Incorporation of Various Nanoclays in Semi-refined Carrageenan Film Composite

B B Sedayu1,3, D Fransiska2, P Wullandari1, T D Novianto1, W T Handoyo1 and L Assadad1

1Indonesian Research Institute for Fisheries Postharvest Mechanization. Ministry of Marine Affairs and Fisheries. Jl.Imogiri Barat km.11.5. Bantul. Yogyakarta. Indonesia. 55781.
2Research and Development Center for Marine and Fisheries Product Processing and Biotechnology, Ministry of Marine Affairs and Fisheries. Jl.KS. Tubun, Petamburan VI. Jakarta. Indonesia. 10260
3Corresponding Author’s Email: baktibsedayu@gmail.com, bakti.sedayu@kkp.go.id

Abstract. In current investigation, various commercial nanoclays with different level of hydrophilicity i.e., hydrophilic bentonite (HB), cloisite 10A, and cloisite® 30B were incorporated to a hydrophilic semi-refined carrageenan (SRC) films to observe their presence in film matrix in regards with the final film’s properties. High shear mixing and sonication were applied to the film preparation to obtain high dispersion of nanoclays in the matrix. As expected, the hydrophilic clay showed better dispersion within the matrix as shown in Energy Dispersive X-Ray Spectroscopy (EDS) image. The more hydrophilic clay inclusion resulted in higher tensile strength, while the more hydrophobic resulted in higher stiffness of the films. The water vapour permeability was decreased in corresponded to the more hydrophobic clay incorporated, and the thermal properties of the films were overall enhanced by the nanoclays reinforcement. In general, nanoclays incorporation in SRC film improved the overall properties of the SRC film.

1. Introduction

Among many potential bio-based materials for replacement of conventional synthetic plastics, seaweed has recently attracted scientists for bioplastic development, as a promising candidate of biopolymer showing more advantages over other biomass particularly in term of its availability and sustainability [1]. Farmed seaweed from red algae species has been well known to be grown massively in tropical waters with consistent production increase every year. From this red seaweed species, we can harvest their main component polysaccharides namely carrageenan, and develop this material further into bioplastic [2]. There are two common types of carrageenan products available in market namely a refined-carrageenan (carrageenan) and a semi-refined carrageenan (SRC). For bioplastic production purposes, the latter product is economically preferable due to its lower price. In comparison with carrageenan, SRC still contains residual cellulose since it takes less processing steps for the production.

Nonetheless, like many other bio-based plastic materials, carrageenan-based plastic has also exhibited some weaknesses such as high-water sensitivity and poor gas barrier properties [3] which are essential whenever they are used for food packaging applications. To obtain a fully functional bioplastic made of carrageenan, it requires some modification to enhance its properties such as blending with other biopolymer, incorporated with hydrophobic elements, or reinforce with nanoparticles [4-6].

The aforementioned techniques are common to be applied in biodegradable plastics production to obtain improved properties such as higher water resistant and greater mechanical or barrier properties. For example, starch that has been blended with hydrophobic biodegradable polymer like polylactic acid (PLA), polycaprolactone (PCL), and other polymers to improve its water sensitivity
and tensile properties, and gas barrier properties [7]. Moreover, another more efficient method is also frequently applied in many biopolymers composite production i.e., nanoparticle reinforcement, which only incorporating a low level of nanofiller in the formulation, but it can improve the final biopolymer composite properties that equally loaded with 40–50 % of classical fillers [8, 9]. Among many commercially available nanomaterials used in biopolymer composite preparation, nanoclay has been well known as one of the most prevalent filler showing an ability to enhance the mechanical, barrier, and thermal properties of biopolymer film composites [10-12]. However, the successful reinforced polymer is dictated by interaction and interfacial chemistry between incorporated nanomaterials and polymer molecules, which results in intercalation or exfoliation morphologies within the polymer matrix [13]. Regarding this, compatibility between nanofillers and biopolymer matrix is a key factor to obtain property enhancement, as well as their amount in the biopolymer formulation [11].

