Characteristics of Thermoplastic Potato Starch/Bentonite Nanocomposite Film

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Abstract. The aim of this study is to investigate the effect of bentonite towards thermoplastic potato starch nanocomposite films on the mechanical, microstructure and physical properties. The nanocomposite films were prepared using bentonite nano filler (0, 1, 5, 10, 15 and 20%) through solution casting technique. Obtained result indicate that, tensile strength increased significantly with increasing bentonite content and the highest tensile strength was recorded for nanocomposite film with 20% bentonite content. Meanwhile, elongation at break increased as the bentonite content increased from 0 to 15%, however significantly decreased at 20% bentonite content due to ductile structure and anti-plasticizing effect. Besides, good dispersion between bentonite nano filler and starch matrix with slightly remaining angglomerates was evident in scanning electron microscopy (SEM) image. Overall result shows that the addition of bentonite nano filler in potato starch film significantly influenced the properties of the films.

1. Introduction

Nowadays, there has been vast applications in biomaterials for biomedical engineering, and one of the growing interest is biodegradable starch based biopolymer. Starch is a natural source which can easily extracted from agricultural raw materials and known as the most abundant, renewable, non-toxicity, biocompatibility and readily biodegradable with thermoplastic behaviour at low cost [1–3]. Besides, starch possess similar properties to synthetic polymer and thus they are one of the potential candidates for replacing current synthetic materials.

Starch possible to process into thermoplastic materials through disruption and plasticization of starch macromolecules by heating in the presence of water and plasticizer, such as glycerol. Nonetheless, thermoplastic starch (TPS) products are water sensitive and would lead to poorer mechanical and physical properties, due to their hydrophilic nature. In order to improve the mechanical properties and water resistance, starch can be altered by incorporation of an inorganic reinforcing material to form composite products [4, 5]. Recently, special attention has been focused on the use of nano sized fillers into starch matrix to form nanocomposites. The application of nanocomposites could yield significant enhanced mechanical properties of starch based materials as...
compared to conventional micro composites. This is because the mutual effect between filler at nanometer size permits them to form molecular bridges in polymer matrix.

Nanoclays are the most employed nanofiller for polymers because of its natural source and high modulus of clay platelets which mains a significant role to improve the mechanical properties in nanocomposites film. Furthermore, nanoclay is a naturally abundant toxin-free mineral and relatively low cost which can be used as one of the components in biomedical application [6]. Several studies have investigated the development and characterization of starch nanocomposites film using bentonite clay. The results showed significant improvement in mechanical properties of potato starch nanocomposite films [7]. Hence, resolving the barrier of starch-based film, usage of clays has proved to strengthen the mechanical properties of TPS.

Therefore, in this study natural bentonite was introduced as nanofiller to prepare potato starch nanocomposites film through solution casting method. Nanocomposites film with different bentonite content were prepared to investigate the effect on the tensile and microstructure properties.

2. Materials and method

2.1. Materials

Commercially available potato starch, \((C_6H_{10}O_5)_n\) (HmbG Chemicals) was used as matrix material and bentonite powder from (Multifilla Bhd) was used as nanofiller. Glycerol, \((C_3H_8O_3)\) obtained from (HmbG Chemicals) was used as plasticizer. The selection of the materials were determined according to the requirement of biomedical application, as the investigations reported that:

i. Potato starch have ability to improve its durability, good tissue integration and did not induce a pathological foreign body reaction.

ii. Bentonite is from natural source and have high modulus clay platelets to attain mechanical properties. The bentonite also have barrier properties in which able to inhibit the diffusion of water and oxygen.

iii. Glycerol have better performance in producing biodegradable film compared to sorbitol.

2.2. Preparation of the thermoplastic starch films

Starch nanocomposites films were prepared via solution casting technique. About 5g of potato starch was first dispersed in 100 ml deionized water with (30% relative to dry starch) of glycerol content according to the corresponding run of experiments. The mixture was then heated to 85°C in a water bath for 30 min under constant stirring. Specified amount of dried Bentonite and HA were dispersed at room temperature in 40 ml deionized water with the following mixing modes:

i. Mechanical mixing at 1000 rpm for 30 minutes, using a RW 20 mixer (IKA, USA) in a 100 ml beaker.

ii. Sonication mixing for 30 minutes, perform on a HD 2200 ultrasonic homogenizer (Bandelin, Germany) with the high frequency power at a frequency of 20 kHz and 6 mm probe diameter.

| Table 1. Formulation of thermoplastic potato starch nanocomposites film. |
|-----------------------------|----------------------------------|---|---|---|---|
| Material                    | B1 | B5 | B10 | B15 | B20 |
| Potato starch (g)            | 5  | 5  | 5   | 5   | 5   |
| Distilled water (mL)         | 100| 100| 100 | 100 | 100 |
| Glycerol (%)                 | 30 | 30 | 30  | 30  | 30  |
| Mixing temperature (°C)      | 85 | 85 | 85  | 85  | 85  |
| Bentonite (%)                | 1  | 5  | 10  | 15  | 20  |

The nanofiller suspension was added to the aqueous dispersion of starch and the mixing was continued for 30 minutes at 85°C. Subsequently, the mixture was poured homogeneously onto petri dish of 14 cm diameter. The mixture were then dried at 45°C in an oven with air force circulation. The dry films were removed from the petri dish and stored in a dessicator (40% of relative humidity) in a plastic bag for a week prior to testing. Thermoplastic starch films with varies content of bentonite was
denoted according to bentonite content as (B1, B5, B10, B15 and B20). Table 1 shows the formulation of thermoplastic potato starch nanocomposites film.

