

BIOREMEDIATION SCIENCE AND TECHNOLOGY RESEARCH

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The Development of Banana Peel/Corn Starch Bioplastic Film: **A Preliminary Study**

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HISTORY

Received: 7th Mar 2017 Received in revised form: 20th May 2017 Accepted: 6th of June 2017

KEYWORDS

bioplastic film banana pee corn starch FTIR

ABSTRACT

The aim of this study is to develop bioplastic film from a combination of two biopolymers of same source, namely banana peel and corn starch. Five banana peel films (BP film) were prepared with different concentrations of corn starch (1% up to 5%) as co-biopolymer and film without corn starch acted as a control. The films were carried out with several durability tests and characterization analyses. Based on the results obtained, the BP film with 4% corn starch gave the highest tensile strength 34.72 N/m² compared to other samples. The water absorption test showed that BP films with 3% corn starch were resistant to water uptake by absorbing water up to 60.65%. In terms of characterization, spectra of Fourier Transform Infrared Spectroscopy (FTIR) obtained for BP control film and BP film with 4% corn starch were comparable with most of the peaks were present. The thermal analysis by differential screening calorimetric (DSC) detected the melting temperature for both BP control film and BP film with 4% corn respectively at Tonset of 54.41°C and 67.83°C. Overall, combination of starches from two different sources can be used as an alternative in producing bioplastics.

INTRODUCTION

As the world need plastics for our daily purposes, about 265 million tonnes of plastics were produced worldwide in 2010, of which 57 million tonnes were produced in Europe alone [1]. Polymer film is selected as the best packaging materials due to its versatility, low cost, and permeability. Low-density polyethylene, high- density polyethylene and polyvinyl chloride are some of the most commonly available plastic polymers in the packaging industry. However, these synthetic materials are unable to be degraded by present natural microorganisms upon their disposal to the environment [2]. As a result, these nonbiodegradable plastics remain in the environment for a long time and cause an increase in solid waste production.

The keen interest in bioplastics has begun since the early 20th century when Henry Ford used corn and soybean oils to manufacture his automotive parts [3]. Currently, the bioplastic industry promises good opportunities as this new era, there is a high demand for plastic in global markets. Macromolecules from natural polymers and smaller molecules such as sugar, disaccharides and fatty acids are becoming major raw materials in the production of bioplastics.

Starch is one of the major sources in the development of bioplastic. Many previous studies have been conducted by using starch as a natural biopolymer. Starch consists of a long chain of two glucose units joined together, namely branched polymerized amylopectin and amylose, which gives its granular structure. Due to its large availability, low cost, renewability and biodegradability, starches are commonly used in the production of bioplastics. Starch can behave like a thermoplastic in the presence of plasticizer, with application of heat and mechanical treatment [4]. As native starch-based films are limited to high water affinity and brittleness, other natural biopolymers are often added as fillers to modify and improve films' properties [5].

One of the most common waste form of starch is the banana peels. The waste management problem is also faced due to the disposal of tonnes of banana peels in some parts of the globe, especially in developing countries. In Malaysia, there are several industries based on banana products such as manufacturing of banana cake, banana chips, banana fritters and many more. These industries use banana flesh as raw materials and discard the peels into the waste at end of the process. The disposal of these large amounts of wet organic waste can eventually harm the environment and lead to health problems such as respiratory disorders [6].

Banana peels consists high sources of starch, which is about 18.5% [7]. As banana peels ripen, the glucose level increases. However, if the peels are too ripe, the starch will be converted into glucose while the least ripened peels, becomes too firm although high in starch molecules [8]. Therefore, banana peels can be suggested as a suitable source for the manufacturing of bioplastics. Meanwhile, corn is a well-known source for starch and has become one of human's main sources of food. But, some parts are still being discarded as waste. In fact, studies on using corn as potential biopolymer for bioplastics have been widely explored. Hence, in this paper, a new approach was developed by adding corn as co-biopolymer with banana peels acting as the main biopolymer. Previous studies also only focused on the potential of banana peels in forming starch based plastic film. Even though several studies have been done using cellulose as natural reinforced filler in starch based films [9], yet in this study a new derivative was prepared by combining starches from two different sources. Therefore, this study aims to investigate the tensile properties of banana peel/corn starch films, to determine the maximum water uptake and to characterize the films in term of functional group and thermal properties. The study also intended to show the bioplastic film from combination of organic waste has potential to become alternative resources in plastic making industries, to reduce the amount of discarded organic wastes and to contribute to waste-to-wealth industry development in Malaysia.

