Preparation, Characterization and Mechanical Properties of Na⁺ Alginate/Na⁺ Bentonite Nanocomposite Film

Prasetia, Jemmy A. a)*, Saleh Wikarsa b), Sukmadjaja Asyarie b)

a) Department of Pharmacy, Universitas Udayana
b) School of Pharmacy, Institut Teknologi Bandung

Abstract

The clay-containing polymeric nanocomposites (CPNC) is a nanocomposite in which a nanoclay filler is added into polymer matrix. It causes change that exceeds of polymer mechanical characteristics initially. Sodium bentonite (NaB) is one of natural clay and contains about 80% montmorillonite. Sodium alginate (NaA) is a polymer that has a low mechanical properties. By cpnc system, it was expected that can improve the mechanical properties. The experiment was began by choosing the proper of swelling clay method (stirring, ultraturax and sonication) at concentration of 5%. The swelled clay was then added in various concentrations of 0, 2, 3, 4 and 5% into solution of polymer sodium alginate of 1%. These mixtures were then formed a film by film casting method. This thin solution was dried at 50 °C for 20 hours to form the NaA/NaB nanocomposite films. The characteristic of nanocomposite films were evaluated by using XRD and SEM and also the mechanical properties (tear resistance, tensile strength, percent elongation and modulus of elasticity), solubility test, water vapor permeability and bursting test. The clay swelled by stirrer, ultraturax and sonication produced the viscosity of 1263.33±5.77; 1740.00±0.00 and 2883.33±5.77 cPs respectively. The identification of nanocomposite films showed that the nanoclay experienced the exfoliation. While the mechanical properties showed that the tear resistance (TR) of each formula were 6.86±0.00; 16.01±1.13; 16.99±2.47; 18.62±1.70 and 23.52±1.70 N respectively. Tensile strength (TS) were 17.15±0.00; 40.02±2.83; 42.47±6.17; 46.55±4.24 and 58.80±4.24 MPa. Percent elongation (PE) were 18.97±0.69; 4.97±0.00; 6.11±0.62; 5.64±0.28 and 5.30±0.29. Mean while the modulus of elasticity (ME) for each formula were 90.48±2.90; 80.57±56.96; 694.12±58.03; 824.68±64.58, and 1108.70±20.32 MPa. In conclusion, the sonication was the best swelling clay method to produce nanoclay and there was enhancement mechanical properties along with increasing concentration of nanoclay in polymer matrix.

Keywords: clay-containing polymeric nanocomposites film, natrium bentonite, natrium alginate, characterization, mechanical properties

Introduction

Alginate is a natural polymer that has been widely used in pharmaceutical formulations such as emulsion stabilizers, suspending agents, binders and disintegrant tablets (Sudhakar, 2006). Alginate or alginic acid is a polysaccharide which can be obtained from brown algae (Phaeophyceae) and marine algae such as Laminaria Hyperborea, Ascophyllum nodosum and Macrocystis pyrifera. It is composed approximately 700-1000 of α-L-guluronic acid (G) and ß-D-mannuronic acid (M) that was normally found in the wall of the cell. Alginic acid in generally found as calcium, magnesium and sodium salts (Laurienzo, 2010). ß-D-mannuronic acid have an equatorial bond 1C4 while α-L-guluronic acid in axial bond 1C5.

Sodium alginate (NaA) can be used in a sustained release oral dosage form for its ability to delay the dissolution of the active ingredient. In addition, its benefits have also been studied in a microencapsulation. Gelation properties of guluronic residues with polyvalent ions such as calcium and aluminum, leads to form a cross-bonding connection (Sarmento, 2007). For example, coating material that made with alginete cross connection can withstand the release of active substances in artificial gastric fluid but not in intestinal fluid (Lee, et al., 1998). This fact causes the alginate has the potential to be developed into an enteric coating material. Based on the other studies, alginate films can be deformed so that it looks like a fracture line.
on the surface of the film. This fracture can be reduced by adding cross junction substance such as calcium. In addition, compared with other films of cellulose derivatives, alginate films have lower distance of break and elongation at break (Park, et al., 1993).

