Effect of bentonite nanoclay filler on the properties of bioplastic based on sago starch

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Abstract. The non-biodegradability of plastic packaging has led to a renewed interest in packaging materials based on biopolymers. The biopolymer used in this study which is sago starch is versatile and abundantly available in nature. In the present study, sago starch (SS)/polyvinyl alcohol (PVA) films were plasticized with glycerol (GLY) and reinforced with nanoclay bentonite (BEN) at 1 wt.%, 3 wt.% and 5 wt.% using solution casting method. The films prepared were characterized for their physic-chemical properties using conventional methods. Findings have shown that 5 wt.% BEN reinforced thermoplastic sago starch (TSS) showed highest weight loss in degradation test, greatest improvement in tensile strength and the lowest water absorption in swelling test. The introduction of BEN in the TSS showed changes in the intensification of O-H bond and Si-O bond. Furthermore, inclusion of BEN had reduced the vacant spots of SS/PVA/GLY matrices. Hence, the introduction of BEN in TSS composite had improved the film's properties. This study suggests that SS/PVA/GLY/BEN film has the potential for packaging application to lessen the dependence on non-degradable plastic packaging.

1. Introduction
Recent studies on biodegradable films indicates a progressive advancement in utilization of starch as potential source. Sago starch (SS) is the most underutilized and novel source of starch as compared to maize, cassava, and potato starches mainly because of the sustainability of the crop [1,2]. SS is produced from the trunk of sago palm (Metroxylan sangu) which is indigenous to Southeast Asia region. Malaysia is the third sago production in the world after Indonesia and Papua New Guinea, where sago plantation can be widely found in Mukah districts, Sarawak [3]. According to Ismail & Zaaba [4], SS is a viable source for bioplastics due to its high amylopectin content which contributes to better tensile properties. Abral et al., [5] supported that apart from this unique characteristic, SS exhibits physicochemical properties like cassava and potato starches.

SS can be used as raw material for bioplastic due to its abundance, low cost and renewable. [6,7]. However, due to its hydrophilic nature of the starch, starch-based plastics are brittle, have poor mechanical properties [9], and water barrier [8]. To overcome these disadvantages, plasticizers such as glycerol (GLY) and polymer blending such as polyvinyl alcohol (PVA) are often added to increase the flexibility and overcome brittleness of the plastic films [10,11,12,13]. Studies have shown that PVA is highly compatible with starch due to its ability to form stable hydrogen bonding in the polymer network...
Furthermore, incorporation of nanoclay filler in nano-scale between the range of 0 to 5 wt.% to the starch-based polymer matrix capable to enhance the mechanical and water barrier quality [15-17] as well as improved biodegradability of the bioplastic films [17]. Bentonite (BEN) clay is derived from alteration of volcanic ash. It is relatively low cost, non-toxic and naturally abundant [18]. Starch-based plastics reinforced with BEN have shown improved mechanical strength, thus solved the water barrier limitation. This due to its fine particle size that leads to good penetration into starch composite matrices which ensure great interaction with other molecules in composite matrices [18-20].

The aims of this study are to develop sago starch-based bioplastic from raw material and characterize its properties. Specifically, the objective of this work was to investigate the effects of incorporating BEN nanoclay on the mechanical, physicochemical, and biodegradability to produce a good biodegradable plastic in hope to provide alternative to plastic packaging.

2. Methodology

2.1 Raw materials

Food grade of SS, PVA (molecular weight of 85 000-146000, hydrolysis degree of 99%), GLY (molecular weight: 92.09 g/mol, 60–100% concentration) and BEN hydrophilic nanoclay.

2.2 Preparation of SS/PVA/GLY/BEN bioplastic film

10 wt.% SS solution was prepared by heating at 50 °C with continuous stirring for 30 minutes. 10 wt.% of PVA solution was prepared by mixing PVA in distilled water with continuous stirring at 90 °C until fully dissolved. Both solutions were mixed with ratio of 6:4. While mixing, 30 % of GLY was added slowly to the solution. Solution was continuously stirred for at 50 °C for 30 minutes until homogeneously mixed [11,12]. The solution mixture was casted onto a petri dish and air dried. After completely dry, the SS/PVA/GLY pristine film was peeled off and cured at 60 °C for 2 hours.

