysis. The starch was modified by an acetylation process in which -OH group was substituted in the starch solution. Fourier-transform infrared (FTIR) analysis was used to analyze the presence of functional group of starch acetate. The biodegradable plastic film composed of plantain peel starch and PVA blend was made through solution casting method. The degradable film was produced by compounding the starch with PVA and the use of glycerol as a plasticizer. The blend was spread on the flat glass plate in order to produce the film with even thickness. The casted film is dried in an oven at 90°C for about one hour. The elasticity and strength of the film then was analyzed through tensile test. It was found that the film produced from modified starch has more flexibility and reliability compared to non-modified starch. The highest tensile strength and elongation at break of the film produced was found at 15g of the starch-PVA blend. Meanwhile, the Young’s modulus obtained is concurrent to the tensile strength of produced film.

Keywords: chemical modification, plantain peel, polyvinyl alcohol, tensile properties.

1. INTRODUCTION
Recently, the awareness of environmental issue has renewed great interest in the development of biodegradable materials. These environmentally friendly materials can help in lowering the production of petroleum-based packaging, which has a negative impact on our environment. Biodegradable polymer such as protein and polysaccharide has the potential in producing biodegradable packaging. Starch is known as one type of polysaccharide that is widely employed in film preparation due to its low cost, abundance in nature and also renewable [1]. Thus, as suggested by [2], starch can be an ideal candidate to replace petroleum derivatives which commonly used as the raw materials in producing biodegradable packaging.

Variety types of crops have a great amount of starch. This can be proven by a study conducted by [3] which found that cereals like corn, wheat, rice, oat and barley contain carbohydrates up to 80%, legumes like bean and pea contain up to 50% carbohydrate, 90% contained in tuber like potato and cocoyam and some green or immature fruit like banana and mango contained 70% starch in dry base. Fruits such as banana and mango are considered to be the most important sources of starch since they already form part of the worldwide food system.

The use of starch from different sources has been reported in the preparation of films and coatings with different properties. In [4, 5, 6] for example, used natural starch such as corn, potato and sago starch in preparation of polymer blends on the basis of Polyvinyl Alcohol (PVA). Meanwhile, in [7, 8] used fibers coconut shell powders, corn fiber and cellulose whisker. All of these studies show that these carbohydrates are promising materials in this regard. However, there is still limited in study reported on the use of starch which derives from green banana for the production of films. In an effort for this, plantain peel has been chosen to be the source of starch for producing biodegradable film in this study. This is because plantain peel starch has the ability to be a commodity starch owing to its abundantly available in nature and involves low cost [1]. In spite of that, the fiber content in plantain peel also act as the reinforce additive. This is due to the fiber function which promotes the mechanical properties of scattering the external tensile stress throughout the composites [9].

Plantain is the largest herbaceous plant in the world. According to [3], Musaceae is the family of plantain which has probably over 30 well-known species within the genus Musa and consist more than 700 varieties. This edible fruit was derived from Musa acuminate which is hybridized between Musa acuminate Colla and Musa balbisiana Colla, which contribute to A and B genome respectively. This genome hybridization producing diploid, triploid and tetraploid bananas. Musa paradisiacal is a type of plantain that belong to triploid group AAB [10]. The differences of banana and plantain is generally can be seen based on their size of plantain is larger than a banana and also has starchy flesh rather than sweet that make it suitable for cooking [11].

Starch concentration in an unripe banana is higher than those in ripe banana, and this starch degrades to a relatively small monosaccharide [3]. In [1] in his study was found that unripe banana is a good source of starch because it contains about 36.2% amylose, the starch component that's responsible for the film forming capacity of starch. Furthermore, the amount of starch in green banana is equivalent to those in corn grain and white potato pulp [11]. Thus, it is once again proving that plantain starch is ideal to use for preparing film packaging. However, or the purpose of commercialization, the properties of the plantain starch are still need to be further
improved, either through physical or chemical modification.

Pure starch has some mechanical properties barrier such as lack of strength, water resistibility, process ability and thermal stability [12]. To overcome all of these problems, starch has to be chemically modified through a process known as acetylation. Acetylated starch should have better thermo plasticity and processibility than native starch [13]. Therefore, through acetylation, the hydrophilic hydroxyl groups are substituted with hydrophobic acetyl groups that prevent the formation of hydrogen bonding between the hydroxyl groups and water molecules. Thus, the water resistance of starch will be increased [13-14] and at the same time, decrease the glass transition temperature \( T_g \) [15] and also gelatinization temperature [16].