Clay-polymer nanocomposite is a combination of polymer matrix and a clay as a filler that has at least one dimension in the nanometer range (Kato and Usuki, 2006). Clay-polymer nanocomposite can be very interesting to study for academics and industries due to the addition of a small amount of filler in the polymer that will be able to improve the mechanical properties such as elasticity and strength properties of the polymer, permeability and also to the heat retention properties of the polymer exceeds the initially (Lagashetty, et al., 2005).

Clay is a material that is often used as filler in nanocomposite system because it is strong, rigid, abundant in nature, easily obtained at low cost and has a high surface area (± 750 m²/g). In addition, the clay has a simple structure that can be intercalated or exfoliated and can be chemically modified so that the system is compatible with the polymer dispersion to the nanometer scale. It is called with nanoclay (Gupta, 2008).

The material most commonly used as the nanoclay filler is sodium bentonite (NaB). Montmorillonite is the main constituent of bentonite. Montmorillonite, as well as a member of smectite clays groups, has a colloidal structure with very small particle size. It can only be identified by X-ray diffraction (Utracki, 2004). Smectite clay has a high capacity cation replacement, a good swelling in water and it is widely available in nature (Sorrentino, et al., 2006).

The purpose of this study was to produce a nanocomposite film from NaA as a polymer matrix and NaB as a filler at various concentration (2%, 3%, 4% dan 5%). It was expected that by clay-polymer nanocomposite method could improve the physical properties of NaA.

Material and Methods

Materials

Sodium algin ate was purchased from Wako Pure Chemical Industries, Ltd., Sodium bentonite (Opazil AM®) was obtained from PT. Sud-Chemie Indonesia, sodium dioctolene was purchased from Yung Zip Chemical Ind-Taiwan, PVP K-25 was purchased from ISP Technology Inc., Avicel PH 101, Amprotab, Primogel, Mg Stearate, Talc, Potassium Chloride, Hydrochloric Acid, Potassium phosphate monobasic, sodium hydroxide, distilled water.

Methods

Preparation of NaB magma

5 grams NaB was weighed and then dispersed over the 100 mL distilled water. Let it stand for 30 minutes. The magma swelling is done by 3 different ways. First, NaB was swelled by using stirrer at 1300 rpm for 1 hour. The second method, NaB was swelled by ultraturax at rotating of 8000 rpm for 30 minutes. The third method used sonicator at 60 amplitude for 30 minutes.

Preparation of NaA/NaB nanocomposite film

NaB magma weighed according to the percentage of a formulation (0, 2, 3, 4 and 5%) where the weights are based on dry weight of NaA used. 1% solution of NaA was prepared by taking the NaA into the water and then heated at temperature 60°C. This warm solution was then cooled until room temperature was reached. A weighed NaB magma was added into NaA solution under stirrer at 500 rpm for 1 hour. After that, the mixture was poured into film moulder and allowed at temperature 50°C. The dry films were peeled of and kept in desiccators before evaluation.

Minimum Film Forming Temperature (MFT)

15 mL of solution NaA/NaB nanocomposite films was poured into a petri dish diameter of 9 cm and then dried at different temperatures such as room temperature, temperature of 30°C, 40°C, and 50°C for 24 hours. The film formed was visually observed.

Surface Morphology

Surface morphology of the films was observed by scanning electron microscopy (SEM) JEOL ® JSM-6360LA. Nanocomposite film was cut to fit the size of the specimen container that has been spread with silver paste at some earlier point. The sample was then placed on top of the container, then dried at a temperature of 20 °C. The sample was then inserted into the device fine coat that has been set at voltage of 1.2 kV, 6-7.5 mA of electric current and 0.2 Torr of air pressure, for 4 min to obtain film with thickness about 400 Å.