MATERIALS AND METHODS

Materials

Bananas were purchased from the local market in Jalan Pudu and commercial corn starch was purchased from the local grocery shop. Analytical grade hydrochloric acid (HCl; 36 % v/v) and glycerol (99.5 % v/v) were purchased from Accot Lab Supplies (Balakong, Selangor). Analytical grade sodium hydroxide was purchased from RND I-TECH (Petaling Jaya, Selangor).

Preparation of the Banana Peels

The banana peels were removed from the flesh by using a stainless knife. Approximately 300 g of banana peels were dipped in acetic acid solution and the peels were then placed into a beaker containing 800 mL water and boiled for 30 minutes. The water was decanted off and the peels were left to dry for 30 minutes at room temperature. The banana peels were then placed in a clean 500 mL beaker.

Preparation of Bioplastic Film

The banana peels were pureed using the hand blender. 25 mL of the paste was placed in a 50 mL beaker. 3 mL of 0.5 M HCl was added and the mixture was stirred using a spatula. Then 2 mL of 15% glycerol solution was added and the mixture was stirred. A 3 mL of 1% corn starch was then added as co-biopolymer and the mixture was stirred again. Then, a 3 mL of 0.5 M NaOH was added to the mixture and stirred. The mixture was poured into a mould and spread into a thin layer with a wooden rod. The mould was then placed in a 130°C oven and baked for 30 minutes.

Load Test

A small piece of the bioplastic film was cut into $2 \text{ cm} \times 6 \text{ cm}$ size. The film was then hooked onto the retort stand placed 3.5 cm apart. A spring balance was hooked onto the middle of the film and weight load was added until sample broke apart. The steps were repeated with three replicates to obtain an average value. The tensile strength was calculated by using the following formula:

Tensile Strength =
$$\frac{\text{Weight Load (N)}}{\text{Area of cross section of biofilm (m2)}}$$

Water Absorption Test

A small piece of the sample was cut into $1 \text{ cm} \times 2 \text{ cm}$ size. The initial weight of the sample was recorded. The sample was then placed into a beaker containing 60 mL of water at room temperature for 24 hours. The sample was then taken out from the water and wiped off. The final weight was recorded. The amount of water uptake was calculated by using the following formula:

WA (%) =
$$\frac{\text{Final weight (g)-initial weight (g)}}{\text{initial weight (g)}} \times 100$$

Fourier Transform Infrared Spectroscopy (FTIR) Characterization

A small piece was cut from the bioplastic film and placed onto the germanium plate. The spectra were taken in 256 scans between 4000 and 400 cm⁻¹ using Spectrum 100 Perkin Elmer FTIR.

Differential Screening Calorimetric (DSC) Analysis

The DSC analysis was performed using DSC Mettler Toledo 822e at -10 $^{\circ}$ C to 250 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C/min under nitrogen atmosphere.

RESULTS AND DICUSSION

Banana Peel/Corn Starch Bioplastic Films

Fig. 1 shows the BP films with different percentage of corn starch. It is probable that the development of brownish color was due to the caramelization of the sugar in the ingredients.



Fig.1. BP films with different percentage of corn starch. a) 1% b) 2% c) 3% d) 4% e) 5%.

Load Test

Based on **Fig.2**, BP film with 4% corn starch provided the highest tensile strength. Compared to BP film with 0% corn starch, this film was able to withstand stress up to 34.72 N/m^2 with the maximum load of 4.71 N. The second highest tensile strength is discovered to be BP film with 5% corn starch. However, the trend graph decreases for 5% corn starch as due to the increase in starch-starch chain molecules. According to Azhari et. al [10], as the filler-filler interaction became more prominent due to the increase in the amount of starch, the tensile strength tended to decrease. This shows that 4% of corn starch is the maximum amount to be added for the film The tensile strength of the films is far smaller compared to previous studies on starch based films. Previous study stated that potato based bioplastics have the strength of 4870 kN/m², cassava with 4500 kN/m² and corn based bioplastics with 3590 kN/m²[11]. However, the films tensile

strength values correspond to the value obtained by Mohapatra et. al [12] which is in the range of 164.750 to 343.511 kN/m² in neutral medium. This shows banana peel film provides a small value of strength compared to other starch based sources.



Fig.2. Tensile behavior of BP films with different compositions of corn starch. The error bars depicts the standard error of the average tensile strength.

