Optimization Properties of Environmentally Friendly Paper Coating Based Starch-Polyethylene glycol (PEG) Mixture

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Abstract. The use of starch as biodegradable base material for packaging application was of great interest as an environmentally friendly alternative to the present use of polyethylene and polyvinyl chloride. However, starch tended to be brittle and had a lack of stability due to exposure to water. Several approaches have been done to improve shellac properties including through chemical modification, mixing with polymers, clays, and plasticizers. The present study related to optimization of starch properties when mixing with polyethylene glycol (PEG) coated on the paper. The aim was to obtain the temperature and mixing time between starch and PEG so produced composites with optimal barrier properties. The composites of PEG/starch 10 % w/w were prepared using solvent casting and coated on paper surface, and dried in the oven for 12 hours at 40°C. Water Vapour Transmitter Rate (WVTR) (Payne cup method) showed that 70 °C was the optimum temperature when mixing time was 30 minutes. Moreover, it showed that the optimum mixing time was 30 minutes when mixing temperature was 80 and 70 °C. Fourier Transform Infra Red (FTIR) showed a strong interaction between PEG400 and starch.

1. Introduction
Packaging was of great concern as it played important role in food and pharmaceutical industry. The issue was driven by the need to develop new material as an alternative to present material synthesized from a chemical compound [1]. One type of such packaging was conventional paper made from polyvinyl chloride (PVC), polyethylene (PE) [2]. This material was difficult to degradation naturally when it was disposed in nature leading to environmental problem [2]. This synthetic polymers have been widely used for food packaging because they were affordable and good for their mechanical and chemical properties.

Biodegradable polymers are polymers having ability to degrade naturally by breaking the polymer chains or inter-monomer bonds on the main chain of polymers into short chains by living organism such as fungi, bacteria, and enzymes [3]. This type of polymer exists in nature and derived from renewable natural such as tubers, corn, and
others [4]. One of the most potential natural polymeric is starch. It is a mixture of amylose and amylopectin which is a complex carbohydrate in the form of white powder, tasteless and odorless. It is a potential material to use because of its relative cheap, abundant, renewable, and biodegradable [4], so it can be applied in food packaging. However, it has poor mechanical and water barrier properties [5].

Many effort have been done to improve the properties of starch. One of the effort was to mix starch with Poly vinyl alcohol (PVA) [1,6]. Another approach is to mix starch with clays [7]. However, it produced brittle composite. Recently, plasticizers also have been applied to starch. Those included sorbitol [8,9], glycerol [10], glycerol and urea [11].

In this work plasticizers polyethylene glycol (PEG) was applied to improve the properties of starch. It was water soluble, non-toxic, and safe for packaging. The addition of PEG may affect the permeability of water vapor in the coating [12]. Starch has gelatinating temperature where the properties of starch change drastically. The gelatinization temperature also depends on the types of starch [13]. Therefore, the purpose of this study is to obtain time and temperature of starch and PEG mixture giving optimum properties. The interaction between starch and plasticizer PEG was explored using Fourier Transform Infrared (FTIR).

2. Materials and methods

2.1. Sample Preparation
The starch was cassava (amylum manihot) from local resources and plasticizer was PEG having molecular weight 400 supplied by Sigma Aldrich. Starch of 0.9 gram was dissolved in 10 ml of distilled water and stirred for 30 minutes from 55°C to 80°C and then held for a heating rate of 1 hour.

PEG 400 of 0.1 gram was dissolved in 5 ml of distilled water and stirred for 2 hours. Starch and PEG 400 solution were mixed and heated for 30 minutes at different temperature i.e. 60°C, 70°C, 80°C. The PEG 400 starch suspension was then coated on the surface of paper and dried for 12 hours at 40°C.

2.2. Sample characterization
2.2.1. Water Vapor Transmitter Rate (Payne cup method)
The nature of barrier properties of the paper coating was determined by Water Vapor Transmission Rate (Payne cup Analysis method) at 85% humidity. The humidity was achieved by saturated KCl solution placed in humidity chamber.