For the reinforced SS bioplastic, firstly, nanoclay BEN suspension was prepared by dispersing 1 wt.% BEN into 50 mL distilled water. Then, it was sonicated at 25-kHz frequency for 10 minutes. BEN suspension was added slowly to 100 mL SS/PVA/GLY solution with continuous stirring. Next, the mixture was sonicated for 30 minutes [21–23]. Mixture was casted onto a petri dish and drying process was performed as previously stated. SS/PVA/GLY bioplastic of reinforced BEN with 3 wt.% and 5 wt.% loadings, were prepared following the similar method. Table 1 shows the composition of SS/PVA/GLY/BEN bioplastic films prepared.

| Sample  | SS (%) | PVA (%) | GLY (% based on total weight of SS and PVA) | BEN (wt.% based on total weight of SS and PVA) |
|---------|--------|---------|------------------------------------------|-----------------------------------------------|
| C1 (pristine TSS) | 60 | 40 | 30 | 0 |
| C2      | 60 | 40 | 30 | 1 |
| C3      | 60 | 40 | 30 | 3 |
| C4      | 60 | 40 | 30 | 5 |

2.3 Characterization of SS/PVA/GLY/BEN bioplastic films

2.3.1 Soil burial test. Film was cut into 50mm x 60mm and buried in containers that contain 4cm depth of natural soil. The containers were kept in the laboratory and maintained at ambient temperature [25]. Degree of degradation of the film was recorded by measuring its lost in weight over time. Films initial weight was taken before burying and the buried films were weighed every 5 days for 30 days. The films were cleaned to remove soil and contaminant and then dried before weighing. The weight loss percentage was calculated using the following equation,
Weight loss (%) = \frac{W_i - W_d}{W_i} \times 100 \quad (1)

where: \( W_i \) is the initial weight of the film (g) and \( W_d \) = dry weight of film after being cleaned and dried (g).

2.3.2 Swelling test. Films were cut to 60mm x 10mm dimension and measurement were performed according to ASTM D570. Films were dried in the oven at 50 °C for 24 hours until reaches a constant weight. The films were immersed in distilled water for 24 hours. Next, films were blotted with a dry cloth and weighed. The swelling test was performed for 10 days. Water absorption was calculated as,

\text{Water absorption} (%) = \frac{M_1 - M_0}{M_0} \times 100 \quad (2)

where \( M_1 \) is the final weight of the film (g) and \( M_0 \) = dried weight of film (g).

2.3.3 Tensile analysis. The test was performed according to ASTM D882 using texture analyser. Films were cut into dimension of 60mm x 10mm. the test was performed at 5 kg load cell and initial grips distance of 30mm, and crosshead speed of 10mm/s [10,26]. The tensile strength, elongation at break and Young’s modulus were calculated as follows,

\text{Tensile strength} (\text{Pa}) = \frac{\text{mass}(kg) \times \text{distance}(m)}{\text{time}(s^2) \times \text{area of film}(m^2)} \quad (3)

\text{Elongation at break} (%) = \frac{\text{change in length before break}(m)}{\text{initial film length}(m)} \times 100 \quad (4)

\text{Young’s modulus} (\text{Pa}) = \frac{\text{tensile strength}}{\text{elongation at break}} \quad (5)

2.3.4 Scanning Electron Microscopy (SEM). The fractured surfaces of the samples were observed using SEM at 15kV after undergoing tensile test. [21,24].

2.3.5 Fourier Transformed Infrared (FTIR). The spectra were recorded at a resolution of 4 cm^{-1} with spectral range from 500 to 4000 cm^{-1} [13,24].

3. Results and Discussion

3.1 Biodegradability of SS/PVA/GLY/BEN bioplastic films
The degradation of films was due to the moisture loss and growth of microorganism presence in the soil. After 30 days of degradation test, the samples lose their shape and structural integrity. The SS/PVA/GLY blends and SS/PVA/GLY/BEN nanocomposite films shrank in their original sizes and were more fragile with wrinkle appearance as shown in figure 1. These samples also observed colour changes and become slightly yellowish after degradation test compared to the initial appearance as depicted in figure 2. This was due to the presence of SS that is prone to the strong attack by microorganism. The microorganisms consume the SS and weaken the structure the films [27,28].
In Figure 3, the percentage of weight loss after soil burial is continuously increasing with days. However, the weight loss speed reduces as the time of test progresses. This is because there were lesser biodegradable components such as SS, PVA, BEN to be degraded in the samples as time goes by [29]. After 30 days of observation, SS/PVA/GLY composite film exhibited lowest weight loss percentage of 30.94% while nanocomposite film with the highest BEN loadings (5 wt.%) showed highest weight loss of 40.02%. The biodegradability rate increased with BEN loadings. The biodegradable nature of BEN enhanced biodegradation rate of BEN reinforced TSS [29]. Biodegradability of pristine SS/PVA/GLY bioplastic was improved after incorporating BEN into the blend. This could be due to the nature of the pristine-layered silicates. The intercalated-layered silicates of BEN were well distributed in TSS composite matrix in which leads to improve contact between the matrix and BEN surface. This good interaction caused SS bioplastic to fragment readily and enhances the degradation rate [30,31].