X-Ray Diffraction (XRD)

X-ray diffraction pattern of film were recorded using X-Ray tool Diffraetometer type PW1710 BASED with a Cu radiation source with a wavelength of 0.154 nm, generated at 50kV and 300 mA as X-ray source. The samples were scanned in the range of diffraction angle (2θ) 5-50° with a speed of 1°/minute at room temperature, temperature of 30°C, 40°C, and 50°C for 24 hours. The film formed was visually observed.

Solubility in gastric fluid

A certain quantity of film was incubated in 25 mL HCl pH 1.2 for 2 hours at 37 °C under static conditions. Gastric fluid was removed and the film was dried in the oven until the weight constant. The diminution
weight was defined as the solubility of the film in gastric fluid (Dimantov, et al, 2004).

**Solubility in gastric fluid - intestinal fluid**
Firstly, a certain quantity of film was incubated in 25 mL HCl pH 1.2 for 2 hours at temperature 37 °C under static conditions. After 2 hours, the gastric fluid was removed and replaced with 25 mL of phosphate buffer pH 6.8 for 45 minutes at temperature 37°C in a static state. After 45 minutes, intestinal fluid removed and the film was dried in the oven until the weight constant. The diminution weight was defined as the solubility of the film in gastric fluid - intestinal fluid (Dimantov, et al, 2004). At the same time, it also observed the time taken by the film to dissolve in intestinal fluid.

**Water vapor permeability (WVP) studies**
The film was cut into a disc shape with a diameter of 1 cm, placed on open glass vials containing silica beads and held in place with a screw lid with a 0.61 cm² test area (Remunan-Lopez and Bodmeier, 1997). The vials were placed in a desiccator kept at 25±1°C and containing a saturated aqueous sodium chloride solution (75% RH). The weight gain was periodically recorded over 72 hours. The amount of water vapor permeated per-area was plotted against time and the slope of this relationship was the water vapor permeation rate (WVPR). The WVP coefficients of the films were calculated using the following equation (Pongjanyakul et al.,2005):

\[
WVP \text{ coefficient} = \frac{M}{A \Delta P_v h}
\]

Where M is the WVPR, h is the film thickness, A is the area of the exposed films, and \( \Delta P_v \) is the vapor pressure difference.

**Mechanical properties of films**
Mechanical properties such as tear resistance (TR), tensile strength (TS), percent elongation (PE) and modulus of elasticity (ME) of films were measured using a Texture Analyzer (Shimadzu® AGS 500D). The films were cut into 3 cm × 1 cm strips, and kept in desiccator before testing (ASTM, 2002; Pongjanyakul et al., 2005). The measurements were performed using a 5 kg loaded cell, a gauge length of 5cm, and a cross-head speed of 0.2 mm/s.

**Bursting Strength**
This test was based on ISO 2759:2001 on “Determination of Bursting Strength” using Digital Bursting Strength Tester UBS 700. The nanocomposite film was placed on a ring-shaped plate made of stainless steel with a diameter of 3.15 cm. The tool is then run to produce an air pressure on the surface of the film. The power of air pressure that causes film cracking is defined as bursting strength.

**Results and Discussion**

**Swelling clay method**
At the first measurement, the stirring method produced the viscosity 366.67±5.77 cPs, while ultraturax and sonication methods were 846.67±5.77 and 1316.67±5.77 cPs, respectively (Table 2). As addition, for all swelling method, at the first day until forth, the viscosity was quickly increase. It seems that the viscosity after 13 days was constant and the viscosity of stirring, ultraturax and sonication method were 1263.33±5.77, 1740.00±0.00, and 2883.33±5.77 respectively (Fig. 1).