In the present study, three different types of commercial nanoclays (montmorillonite nanoclays) were used in semi-refined carrageenan (SRC) film preparation, and their effects on the mechanical, barrier and thermal properties of the final film composites were investigated.

2. Materials and Methods

2.1. Materials

A food grade powdered semi-refined carrageenan (SRC) derived from red algae Eucheuma cottonii was purchased from W-Hydrocolloids, Inc. (the Philippines). Hydrophilic bentonite (montmorillonite clay), closite 10A (Clo.10A), and cloisite® 30B (Clo.30B) were purchased from Sigma Aldrich (Australia). Glycerol (92.08 g mol⁻¹ MW) obtained from Sigma Aldrich was used as the plasticizer during film preparation.

2.2. Film preparation

For each film composite, a 5 percent mass of nanoclay relative to SRC (w/w) was firstly dispersed in 250 mL of Milli-Q and stirred for a night (±16 h) at 40 °C in a lid Pyrex bottle. It was then followed by high-speed shearing at 20,000 rpm for 10 min using a homogenizer CAT Unidrive X1000 (Germany) and sonication at 50 Hz and 80% amplitude for 10 min using a Hielscher ultrasonic processor UP400S (Germany). After allowing the solution reached ambient temperature, a 5 mg of SRC was added into the nanoclay solution and stirred for 10 minutes. The mixture was then heated at 90 °C for 30 minutes while stirring. During heating, a 40 % of glycerol relative to SRC (w/w) was added into the mixture. The mixture was then poured onto a 38 X 18 cm² acrylic rectangular tray and allowed to dry at ambient temperature for 36 hours.

2.3 Film’s properties

Thickness. Three random locations on each film composite were measured the thickness using digital micrometer. The measurement was performed in triplicates.

Opacity. Prior to the measurement, each of film formulations was cut into an 80 × 12.5 mm² film strip, and at least three specimens were measured for each formulation. Film strip was mounted directly into the test cell of spectrophotometer (Biochrom Libra S12) and measured at λ = 550 nm following procedure by Gómez-Estaca, Giménez, Montero and Gómez-Guillén [14].

Water vapor permeability. Water vapor permeability (WVP) of the film specimens was measured following the previous method performed by Sedayu, Cran and Bigger [15].

Mechanical properties. Each of film formulations was cut into film strip of 120 × 20 mm² before testing by using Instron Universal Testing Machine Model 4301 (US). A 5 kN loadcell was used to measure the film samples with initial grid separation of 2.5 cm, and the testing was performed in accordance with the ASTM D 882-12 method [16]. The tensile strength (TS), E-modulus (EM), and
elongation at break (EAB) values of the tested specimens were recorded and calculated automatically using an Instron BlueHill Universal software.

**Fourier transform infrared (FTIR).** Structural properties of the film specimens were observed using PerkinElmer Frontier FTIR spectrometer (USA) with attenuated total reflectance (ATR). The transmittances of infrared spectra were measured at ranges of 4000–600 cm\(^{-1}\) frequency by 16 scans. **Thermal properties.** Thermographic analysis (TGA) was performed using Mettler Toledo Thermal Analyzer (Switzerland). Approximately 5 – 8 mg of composite film was placed into alumina sample pan and heated from 30 to 400 °C under nitrogen circumstance at a 10 °C/min heating rate to obtain TGA data with non-oxidative decomposition.

**Statistical Analysis.** The collected data were analyzed using One-way analysis of variance (ANOVA), and the significant different among the mean values were determined using a Duncan test at 5% significant level.

