Water vapour and grease resistance properties of paper coating based starch-bentonite clay

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Abstract. In the present study, the water vapour and grease resistance properties of paper coating based starch – bentonite clay has been investigated. The clay concentration was 0%, 10%, 15%, 23%, 30%, 40% dan 50% w/w. The composites were prepared by solution casting and coated on the surface of the paper, and analysed using Payne cup method (water vapour transmitter rate-WVTR), grease resistance test and X-Ray diffraction (XRD).

The WVTR results showed that the addition of clay improved water vapour barrier properties and the most optimal improvement was obtained at clay concentration in the range of 10 – 23 wt %. However, the opposite trend was observed for grease resistance properties which showed that the grease resistance decreased with increasing clay concentration. XRD results showed that starch entered clay gallery and formed intercalated bilayer structure both at clay concentration of 10 and 23 wt % wt. The clay/starch composite (23 wt %) was more ordered and higher amount of starch chains entered gallery than than those of clay/starch (10 wt %) supporting better water barrier properties at high clay concentration.

1. Introduction

Studies and developing of food packaging material based green material was of great interest in the recent decade [1]. Packaging was used to keep freshness and quality of food during storage. One of method to use polymer is by coating it on the surface of a paper. Conventional paper coating available in the market applied synthesis polymer such as Polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polystyrene (PS) [2]. The synthesis polymers were attractive due to their cheap, superior gas and barrier properties compared to natural polymer. These synthesis polymers are non renewable and non biodegradable leading to waste disposal problems, global warming, and health issue. Therefore, natural polymers such as shellac, polylactic acid (PLA), polyhydroxyalkanoates (PHAs), and starch may be an alternative solution to those problems.

In the present studies, starch is used as paper coating material. It is produced in Indonesia, abundant and cheap. However, starch tends to have poor water barrier and mechanical properties [3]. Many efforts have been done to improve the properties of starch. One of them was to mix starch with other polymer such polycaprolactone [4], poly vinyl alcohol (PVA) [5-7] and polylactic acid (PLA) [8]. The use of PVA improved significantly the mechanical properties of starch. However, PVA has poor water barrier properties and also the price is expensive. Other method is to apply silica and clay [3]. In the present report, bentonite clay with different concentration has been applied to starch from local resources. The composite was then coated onto the surface of a paper. As the properties of starch were very affected by
heating temperature [9,10], and source/type [11], in the present studies investigation was conducted to obtain the optimal heating temperature, and was focused on water vapour barrier properties and grease resistance properties.

2. Experimental Methods
The cassava starch was obtained from local resources and bentonite clay was supplied by Southern Clay Products with the tradename Cloisite Na+. The starch composites were prepared by solution casting by heating and stirring 1) at 60,70,80, 95 °C for 60 minutes, 2). at 95 °C for 30, 60, 180 minutes, while the clay/starch composites were prepared by heating and stirring at 80 °C for 60 minutes. The composites were then coated on the surface of papers.

The water barrier properties of the samples were determined by Payne cup Analysis method at 85% relative humidity, and the water vapor transmission rate (WVTR) was calculated by the following equation [12]:

\[
WVTR = \frac{(240 \times m)}{(S \times t)}
\]

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.

The XRD measurements conducted in this report used CuK\(_{\alpha1}\) as the source of x-rays (1.54186 Å) at 40 mA and 40 kV. A divergent slit of 0.5°, anti scatter slit of 1°, and mask of 15 were used.