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula (grams)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natrium alginate (NaA)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Natrium Bentonite (NaB)</td>
<td>0</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Aquadest</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

*) Based on dry weight of NaA used

By this fact showed that the sonication method was able to perform a highest viscosity and the time needed for processing was shorter than the others. This phenomenon occurred may be due to the sonication produced the higher energy. This energy make the silicate layer of clay is open. This condition also lead cationic ion that exist in interlamellar species of clay become free. The water molecules easily diffuse into interlamellar species causing a lateral expansion of the clay (Utracki, 2005).
The dispersing clay in distilled water caused the associated ions that are associated with the clay surface to diffuse out. The osmotic pressure pulls the ion away from the clay surface, whereas the electrostatic change tends to hold them near the surface. Eventually, a steady state is achieved and the electrostatic double layer is formed that keeps the clay platelets apart (Utracki, 2005).

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>596.67±5.77</td>
<td>1223.33±5.77</td>
<td>1896.67±5.77</td>
<td>783.33±5.77</td>
<td>1376.67±5.77</td>
<td>2193.33±5.77</td>
<td>1113.33±5.77</td>
<td>1606.67±5.77</td>
</tr>
<tr>
<td></td>
<td>990.00±5.77</td>
<td>1523.33±5.77</td>
<td>2493.33±5.77</td>
<td>1203.33±5.77</td>
<td>1683.33±5.77</td>
<td>2793.33±5.77</td>
<td>1263.33±5.77</td>
<td>1740.00±5.77</td>
</tr>
<tr>
<td></td>
<td>1326.67±5.77</td>
<td>1810.00±5.77</td>
<td>2893.33±5.77</td>
<td>1326.67±5.77</td>
<td>1810.00±5.77</td>
<td>2893.33±5.77</td>
<td>1326.67±5.77</td>
<td>1810.00±5.77</td>
</tr>
</tbody>
</table>

Data are the mean±SD. n=3

Minimum Film Forming Temperature (MFT)
For determining the MFT, the film was dried at room temperature, 30°C, 40°C dan 50°C for 24 hours. The result represent that at room temperature, the film was not formed as well as in temperature of 30°C. At temperature of 40°C, the film was still humid and sticky, while at temperature of 50°C could produce a dry film, clear and transparent. It is also easy to be detached from the film moulder.

Surface Morphology
NaB was swelled by sonication method then added into the NaA solution in several concentration according to the formulation of nanocomposite film (Table 1). All the formula were successfully prepared using film casting method at temperature 50°C. All film obtained were smooth and transparent with thickness 0.02 cm.

Figure 2-4 give SEM picture of surface NaA film, NaA/NaB nanocomposite film in concentration 3% and 5% respectively. They show the disperse degree of NaB as composite in NaA solution. It seems that the both figure was equal. It could be caused by the low concentration of NaB that added into the NaA solution. Moreover, NaB was in exfoliated condition that made it could not be detected in the picture (Yang, et al., 2009)

X-Ray Difraction (XRD)
The nanocomposite formation between NaA and NaB in the films was investigated using XRD (Fig. 5). NaB powder showed a diffraction peak at 31,14° (2θ), indicating the basal spacing peak and a thickness of the NaB silicate layer of 0,28 nm. Meanwhile, the NaA/NaB nanocomposite film at concentration 2%, 3%, 4%, 5% have no obvious basal spacing peak of NaB respectively. This supposed that the formation of exfoliated nanocomposite films was formed. The exfoliation can be formed because a low content of NaB that dispersed in the NaA polymer matrix (Alexandre and Dubois, 2000; Ray and Okamoto, 2003). Utracki, 2004, explained that
Table 3 Characteristic of nanocomposite film