2.3. Tensile Test
The tensile test were performed as suggested by Sanyang et al. [8], and the tensile strength and elongation at break were determined according to the ASTM standard (D882-02) by using a 5kN INSTRON tensile machine. Film strips were cut into 70mm x 10mm sections are subjected to crosshead speed of 2mm/min and initial grip separation of 40mm. The test was conducted with three replication for each sample and the average value was calculated.

2.4. Microstructure Analysis
The microstructure of the film was observed by using scanning electron microscopy (SEM) model (Hitachi TM-3000) operated at acceleration voltage of 15kV.

3. Results and discussion
3.1. Tensile Test
The mechanical properties of thermoplastic potato starch nanocomposites films were studied through a tensile test. This test was conducted in order to investigate the influence of bentonite content onto the mechanical behaviour of the starch film. The results of tensile strength and elongation at break are illustrated in Figure 1. As shown in Figure 1(a), it is clearly indicated that the tensile strength of the starch films increased significantly with increasing bentonite content. The highest tensile strength value of 5.74MPa was recorded for films prepared with 20% bentonite content, meanwhile neat starch films prepared without bentonite filler showed the lowest tensile strength value of 2.5MPa. The improvement in tensile strength as the bentonite content increased were reported by several studies [9-11]. This behaviour proved that bentonite filler have reinforcing capability, which can optimize the host polymer properties when added at high content.

Figure 1. Tensile properties of potato starch film with different bentonite content, (a) tensile strength and (b) elongation at break.

Figure 1(b) shows the effect of mixing temperature on the elongation at break of the potato starch film. The significant drop in the in elongation at break (13 mm to 12.2mm) was observed as the increased in bentonite content (0% to 10%). This fact is probably due to poor dispersion of bentonite in the starch matrix that create high localized stresses in the matrix during tensile loading. However, a sudden increased in elongation (13.7 mm) was observed at 15% of bentonite content. This finding might be associated with better dispersion of bentonite into starch matrix and thus improve strength.
and flexibility of the films. On the other hand, the starch nanocomposites film with higher bentonite content shows reduction in elongation at break. This could probably due to reduce quality of bentonite dispersion which lead to the formation of bentonite tactoids.

3.2. Microstructure Analysis
Gelatinization process and dispersion of nanofillers into thermoplastic starch nanocomposites produces measurable changes by microstructures characterization. The changes between shape and size, as well as contacts between the phases are commonly observed during gelation process. Figure 2 shows the microstructure of potato starch nanocomposites films containing bentonite filler with different content of (0%, 1%, 5%, 10%, 15% and 20%).

![Figure 2. SEM image of potato starch nanocomposites film with different bentonite content: (a) B1, (b) B5, (c) B10, (d) B15, (e) B20 and (f) B20 tactoids.](image-url)
Observation from SEM image reveal the changes in microstructure development with increasing bentonite content. The surface morphology of potato starch nanocomposites film for all nanofillers content illustrated homogenous distribution structure on the surface area with no remaining starch granules. Figure 2(a) showed rougher surface with slightly agglomeration of nanofiller on the certain surface area which could be due to poor dispersion of bentonite filler onto starch matrix. Meanwhile, the nanocomposites film with 15% of bentonite content showed good dispersion and gradual smoothing with less visible agglomerates which can be observed in Figure 2(d). This is in good agreement with tensile result, which identified the nanocomposites film with 15% of bentonite content showed higher flexibility and strength. However, several agglomerates and tactoids in the size range of 55 μm was observed in the nanocomposites film with 20% of bentonite content due to poor dispersion as showed in Figure 2 (e) and 2 (f). This is in line with the elongation result that exhibited the lowest value.

4. Conclusions
Potato starch nanocomposites films, reinforced with different amounts of natural bentonite was successfully fabricated through a solution casting technique. The varying bentonite content significantly affected the properties of potato starch film by increasing the mechanical properties. The results displays that thermoplastic potato starch nanocomposites prepared with 15% of bentonite nanofiller shows the better strength and flexibility properties, and thus identified as desired nanofiller content in this study. This result was supported by microstructure analysis of the nanocomposites, which revealed more smooth and homogeneous surface of the film. These finding presents starch based nanocomposites film as a potential biopolymer for the development of biodegradable materials.

5. References
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