As starches from different sources are present in the BP film, the value of tensile strength might also be affected by the concentration of plasticizer. The plasticizer used in this study was glycerol. It was reported that glycerol has a small molecular size which allows it to incorporate easily with the polymer chains. As glycerol is added, the starch networks combine with glycerol molecules and reduce starch-starch interactions. Thus, at addition of starch of more than 4%, the presence of starch-starch chains is greater which causes the glycerol molecules the inability to fit in as the polymer chain is saturated. According to Leerahawong et. al [13], glycerol has the ability to decrease tensile strength and elongation at break of films when the same plasticizer concentration is used. As glycerol is added, it disrupts the starch chains causing reduction in rigidity and increase chain mobility.

Water Absorption Test

Water resistance is an important characteristic in determining a suitable source for bioplastic. The water absorption of the plasticized starch BP film was carried out at room temperature for 24 hours to obtain the maximum water uptake data. Based on **Table 1**, the highest water uptake is by BP film with 1% corn starch which is 108.98%.

 Table 1. Data for tensile property and water absorption of BP films with the standard error for the average load applied.

Sample	Tensile property Average maximum load (n)	Water absorption Water uptake (%)
0% corn starch (control film)	1.60 ± 0.0288	63.95
1% corn starch	1.47 ± 0.0440	108.98
2% corn starch	1.07 ± 0.0666	73.76
3% corn starch	3.00 ± 0.2886	60.65
4% corn starch	4.17 ± 0.3333	63.87
5% corn starch	3.50 ± 0.2886	65.50

This may be due to the initial presence of water molecules in the film during film casting. Upon drying, some water molecules may have remained in the film as water can also act as a plasticizer. Amorphous materials plasticized with water results in lower stability and increase mobility [14]. BP film with 3% corn starch concentration showed lower percentage of water uptake of 60.65% followed by 4% with uptake of 63.87% respectively. Comparing the result with the study conducted by Sujuthi et al. [11] the bioplastic sheet from corn starch had the water absorption percentage of 22.69%, followed by potatobased bioplastic sheets with 32.35% and cassava-based bioplastics sheets with 39.48% which is lower than the result obtained. The films were determined to have a water uptake percentage more than 50% because biopolymers are hydrophilic in nature. Besides, the water molecules interact with hydroxyl group in starch structure, the plasticization of biopolymer with glycerol is also an important factor in this study. As glycerol is a hydrophilic low molecular carbohydrates, it has the tendency to adsorb water depend on the number of hydroxyl group present and molecular weight of it structure [15]. Glycerol has three carbons attached to their backbone with one hydroxyl group attached to each carbon which causes the molecules to bind to the highest amount of water corresponding to the weight portion. Increasing sizes of hydroxyl groups concentration centre in biocomposite matrix increases the water absorption of the film.

FTIR Characterization

FTIR analysis has been carried out to compare the spectra of both control and bp film with 4% corn starch. Based on the spectra in Fig.3, the peaks obtained for both BP film are similar to each other with the film containing 4% corn starch showing slight shift to the right. This is due to the presence of -OH group in the starch structure that is involved in the hydrogen bond formation. Four major peaks have been discovered to be present in both the spectra. The major peak determined from both the spectra of control BP film and BP film with 4% corn starch, is the C-O peaks which were found at 1026.41 cm⁻¹ and 1013.86 cm⁻¹ respectively. According to Jumaidin et al. [16] peaks obtained approximately at 1089 cm⁻¹ and 1020 cm⁻¹ were due to the characteristics of anhydro-glucose ring of the C-O stretch. This bond is commonly found in the structure of carbohydrates due to the stretching of C-O-H groups. The peaks observed between 3100 to 3700 cm⁻¹ in both spectra corresponds to the hydrogen bonded hydroxyl group (O-H) due to the complex vibrational stretching that naturally occurs in the carbohydrate structure. However, the band is shifted to lower wavenumber in the presence of 4% corn starch which was assigned to increase intermolecular hydrogen bonding [16].