The modified starch then has to be blended with some biodegradable synthetic polymer such as PVA to increase the mechanical properties of films produced. The blending process is known as solution casting method. Solution casting is the simplest method used to create thin films from solution using centrifugal force. By drop small amount of polymer solution onto spinning head, then spin the solution, the centrifugal force will provide enough force to spread the solution into thin film layers spreading out on top of the surface. The purpose of this blend is to reduce the sensitivity of starch to water [17]. PVA was chosen in this study because it has good potential for plastic and packaging applications as well as due to its potential as a water-processable or melt-processable polymer [12]. Therefore, the main objective of this paper is to determine the effect of modified plantain peel starch-PVA blends on the tensile properties of the biodegradable film.

2. MATERIALS AND METHOD

Unmodified plantain peel from the type of Musa Paradisiaca was collected from various local stall in Dungun, Terengganu, Malaysia. Other materials used include Sodium Hydroxide (NaOH), Hydrochloric Acid, Acetic Anhydride, Ethanol, Glycerol and PVA. Meantime, the Fourier-transform infrared (FTIR) instrument was used for the analysis in this study.

Film formation process

The Unripe plantain fruits were peeled to separate the peel with the pulp. The peels were cut into 6mm slices and the slices were then cut into four pieces. The peels were macerated immediately in a NaOH solution, \((0.25 \text{ g/l})\) in \(2:1\) (v/w) proportion at 40\(^\circ\)C for about 4 hours. After that, the peels were blended at low speed (100 rpm) for five minutes. Then, the resultant slurry was filtered by centrifuged at 3000 rpm for 15 minutes and washed several times with water until the waste solution was clear. The starch suspension was then left overnight in refrigerator at 6\(^\circ\)C. The brownish sediment was dried at 40\(^\circ\)C in a convection oven for 48 hours, sieved by 250 micrometer sieve, stored at room temperature in a plastic sealed and placed in a desiccator as proposed by [18].

The plantain peel starch was then dispersed in distilled water for one hour at 25\(^\circ\)C as suggested by [19]. NaOH was added into the solution to adjust the pH value up to 8.0. This is followed by the addition of acetic anhydride \((6g)\) drop by drop to the stirred slurry, while the pH was kept maintained in the range of 8.0 to 8.4 by using NaOH solution. As the acetic anhydride is completely added, the reaction was allowed to proceed for one hour. The slurry was then adjusted to the pH of 4.5 by using 0.5 M HCl to terminate the reaction. After sedimentation, it was then washed twice with distilled water and once with ethanol for the purpose of free acidity. Last but not least, the sediment was dried by oven at 60\(^\circ\)C until the constant weight was achieved.

Then, distilled water was heated to 90\(^\circ\)C before it being added into the modified starch and PVA for the preparations of starch-PVA blend. For each solution, 150 ml distilled water was used to disperse the plantain peel starch and PVA. Ten samples were prepared in the ratio of starch to PVA. From the ten samples, it was then divided into five samples of modified starch and five samples of non-modified starch as shown in Table 1.

During the heating process, the slurry was stirred at a medium speed which is 700 rpm to avoid formation of bubbles that present when the slurry is stirred at maximum value. The starch-PVA blends were then mixed with glycerol and heated continually until the mixture has started to become viscous. The stirring process was continued for 20 minutes until a viscous homogenous starch paste was obtained. After that, the viscous and gelatinized compounding mixtures were spread on a flat glass for the casting process. The casted mixtures were then dried in an oven at 95\(^\circ\)C for one hour. Then, the casted films were left at room temperature for an hour, to be cooled, before it can be easily removed from the glass.

The films obtained were kept in sealed plastic bags and stored in a dry and cool place in order to protect it from the exposure of humidity and moisture content and to avoid degradation. Lastly, the films were ready to be tested with respect to their mechanical properties.

Table-1. Experimental design for the solution casting of modified plantain peel starch-PVA films.