<table>
<thead>
<tr>
<th>Evaluation</th>
<th>Formula 1</th>
<th>Formula 2</th>
<th>Formula 3</th>
<th>Formula 4</th>
<th>Formula 5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solubility test</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gastric fluid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (minute)</td>
<td>120.00±0.00</td>
<td>120.00±0.00</td>
<td>120.00±0.00</td>
<td>120.00±0.00</td>
<td>120.00±0.00</td>
</tr>
<tr>
<td>Solubility of film (%)</td>
<td>23.07±0.18</td>
<td>20.67±0.48</td>
<td>18.24±0.48</td>
<td>17.82±0.96</td>
<td>16.71±0.67</td>
</tr>
<tr>
<td><strong>Gastric fluid – intestinal fluid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (minute)</td>
<td>10.33±2.89</td>
<td>22.33±1.15</td>
<td>23.67±7.37</td>
<td>31.33±0.58</td>
<td>34.67±2.89</td>
</tr>
<tr>
<td>Solubility of film (%)</td>
<td>100.00±0.00</td>
<td>100.00±0.00</td>
<td>100.00±0.00</td>
<td>100.00±0.00</td>
<td>100.00±0.00</td>
</tr>
<tr>
<td><strong>Water vapour permeability coefficient (x10^3 g h^-1 cm^-1 mmHg^-1)</strong></td>
<td>3.37±0.05</td>
<td>2.23±0.12</td>
<td>2.21±0.14</td>
<td>2.12±0.00</td>
<td>1.86±0.03</td>
</tr>
<tr>
<td><strong>Mechanical strength</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tear resistance (N)</td>
<td>6.86±0.00</td>
<td>16.01±1.13</td>
<td>16.99±2.47</td>
<td>18.62±1.70</td>
<td>23.52±1.70</td>
</tr>
<tr>
<td>Tensil strength (MPa)</td>
<td>17.15±0.00</td>
<td>40.02±2.83</td>
<td>42.47±6.17</td>
<td>46.55±4.24</td>
<td>58.80±4.24</td>
</tr>
<tr>
<td>Percent elongation (%)</td>
<td>18.97±0.69</td>
<td>4.97±0.00</td>
<td>6.11±0.62</td>
<td>5.64±0.28</td>
<td>5.30±0.29</td>
</tr>
<tr>
<td>Modulus of elasticity (MPa)</td>
<td>90.48±2.90</td>
<td>805.70±56.96</td>
<td>694.12±58.03</td>
<td>824.68±64.58</td>
<td>1108.70±20.32</td>
</tr>
<tr>
<td><strong>Bursting Strength (kgf/cm²)</strong></td>
<td>1.32±0.31</td>
<td>1.69±0.44</td>
<td>1.48±0.19</td>
<td>1.48±0.40</td>
<td>1.48±0.41</td>
</tr>
</tbody>
</table>

Data are the mean±SD. n=3

Exfoliated nanocomposite film has basal spacing > 8.80 nm with the depiction of the separated platelets. Silicate layers that was exfoliated into the polymer matrix will be produced x-ray diffraction where the spectrum of the silicate is disappeared into spectrum of the polymer. This condition was not occurred in intercalation ones (Ray and Bousmina, 2005, Blanton, et al., 2000).

Solubility test

The solubility of film in gastric fluid from each formula (0%, 2%, 3%, 4% and 5%) were 23.07±0.18%, 20.67±0.48%, 18.24±0.48%, 17.82±0.96% and 16.71±0.67% respectively (Table 3). Meantime, the solubility of film in gastric fluid – intestinal fluid were 100% but each formula need a different time to solubilize. The time to solubilize for each formula (0%, 2%, 3%, 4% and 5%) were 10.33±2.89, 22.33±1.15, 23.67±7.37, 31.33±0.58, and 34.67±2.89 minutes (Table 3). In gastric fluid, the time for NaA film significantly decrease with increasing NaB in concentration 2%, 3%, 4% and 5%. Meanwhile, NaA/NaB nanocomposite film in 3%, 4% and 5% were comparable. In gastric fluid – intestinal fluid solubility test showed that the time to solubilize for NaA film was longer, with increment of NaB in polymer matrix. From data in above, it indicated that NaB could be inhibit the solubility of nanocomposite film.

Water vapor permeability (WVP) studies

Water vapor permeability experiments are used to evaluate the effectiveness of a film coating as a barrier to water (Baert, 1993; Guo, 1993; Okor, 1987; Zheng, 2005). The WVP coefficient was calculated using Eq. (2).