Besides, according to Muscat et al [17], the O-H stretching peak decreases from 3324 to 3317 cm⁻¹ upon the addition of 15% glycerol to low amylose starch which indicates a more stable hydrogen bond was formed between the glycerol and the starch molecules. The sharp peaks obtained at wavenumber 2850 to 3000 cm⁻¹ indicates the C-H bond stretching of CH₂ groups in the starch structure [18]. The peaks discovered at wavenumber 1580 to 1700 cm⁻¹ in both spectra assigned to the OH group deflection of water which was specifically due to hydroxyl groups bending mode in water molecules. According to Kizil et al. [19], the band at 1637 cm⁻¹ is a result of water adsorbed in the amorphous region of starch. Based on the spectra, the band at this region is discovered to be wider for BP control film compared to BP film with 4% corn starch. This might be due to the difference in crystallinity of starches present in both films. As each type of starch has different crystallinity values, this band has the potential to be affected due to crystallinity variations.

Other peaks identified in both spectra were between the range of 1400 to 1450 cm⁻¹ corresponding to O-H bending [16], peaks at 1350 to1480 assigned to the CH₂ bending vibrations in the biofilm, peaks at the range of 1240 cm⁻¹ which attributes to C-O stretching and peaks at the range of 1720 to1740 cm⁻¹ due to C=O stretching in the film. The peaks obtained at the region below 800 cm⁻¹ attributed to the pyranose ring skeletal vibrations in the glucose unit of starches [19]. The peaks at the wavenumber of 1534.45 cm⁻¹ and 839.57 cm⁻¹ were only identified in BP film with 4% corn starch concentration. This peaks might be due to C=C stretching and =C-H bending respectively, that might have



Fig.3. The FTIR spectra a) BP control film b) BP film with 4% corn starch.

shifted to a lower wavenumber due to presence of different types of starch in the film. According to Zuraida et al. [20], miscible polymers can cause a distinct interaction of hydrogen bonding which causes the FTIR spectrum to change in band shifting and broadening. Thus, shifting to a lower wavenumber helps to easily identify and compare with reference spectrum.

DSC Analysis

DSC analysis is carried out to study the thermal behavior of the bioplastic film. Based on the thermograms in **Fig.4**, a broad peak corresponding to melting was discovered at T_{onset} 54.41°C for BP control film and 67.83°C for BP film with 4% corn starch. According to Sagnelli et al. [21] the main endothermic peak was identified at onset temperature range of 80 to 105°C which represents the melting of amylose-only starch crystallites. This shows the BP films melts faster compared to amylose-only film. The peaks reach maximum temperature for melting at 106.42°C and 112.88°C respectively for both films.

Stronger interaction of molecular hydrogen bonding between BP starch, corn starch and glycerol attributes to higher melting temperature. The trend of heat flow was determined to be increasing after the melting in BP control film with another melting peak discovered at T_{onset} of 206.42°C, which corresponds to the effect of glycerol plasticization. This peak is absent in BP film with 4% corn starch concentration as the plasticization effect might be too little. According to Sorbal et al. [22] the temperature of melting (T_m) concerned namely with the degree of hydrolysis and plasticizer concentration. There is no glass transition temperature (T_g) identified in the thermal analysis as glass transition provides a similar behavior of T_m [16]. The role of plasticizer that interrupts the polymer chains intermolecular forces might attribute to the T_g value.

CONCLUSION

The bioplastic films from the composite of banana peel and



Fig.4. DSC thermograms for a) BP control film b) BP film with 4% corn starch.

commercial corn starch were successfully formed. The films were able to provide a tensile strength with the maximum value of 34.72 N/m² at 4% corn starch concentration. As the films were made of starches from two different sources, it is suggested that a slight improvement in the concentration of plasticizer will able to give a better tensile strength. The water absorption test showed that the hydrophilic nature of starch molecules increases the water uptake for all the bioplastic BP films with more than 50%. The characterization of functional group by FTIR analysis indicated that BP film with 4% corn starch are comparable with the BP control film and to the previously developed starch based biofilms such as corn and cassava as most of the major peaks was identified. In terms of thermal analysis, only T_m were detected for both the BP control film and BP film with 4% corn starch concentration at Tonset of 54.41 °C and 67.83 °C respectively. The glass transition temperatures were not detected as previous studies indicate that glass transition has an equal behavior to melting temperature. As this is a preliminary study, it is recommended to conduct more tests in the future for a better performance of the film, particularly in terms of mechanical properties. Addition of co-plasticizers such as citric acid is suggested to improve the strength of the films. Thus, new formulations can be developed in the future to achieve the standard bioplastic requirements.

ACKNOWLEDGEMENT

The authors would like to thank the lab staffs of Faculty of Environmental Studies and Faculty of Science (namely FTIR and DSC instrumentation) of Universiti Putra Malaysia (UPM) in providing their support in completing the study.

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