<table>
<thead>
<tr>
<th>Basis (g)</th>
<th>Formulations</th>
<th>Mass of Modified Plantain Peel Starch (g)</th>
<th>Mass of PVA (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5</td>
<td>A</td>
<td>3.15</td>
<td>7.35</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>5.25</td>
<td>5.25</td>
</tr>
<tr>
<td>15</td>
<td>C</td>
<td>4.5</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>20</td>
<td>E</td>
<td>6</td>
<td>14</td>
</tr>
</tbody>
</table>

Mechanical properties analysis

The film produced was cut into a dumbbell shape as shown in Figure-1. Dumbbell shape is the standard shape used for determining tensile strength. The samples were cut into 9.53 mm wide and 63.5 mm long strips. The initial grip separation and the crosshead speed were set at
23.5 mm and 0.1 mm/s, respectively. The reason for using this shape is to ensure that the stress at both ends of the specimen film will be evenly distributed through the entire film when the load begins to pull the film until break. Rectangular shape is not suitable for this specimen film because it will cause the stress to accumulate at the clamped end of the film due to stress concentration. Hence, the resulting rupture will occur only in the clamped region. For every film, five specimens were taken out from the region with least bubble formation and each of the specimen was observed thoroughly for its appearance and presence of bubbles. The thickness of the specimen was then measured by using a micrometer screw gauge and be devoted as gauge thickness. The specimen was then ready for tensile test.

Tensile test was done by using universal tensile machine. To start the testing, the specimens were clamped by the grips to fix their position in the sample space. The value of length, width and gauge thickness was inserted first in software before testing was started. Once the testing started, the machines were pulling according to the acceleration stated and the graphs were plotted automatically. The tensile strength and the elongation at break were computed directly from the stress-strain curve. Meanwhile, Young’s modulus was calculated as the slope of the initial linear portion of the stress-strain curve. The specimen can only be tested once at a time. The value of elongation at break and tensile strength of the blend was determined by the average value of five specimens for each composition.

Tensile strength or stress is measured in unit Newton (N) per millimeter square (N/mm²). The stress is measured as the highest peak in the stress-strain graph during the test of a specimen. The actual reading of the tensile strength is measured by the mean value of specimens tested plus with the standard deviation.

3. RESULTS AND DISCUSSION

FTIR is a technique used to obtain an infrared spectrum of absorption, emission and photoconductivity of a solid, liquid or gas. In FTIR, infrared radiation is passed through the sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through. The resulting spectrums represent the molecular absorption and transmission, creating a molecular fingerprint of the sample. In this study, FTIR spectra were recorded for both non-modified and modified plantain peel starch in order to prove the presence of acetyl group in the modified plantain peel starch. Figure-2 shows that acetic acid presented in the form of acetyl group was substituted in the modified plantain peel starch. It is known that the free hydroxyl groups absorbed energy between the region of 3650-3584 cm⁻¹, where the bands observed in the region of 3292-3327 cm⁻¹ in the spectra of both films can be assigned to the stretching of the -OH groups, caused by the formation of hydrogen bonds in the studied matrices. This result is in line with the finding obtained by [1] which indicate that the stretching of OH group is in the region of 3288-3298 cm⁻¹. Meantime, in [20] also found similar results but noted a 3425 cm⁻¹ band.

The values of second band found for non-modified (2919.98 cm⁻¹) and modified (2919.90 cm⁻¹) plantain peel starch are similar and this indicates the presence of CH₂ groups. As found out by [1], the bands located between 2800-3000 cm⁻¹ can be accredited to variation in the amounts of amyllose and amyllopectin.

Although both non-modified and modified spectrum of plantain peel starch have a quite similar band, there is some difference which prove the starch has been successfully modified. Figure-3 shows the spectrum of modified plantain peel starch. It can be seen the appearance of a band at 1420.21 cm⁻¹ which signify the presence of acetyl group, resulted from the reaction of hydrogen with acetic acid. According to [1, 21], the band appears within the value of 1500 cm⁻¹ related to the symmetrical stretching of carboxyl group COO, C-C, C-O and C-O-H bonds. Meanwhile, the band at the value of 1314.44 cm⁻¹ and 1317.16 cm⁻¹ for non-modified and modified plantain peel starch, respectively are correspond to the existence of amide III. Amides III are normally present in the range of 1200 to 1350 cm⁻¹ [1] due to the some protein traces remain in the raw material.
Tensile analysis is another test that has been done in this study instead of FTIR analysis. Tensile strength, elongation at break and Young’s modulus are three indications of tensile properties that was investigated in this study. The film produced has a plastic-like character due to the characteristics of plantain peel starch itself and also by the addition of glycerol as a plasticizer. Generally, the tensile strength, elongation at break and Young’s modulus of biopolymer film is affected by the composition of plantain peel starch to PVA used to produce the film. Inconsistency thickness of the film produced is determined as the factor that affects the precision of the analysis. Table 2 shows the mean value and standard deviation of tensile properties for the two types of starch. Both of the modified and non-modified starch has the same composition of plantain peel starch to PVA used to produce the film.