The WVP coefficient of NaA free film and NaA/NaB nanocomposite film with NaB content 2%, 3%, 4% and 5% were 3.37±0.05; 2.23±0.12; 2.21±0.14; 2.12±0.00 and 1.86±0.03 x10^3 g h^-1 cm^-1 mmHg^-1 respectively. WVP coefficient of NaA film was decrease with increasing NaB in concentration 2%, 3%, 4% and 5%.

It means that the addition of NaB could retarded the water vapor permeation. This results was analogous to the WVP characteristics of the CS-rectorite films, where rectorite retarded the water vapor permeation (Wang et al., 2007). NaB expand the barrier properties of film by creating a maze or tortuous path that retarded the progress of gas molecules through the polymer matrix (Khunawattanakul, et al., 2010, Sorrentino, et al., 2006).
Mechanical properties of films
Polymer films must be mechanically strong during processing, packaging, shipping, and storage. A series of experimental techniques have been used to assess the mechanical strength of polymer film. These data have been used to predict such properties as dissolution or the possibility of film defects (Rowe, 1983; Satturwar, et al., 2004; Gibson, 1989). Other scientist have also used mechanical testing to evaluate the effectiveness of plasticizers or to predict long-term storage stability (Gutierrez-Rocca, 1994; Fulzele, 2002; Gutierrez-Rocca, 1993; Wu, 1999).

The mechanical properties test showed that the tear resistance (TR) of each formula were 6.86±0.00; 16.01±1.13; 16.99±2.47; 18.62±1.70 and 23.52±1.70 N respectively. Tensile strength (TS) were 17.15±0.00; 40.02±2.83; 42.47±6.17; 46.55±4.24 and 58.80±4.24 MPa. Percent elongation (PE) were 18.97±0.69; 4.97±0.00; 6.11±0.62; 5.64±0.28 and 5.30±0.29. Mean while the modulus of elasticity (ME) for each formula were 90.48±2.90; 805.70±56.96; 694.12±58.03; 824.68±64.58, and 1108.70±20.32 MPa.

Mechanical properties of film such as TR, TS and MY of NaA film was increase by adding NaB in concentration of 2%, 3%, 4% and 5%. The PE of NaA film significantly diminish with replenish of NaB into polymer matrix (Fig. 7). The higher NaB content into NaA/NaB nanocomposite film gave higher TS than the NaA film. It showed that the exfoliation of NaB silicate layer into NaA could create a strong matrix structure of the film. However, enhancement of NaB concentration into NaA polymer matrix could reduce
the PE of the film. This result was in agreement with previous study (Wang et al., 2007). This phenomenon could generally occur in the film loaded with solid particles even if the solid particles did not interact with the polymers (Okhamafe and York, 1984; Felton and McGinity, 2002).

**Bursting Strength**

The objective of bursting strength test is to reflect the resistance of the film due to the pressure. The different concentration of NaB (0%, 2%, 3%, 4% and 5%) into NaA gave the bursting strength were 1.32±0.31, 1.69±0.44, 1.48±0.19, 1.48±0.40, 1.48±0.41 kgf/cm³ respectively. It showed that the addition of NaB at concentration 2% gave a highest resistance of the film to the pressure.

**Conclusion**

In this study, NaB organoclay, which is a type of smectite clay, has a good swelling in the water. The highest swellable silicate clay can produce by sonication method. It is indicate that the structure of the nanocomposite that has been produced was in exfoliated condition. It is proved by the result from XRD. In the mechanical properties, the addition of NaB into NaA polymer matrix could create a strong matrix structure of film. Moreover, the addition of NaB could retarded the water vapor permeation by creating a maze or tortuous path. The NaA/NaB nanocomposite film provide promising applications as water-barrier compounds and delayed release carriers in drug-delivery system.

**References**


AUTHORS’ CONTRIBUTIONS
Authors contributed equally to all aspects of the study.

PEER REVIEW
Not commissioned; externally peer reviewed.

CONFLICTS OF INTEREST
The authors declare that they have no competing interests.