3.2 Chemical properties of SS/PVA/GLY/BEN bioplastic films

Referring to IR spectra in fig. 4, the strong and broad band around 3260 – 3272 cm⁻¹ was assigned to the –OH stretching for SS, PVA and GLY, respectively. [21,22]. Peak observed around 1038 cm⁻¹ was attributed to C–O stretching of SS/PVA/GLY blend [7,22]. The -OH peak reduced to a lower wavelength which was from 3281 to 3271 cm⁻¹ after the introduction of bentonite. The changes in the intensity and wave number of -OH stretching vibration indicated that BEN exhibited good dispersion and compatibility with the SS/PVA/GLY composite system [22]. The -OH peak broaden with BEN concentration reflected the formation of more stable hydrogen bonds between BEN and composite system [32].

C–O peaks was found to shift slightly from 1038 to around 1032 cm⁻¹, 1036 and 1035 cm⁻¹ and experienced intensity reduction which were attributed to the Si–O bonding due to addition of BEN which contain Si [33]. The clear peak observed at 2920–2950 cm⁻¹ and 845 – 850 cm⁻¹ was corresponded to C–H stretching and C–H bending, respectively. Moreover, peaks detected at 1416–1420 cm⁻¹ were
associated with CH$_2$ group [15]. Band observed at 1640–1650 cm$^{-1}$ was referred to OH bending. Reduction of frequency of OH bending after introduction BEN in SS/PVA/GLY matrices indicate the interaction between Al from BEN with OH group [28].

![FTIR of TSS/PVA/GLY at different BEN loadings (wt.%)](image)

**Figure 4.** FTIR of TSS/PVA/GLY at different BEN loadings (wt.%).

### 3.3 Water absorption of SS/PVA/GLY/BEN bioplasic films

Figure 5 shows that the absorption of water occurred rapidly at the initial stage of absorption process because all samples are free of unbound water and have more -OH groups to form hydrogen bonding with water molecules. The absorption rate slowed down gradually after day 1 until equilibrium at day 7. After day 7, the change in weight of composite film were exceedingly small which is not significant and can be assumed that the water uptake of composite films had reached maximum [15,34]. BEN reinforced SS bioplastic experienced a lower water uptake compared to non-reinforced film. Addition of BEN enhanced the water resistance of the nanocomposite system. This is because BEN contain hydroxyl groups that can form hydrogen bonds with the composite system. This strong structure could reduce the diffusion of water molecules in the film [15].

![Water absorption (%) of TSS/PVA/GLY/BEN](image)

**Figure 5.** Water absorption (%) of TSS/PVA/GLY/BEN.
However, the water absorbed by the film reduces as the BEN loadings increases. This could be explained with the increase in -OH groups available to from hydrogen bond with composite system when BEN concentration increases [21]. Referring to the IR spectra in figure 4, -OH peak broaden as BEN concentration increased which indicates more hydrogen bonds were formed. Therefore, free water molecules do not interact as strongly as with nanocomposite films as compared to the composite films alone [17]. Thus, SS/PVA/GLY blend showed the highest water absorption which is 76.22%, while 5 wt.% BEN reinforced nanocomposite film gave the lowest water absorption at 46.59%.

3.4 Morphological studies of tensile fractured surfaces of SS/PVA/GLY/BEN bioplastic films
SEM micrographs of the tensile fractured surface of SS bioplastic at different BEN concentration are depicted in figure 6. As shown in figure 6(a), there were voids or vacant spots in nonreinforced SS bioplastic. The SS bioplastic produced was homogenous as no remaining starch granules can be observed. In figure 6(b), with the addition of 1 wt.% BEN, however, did not show significant improvement as there are still many voids observed on the fractured surface. SS bioplastic reinforced with 3 wt.% BEN in figure 6(c) shows that the vacancies were filled by BEN particles as there were reduction in voids.