The value of the water vapor transmission rate (WVTR) was calculated by the following equation (Standart british, 1996):

\[ \text{WVTR} = \frac{240 \times m}{sx \times t} \]  

Where:

- \( m \) = The weight of gram in a certain time
- \( s \) = Surface area of the test film (cm)
- \( t \) = The time between the last weighing

2.3. Fourier Transform Infrared
A spectrometer along with a mercury cadmium telluride detector cooled by liquid nitrogen was used for all the FTIR analysis. The spectrometer was coupled with a single reflection diamond ATR cell. The film was placed on top of the crystal diamond and the
spectra of the films taken. The wavelength of interest ranges from 700 to 4000 cm\(^{-1}\) and was collected with resolution of 4 cm\(^{-1}\) and 64 scans.

3. Results and discussion

Figure 1. shows that the accumulation of water transmitted through the samples as a function of time. The samples are paper (with no composites, starch heated 70°C for 30 minutes (coated on paper), K+PEG400/70C/30’ (starch and PEG400 mixture heated at 80°C for 30 minutes), K+PEG 400/70C/30’ (starch and PEG400 mixture heated at 70°C for 30 minutes), and K+PEG 400/60C/30’ (starch and PEG400 mixture heated at 60°C for 30 minutes) as a function of time. It shows that the water accumulation increases linearly with time within the period of experiment under studies. The WVTR value is calculated using Equation 1 and given in Table 1. It showed that the WVTR value of the samples compared to the paper on its own reduced ~ 26 % when coated with starch heated at 70°C. However, adding PEG400 to starch reduced the WVTR value only ,~ 1.9 % when heated at 60°C, ~20.5 % when heated at 70C, and ~16.9 % when heated at 80C. These results suggested that the gelatinization of starch did not occur when heating temperature was 60°C. This was supported by previous study that gelatinization only occurred above temperature 60°C [7] The the WVTR value compared to starch on its own increased ~ 6.7 % when PEG400 incorporated into starch. Plasticizer tended to increase the WVTR values of polymers as shown by previous studies (Ghasemlou et al. 2011; Hernández-Munoz et al. 2003; Kristo and Biliaderis 2006; Zhang and Han 2006 ) In overall, heating temperature at 70 C gave the most optimal barres properties when PEG400 incorporated with starch.

![Figure 1. Water accumulation as a function of time of paper, starch, and PEG 400/starch mixture.](image)

Altough our results showed that the addition of plasticizers into the starch reduced the water barrier properties, however, the paper coated with starch only produced brittle composite and easy to crack and break, so it is not applicable in food packaging. In the other side, the incorporation of PEG400 into starch produced flexible composite and readily to use for packaging application. Another studies also showed the same trend [1,6]. The starch was sensitive to water leading to damage of the structure [1].
Table 1. WVTR value of the samples

| Cooking Temperature (°C) | Value of WVTR (g/m² day) |
|-------------------------|--------------------------|
| Starch                  | 752,00                   |
| Paper                   | 1010,67                  |
| K+PEG 400/60C/30’       | 992,00                   |
| K+PEG 400/70C/30’       | 802,67                   |
| K+PEG 400/80C/30’       | 840,00                   |

Figure 2 shows the FTIR spectra of PEG400, starch and PEG400/starch mixture. It shows that four main peaks exists in those samples. The intensity peak in starch sample at 3300 cm⁻¹ attributed to hydroxyl groups [16], 2926 cm⁻¹ attributed to methyl groups [15], and 1149 cm⁻¹ attributed to ether groups. There three peaks in PEG-starch mixture is observed at 3300 cm⁻¹ (hydroxyl), 2881 cm⁻¹ (methyl), and 1145 cm⁻¹ (ether) which are only slightly different from starch. Similar FTIR trends also were shown by Ortega-Toro et al [14] in –glycerol starch coated with PEG.