Table 2. Mean value and standard deviation for tensile properties of modified and non-modified starch.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Modified Plantain Peel Starch</th>
<th>Non-Modified Plantain Peel Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tensile Strength (N/mm²)</td>
<td>Elongation at Break (mm)</td>
</tr>
<tr>
<td>A</td>
<td>14.72 (±3.25)</td>
<td>1.811 (±0.572)</td>
</tr>
<tr>
<td>B</td>
<td>17.89 (±5.05)</td>
<td>2.983 (±0.850)</td>
</tr>
<tr>
<td>C</td>
<td>13.79 (±3.89)</td>
<td>2.309 (±0.630)</td>
</tr>
</tbody>
</table>

Thus, the film produced was analyzed by the effect of different basis of starch-PVA blend on the tensile properties and the tensile value was then compared between both types of films. The blend bases used are 10.5g, 15g and 20g. Figure-4 and Figure-5 visualized the results of tensile strength for both modified and non-modified starch when the composition of starch to PVA is 30:70. It can be seen from both figures that the optimum amount of the starch-PVA blend is 15g since it shows the highest tensile strength value. Besides, it is also can be seen that film produced from modified plantain peel starch has higher tensile strength compared to the film made from non-modified starch. The highest tensile strength for non-modified starch is 13.186 N/mm² (±3.055), Meanwhile, for modified starch the value is 17.890 N/mm² (±5.0467). This result is supported by the research conducted by [18] which found modified starch has better paste clarity and stability, increased resistance to retrogradation and also freeze-thaw stability.

On the other hand, the tensile strength of films against non-modified blend basis when the basis used are 10.5g and 15g with the same ratio of starch to PVA, 50:50, are shown in Figure-6. It is clearly seen that the starch amount was increased as the tensile strength of film decrease. This is due to the presence of amylose which decreases the flexibility of the films [1].
The same formulation was done for modified starch as to compare it with non-modified, but the result shows that the blend is not forming a plastic. The casted blend shows a crack after it has been dried in an oven. This is due to the concentration of starch was dominated over the concentration of glycerol. When the starch concentration is dominated among the blend, glycerol that was used as a plasticizer does not give any effect towards the blend. So, the film produced is like an unplasticized film. According to [22], unplasticized film showed crack or pores and has a fragile and rigid characteristics. Moreover, cracking of the film can also cause by the slurry that are too viscous. As found out by [11], acetylation increase the viscosity of starch paste.

Elongation at break analysis

Elongation at break, also known as fracture strain is the ratio of elongation to the original length of the sample at the break of the test specimen [23]. It expresses the capability of a material to resist change of shape without crack formation. The elongation at break is determined by tensile testing. During the test of a specimen, elongation at break was measured. Elongation at break is the longest length of a material can sustain before breakage. The unit measurement is in millimeter (mm). The data of elongation at break for films produced by the non-modified and modified plantain peel starch increased when the blend used increased from 10.5 g to 15 g. In order to identify the pattern of the elongation at break of the films, the total amount of starch-PVA blend was further increased from 15 g to 20 g. However, this increment does not continually increase the elongation at break but reduce the strain property of the films. This shows that the strain has already achieved its longest extension length at break since the blend basis is 15 g.

The reason for the reduction in elongation at break value of the blend basis of 20 g is the concentration of PVA has dominated the blend. This is because when the blend basis increased, automatically it increase the PVA amount in the blend with the composition of starch to PVA is 30:70.