The 5 wt.% reinforced SS bioplastic as shown in figure 6(d) also exhibited low void content but experienced some BEN agglomeration at the same time. The occurrence of pores and voids would affect the tensile strength, Young’s modulus, and elongation at break of samples as these voids indicated weakness on the rigidity of the nanocomposite [21,35].

Figure 6. SEM image of SS/PVA/GLY fracture surfaces at BEN loadings (a) 0 wt.%, (b) 1 wt.%, (c) 3 wt.%, and (d) 5 wt.%.

3.5 Tensile properties of SS/PVA/GLY/BEN bioplastic films
Table 2 shows the effects of BEN loadings concentration on the tensile strength, Young’s modulus, and elongation at break of SS/PVA/GLY bioplastic films, respectively. Generally, inclusion of BEN improved the tensile strength of SS bioplastic. Tensile strength of SS bioplastic increases with increasing BEN concentration. The high specific surface area and particle size resulted in better dispersion of BEN between SS/PVA/GLY composite matrices which favour the interfacial interaction. Tensile strength increases from 0.3276 Pa for 1 wt.% BEN to 0.4412 Pa for 3 wt.% BEN. Referring to figure 6, it was found that vacant spots within composite matrices reduced with BEN loadings which indicate that BEN
is compatible with the composite matrices as it filled up the voids. When sufficient contact area is provided to react with the SS/PVA/GLY matrices, the wetting and adhesion of the matrices to BEN filler is also enhanced, which subsequently promote stronger bonding at the interfaces [29,36]. On the other hand, addition of 5 wt.% BEN was found to slightly improve the tensile strength to 1.77% from 3 wt.% loading. More BEN promotes agglomeration of fillers to occur, and these agglomerates initiates formation of voids. In figure 6(d) shows that several agglomerated BEN clusters were found on the fractured surface of nanocomposite with 5 wt.% BEN.

Table 2. Tensile properties of SS/PVA/GLY/BEN bioplastic films.

| Sample | Tensile strength (Pa) | Young’s modulus (Pa) | Elongation at break (%) |
|--------|-----------------------|----------------------|-------------------------|
| C1     | 0.2936                | 0.1961               | 149.72                  |
| C2     | 0.3276                | 0.2411               | 135.86                  |
| C3     | 0.4412                | 0.3492               | 126.35                  |
| C4     | 0.4490                | 0.6072               | 73.93                   |

Young’s modulus of SS/PVA/GLY bioplastic films increased with BEN concentration as shown in table 2. Young’s modulus increased gradually from 0.1961 Pa to 0.2411 Pa, to 0.3492 Pa for 0 wt.%, 1 wt.% and 3 wt.% BEN loadings, respectively. Furthermore, a sharp increment to 0.6072 Pa was observed when BEN loading was 5 wt.%. BEN can reinforce the SS/PVA/GLY matrices which hindered the mobility of surrounding chains in the matrices, thus increasing the matrix stiffness [20,29].

Elongation at break of SS/PVA/GLY/BEN bioplastic films decreases with the increasing in BEN loading. The elongation at break dropped slightly from 149.72% to 135.86% for 0 wt.% and 1 wt.% of BEN loadings, and then reduces to 126.35% at 3 wt.% BEN. The elongation at break further reduces drastically to 73.93% after inclusion of 5 wt.% BEN loading. This observation is common for polymeric materials reinforced with inorganic fillers. Inorganic reinforcing fillers are stiffer than the matrices and deformed less which leads to overall reduction in the matrices strain. The filler reinforced TSS was said to undergo improvement in stiffness and brittleness property [17,21,30].

4. Conclusion
SS/PVA/GLY bioplastic with and without BEN had been successfully prepared by casting method. SS bioplastic reinforced with 5 wt.% BEN showed the highest weight loss of 40.02% in degradation test. However, the same SS bioplastic observed the lowest water absorption of 46.59%. SS bioplastic reinforced with 5 wt.% of BEN also exhibited the highest tensile strength and Young’s modulus of 0.449 Pa and 0.6072 Pa, respectively, and the lowest elongation at break of 73.93%. Based on FTIR spectra, increased in BEN loadings contribute to the wavelength reduction of -OH band representing the formation of more stable hydrogen bonds between BEN and composite system. Interaction of Al and Si from BEN with OH and C-O in SS bioplastic matrices was observed after addition of BEN. In SEM micrographs of the tensile fractured surface of TSS, introduction of BEN filler contributed to void reduction in TSS composite.

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