Figure 2. FTIR spectra of starch, PEG 400, and starch/PEG 400.

FTIR spectra of starch/PEG 400 heated at 60°C, starch/PEG 400 heated at 70°C, and starch/PEG 400 heated at 80°C is presented in Figure 3. It shows that the four group (C-O-C, C=O, C-H, O-H also present in PEG/starch mixture heated at 60,70, and 80. The band peak intensities are presented in Table 2.
Figure 3. FTIR spectra of starch/PEG 400 heated at 60°C, starch/PEG 400 heated at 70°C, and starch/PEG 400 heated at 80°C.

The result in table 2 indicated that the band peak position in starch and starch/PEG400 mixture show no dissimilarity with those obtained by Jagadish et al [15] and Yu et al [16] with only slightly peak shift, in the functional group. The incorporation of PEG400 into starch shifted the band position of O-H from 3418.97 cm$^{-1}$ into 3456.59 cm$^{-1}$ as shown in PEG/starch mixture heated at 70°C, indicating there is interaction between starch and PEG. The PEG molecule may disturb the interaction between starch molecules. in starch. The highest shift of peak position of O-H was shown by PEG/starch mixture heated at 70°C. This result is coincident with the trend of WVTR value in table 1. The graph of the data is shown in Figure 3.

Table 2. Peak absorbance in starch, PEG 400, starch-PEG400 (60°C), starch-PEG400 (70°C), starch-PEG400 (80°C).

| Groups | Starch | PEG 400 | S+PEG400 (60°C) | S+PEG400 (70°C) | S+PEG400 (80°C) |
|--------|--------|---------|----------------|----------------|----------------|
| O-H    | 3418,97| 3469,12 | 3449,84        | 3456,59        | 3417,04        |
| Intensity | 0,048421 | 0,088319 | 0,1            | 0,096221       | 0,1            |
| C-H    | 2930,00| 2902,03 | 2931,93        | 2925,17        | 2921,32        |
| Intensity | 0,023248 | 0,067364 | 0,047665       | 0,054608       | 0,069982       |
| C=O    | 1642,46| 1635,71 | 1653,07        | 1637,64        | 1646,32        |
| Intensity | 0,015229 | 0,034638 | 0,041122       | 0,058114       | 0,034113       |
| C-O-C  | 1157,34| 1102,37 | 1166,02        | 1155,41        | 1166,02        |
| Intensity | 0,047919 | 0,1      | 0,032949       | 0,039149       | 0,022622       |
The change of peak position when PEG was present in starch was also observed C-H group where it was shifted from 2930.00 cm\(^{-1}\) to 2925.17 cm\(^{-1}\), the C=O group changed from 1642.46 cm\(^{-1}\) to 1637.64 cm\(^{-1}\), and the C-O-C group change from 1157.34 cm\(^{-1}\) to 1155.41 cm\(^{-1}\). These results again clearly showed that there was a strong interaction between starch and PEG400.

The intensity values of the peaks also increased when PEG400 was added to starch indicating that adding PEG 400 to starch increasing the number of bonds in the group, and similar result also shown by other study [16]. However, the incorporation of PEG into starch did not create a new peak indicating there was no new chemical bonding during the process of coating. Ortega [14] also reported similar result.

4. Conclusions

The processing of starch-plasticizer (PEG 400) for 30 minutes and temperature variation (60, 70, 80) \(^{o}\)C is obtained optimum temperature at 70\(^{o}\)C, the starch processing and the addition of PEG 400 strongly influenced the increase of moisture barrier properties and made the paper have more flexible on the processing of starch.

In the mixing of plasticizer molecules with starch there was a strong interaction with the peak shift in the four groups (O-H, C-H, C=O, and C-O-C) and increased number of bonds in the OH, CH, and C=O groups for mixing starch-PEG1000 shown by increased intensity. Both the starch-PEG1000 and starch-glycerol samples do not form new bonds.

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