According to [12, 13], starch-PVA blend has good compatibility, but too high amount of PVA will contribute to the brittleness of the film. Besides, it is also can be seen that the highest value of elongation at break for films produced using non-modified starch is 2.703 mm ± 0.5812 and 2.983 mm ± 0.8504 for films produced using modified starch. Acetylated starch films have a higher elongation at break properties due to the effect of plasticizer added to the starch. This is because the addition of plasticizer such as glycerol to the acetylated starch will cause the film to have greater flexibility and resilience [22].
Young's Modulus analysis

Young’s modulus is an indicator of film rigidity and elasticity which prepared under normal process condition [1]. It is also defined as tensile modulus or elasticity modulus which measures the stiffness of an elastic material. Young’s modulus is measured by the ratio of stress to strain at low values of strain [23]. The unit for this measurement is Newton per millimeter square (N/mm²). The Young’s modulus data for films produced by the non-modified and modified starch is shown in Figure-9 and Figure-10. In both figures, the Young’s modulus obtained for films produced from non-modified and modified starch is concurrent to its tensile strength. In Figure-9 for example, the Young’s modulus decrease from 10.5 g to 15 g blend basis and increase from 15 g to 20 g of the basis. This result contrasts with the result of tensile strength which achieved the higher value at 15g blend basis. On the other hand, for Young's modulus, at this point, the lowest value was achieved which is 119.475 N/mm². The same performance of Young’s modulus related to tensile strength reported by [23].

The highest value of Young's modulus was achieved at 20 g of blend basis, which is 179.722 N/mm² (+46.7697). This result is incorporating with the highest amount of starch present as compared to the other blend. According to [11] plantain has a significant amount of amylose which is in the range of 10-11%. Thus, the highest value of the Young’s modulus could be explained by the differences in the amylose content of the film, since it is known that films rich in amylose exhibit good mechanical strength but little flexibility [1]. Whereas for Figure-10, the Young’s modulus for films produced by modified starch decreased as the total amount of starch-PVA blend is increasing. The film has the highest elasticity at 10.5 g of the blend basis which is 208.334 N/mm² (+86.8011), and the lowest at 20 g which is 139.440 N/mm² (-28.3186). The film should have the lowest value at 15 g of the blend, but it has reached the optimum elasticity at 15 g which make the film no longer elastic at 20 g blend basis. Thus, it is resulted to have the lowest value at 20 g blend basis.

**Figure-9.** Graph of young’s modulus against non-modified blend basis.

**Figure-10.** Graph of young’s modulus against modified blend basis.

Inconsistent film thickness

Inconsistent film thickness has been determined as a factor that affects the precision of mechanical properties of the blend. Inconsistency is mainly because of the suspension is not evenly spread on the glass plate during the film casting procedure. Besides that, the high heating temperature used for drying the film may induce the fast crystallization of starch solution regardless the effect of amylose content in the starch. The stable structure and strong molecular orientation of the amylose produced film, which exhibit good mechanical strength but little flexibility [1]. Consequently, the film will be formed with inconsistent thickness. As a result, this factor had a significant effect on the precision of mechanical properties of the film. Since the data were believed not accurate at all, the mean and standard deviation for all measurements were computed to obtain the most acceptable and reliable value for each tensile strength, elongation at break and Young’s modulus.

4. CONCLUSIONS

This study has proven that the isolated plantain peel starch was successfully modified by using sodium hydride, acetic anhydride and hydrochloric acid and the biodegradable films were successfully prepared. It is also proven that the films produced from modified plantain peel starch are more flexible and ductile as compared to the films produced from non-modified starch. This is because, the modified plantain peel starch contains acetyl group increases the elasticity of the film and hence makes the film more flexible and ductile. Besides, this study also found that the bio film produced has its own properties of flexibility, hardness and behave according to its composition and amount of starch-PVA used in the blend in a fixed volume of distilled water. For non-modified starch, higher composition of starch used had increased the film flexibility whereas the higher composition of PVA has reduced the tensile strength of films produced. For modified starch, an increment in the composition of plantain peel starch had resulted in dominant effect towards the starch while diminishing the plasticizer effect. Besides, the starch present is associated with amylose content in the starch. High amylose content in starch solution may cause fast crystallization, resulting the
increment of film’s hardness. Meanwhile, a lower content of starch may slow down the crystallization due to the dominant plasticization effect by glycerol. Hence, more flexible and ductile film can be obtained. Thus, it can be concluded that the film cannot be produced at high concentration of starch.

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