3. Results and Discussions
Preliminary studies were conducted to find the optimal temperature and heating time of shellac. The amount of water passed through the paper coating of starch increased with the increase of time for both samples prepared by heating at different temperature i.e. 60,70,80, 95 °C for 60 minutes (Figure 1) and at different heating time at 95 °C (Figure 1b). The WVTR value of samples of Figure 1a calculated using equation 1 was 1026.67, 757.33, 722.67, 930.67 g/(day.m\(^2\)), respectively whereas for samples of Figure 2 was 1088, 930.67, and 984 g/day.m\(^2\), respectively. The WVTR of the paper (no starch) was 928 g/(day.m\(^2\)). These results showed that the water barrier property of starch was affected by temperature and heating time. In our sample, the optimal condition of starch preparation was 80 °C and 60 minutes and used as preparation condition when starch was mixed with clay. It is interesting that heating starch at 95 °C produced starch paper coating having worse water paper barrier properties that the paper. The gelatinization of starch related to crystal structure [9] . Other researchers found that the gelation temperature of starch was 70 [9], and 64 [10]. The gelatinization temperature depends on the type of starch [11].

![Figure 1. The amount of water passed through the starch paper coating prepared at different temperature for 60 minutes](image-url)
Figure 2. The amount of water passed through the starch paper coating prepared at 95 °C for different heating time.

Figure 3 showed the WVTR of clay starch composite coated on paper prepared by mixing at 80 °C and 60 minutes. The concentration of clay was 5, 10, 15, 23, 30, 40 dan 50 wt %. The data in Figure 3 was presented as percentage of water barrier properties improvement in Figure 4. The water barrier properties increased around 22.13% (from 928 to 722.67 g/(day.m²) ) but below previous study (27 %) [13] when paper was coated with starch. The incorporation of 5 wt % clay to starch only improved 1.44 % the barrier properties of starch. The significant improvement of starch barrier properties was achieved significantly when the concentration of clay was 10 until 23 wt% (from 722.67 to 450.67 g/(day.m²)) or 17.24 to 29.31 %. Further clay addition (30-50 wt% still improved the starch properties. The structure of clay is like layers, and the space between the layers called gallery. If polymer chains filled the gallery then small molecules (water or gas) took a longer path when passed through the composite. Hence clay acted as a barrier for the small molecules.

The best water barrier properties produced in this study (400 g/(day.m²) of 50 wt% clay ) was still below the water barrier properties of conventional paper coating of synthesis polymer (90 g/(day.m²)). However, the thickness of paper coating of synthesis polymer was much higher than that of our samples. Thickness of samples affected the barrier properties [14].
Figure 4. Water barrier properties improvement of starch when clay was added.

Figure 5 showed the grease resistance of clay-starch paper coating which showed that the grease resistance decreased with the increase of clay concentration. This may due the interaction between glucose in starch and cooking oil which are both non polar. The addition of clay to starch may reduce the interaction; hence the amount the cooking oil passed the samples increased with the increased clay concentration. The grease resistance of the composite of 5 wt% clay was still lower (110 g/(day.m²) of 5 wt% clay) than that (57 g/(day.m²)) of conventional paper coating.

Figure 6 showed the XRD data of clay, clay/starch (10 wt%) and clay/starch (23 wt%). Three type of structure may be produced when polymers mixed with clay, i.e. microcomposite, intercalated nanocomposite, exfoliated nanocomposite [15]. The XRD showed that the starch chains entered the clay gallery as shown by the shift of the 2θ angles from 7.42 (11.9 Å) in the XRD trace of the clay to 4.96 (17.8 Å) in the XRD trace of the clay/starch composite (10 wt %) and 4.90 (18 Å) in the XRD trace of the clay/starch composite (23 wt %). The structure was intercalated nanocomposite, while bilayer structures were formed for both concentration. The amount of starch entered the clay gallery was higher and the clay
layer was more ordered within the polymer matrix at 23 wt% clay than those of 10 wt% clay as shown lower angle and higher intensity. These results supported the water barrier properties increased with the increase of clay concentration in Figure 3.

Figure 6. The XRD traces of clay, clay/starch (10 wt%), and clay/starch (23 wt%)

4. Conclusion
It has been shown the water barrier properties of starch were temperature and heating time dependence. In this study, the optimal properties were achieved when starch was heated at 80 °C for 60 minutes. The incorporation of clay improved the water barrier properties of starch, and the level of improvement was related to how clay layers dispersed in polymer matrix.

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