3. **Results and Discussion**

3.1. **Physical and barrier properties**

As shown in Table 1, the reinforcement of 5% (w/w) nanoclay in polymer matrix in general did not alter the thickness of the reinforced films, and this might be caused by very little amount of nanoclays included in the matrix, or too thin layer formation of the nanoclays across the polymer matrix, thus the changes were neglected. However, it can be seen that the opacity of composite films was increased after being reinforced with the nanoclays. The hydrophilic bentonite clay appeared to create more opaque film in compared with two other nanoclays with less hydrophilicity. Seems that level of dispersion of the nanoclay particles interfered the opacity of the film, the higher dispersion of the particles in the matrix the opaquer the film. Similar result was also observed by Zakuwan and Ahmad [17] after reinforcing carrageenan polymer with organically modified montmorillonite.

| Film samples | Thickness/mm | Opacity | WVP/g mm cm\(^{-2}\) h\(^{-1}\) Pa\(^{-1}\) (\(× 10^{-8}\)) |
|--------------|--------------|---------|---------------------------------|
| SRC          | 0.069 ± 0.001\(^a\) | 10.92 ± 0.12\(^a\) | 12.60 ± 0.15\(^a\) |
| SRC/HB       | 0.069 ± 0.001\(^a\) | 12.42 ± 0.20\(^b\) | 12.42 ± 0.09\(^b\) |
| SRC/Clo.10A  | 0.069 ± 0.003\(^c\) | 11.40 ± 0.29\(^c\) | 12.36 ± 0.12\(^b\) |
| SRC/Clo.30B  | 0.069 ± 0.001\(^a\) | 11.40 ± 0.41\(^c\) | 12.22 ± 0.09\(^b\) |

Values are given as mean with one standard deviation. Any two means in the same column followed by the same letter are not significantly different (p > 0.05) as determined by a Duncan’s test.

The water vapor barrier of SRC film increased after nanoclay reinforcement. From the results above, hydrophilicity of the clays interferes the barrier properties of the films whereas the less hydrophilic clay inclusion resulted in greater decrease in WVP of the composite films. In principle, decreased WVP of composite film by nanoclay incorporation is attributed to tortuous pathway created by distribution of clay particles within the polymer matrix, which obstructs water vapor diffusion passing through the film [11]. In this investigation, the more hydrophobic clay visibly facilitates more impermeable layer bringing about more effective water vapor barrier than those of the hydrophilic clays. This can be explained by less hydrogen bonding, or physical/chemical interaction, between the hydrophobic nanoclay formation in polymer matrix and surrounding water molecules rendering a lower WVP than those of using hydrophilic nanoclay [18].
3.2. Mechanical properties

Mechanical properties of the composite films i.e., tensile strength (TS), E-modulus (EM), and elongation at break (EAB) are presented in Figure 1. According to the graphs below, incorporation of hydrophilic bentonite nanoclay increased the TS of SRC film by 3% (p < 0.05), however the SRC film’s TS was oppositely decreased by 5−8% after incorporation of the Cloisite 10A and Cloisite® 30B. These different behaviors might be interfered by compatibility of the clay particles within the SRC polymer structure, which is more compatible with the hydrophilic clay. Interaction such as chemical bonding between SRC polymer and clays particles determined the final properties of the film composite, and hydrophilic bentonite nanoclay in the current study appeared to have higher compatibility with SRC polymer. This phenomenon was also observed in our previous study by using energy dispersive X-ray spectroscopy (EDX) showing that the incorporation of hydrophilic nanoclays (hydrophilic bentonite nanoclay) resulting in greater dispersion across the carrageenan matrix in comparison with hydrophobic nanoclay (Cloisite® 30B) [19] (see Figure 2).

Figure 1. Mechanical properties of SRC reinforced films with hydrophilic bentonite (HB), Clo.10A, and Clo.30®B nanoclays. Values are plotted as the mean with a standard deviation error bar. Any labelled with the same letter are not significant different (p < 0.05) as determined by a Duncan test.

E-modulus (EM) value represents the stiffness of a composite film. As can be seen, there was little changes in the EM values of the SRC films due to nanoclay inclusion (p > 0.05), with the most prominent change was found in the Clo.10A inclusion (see Fig.2). While the nanoclay inclusion effects to stretchability (EAB) of SRC film, the increased EAB values were observed in the hydrophilic nanoclay inclusion. On the other hand, hydrophobic nanoclay (Clo.30B) oppositely decreased the film’s stretchability. From these results, we can assume that the more hydrophobic nanoclay inclusion, the more rigid the film is. This result is also in agreement with previous study reported by Müller, Laurindo and Yamashita [3] showing the antiplasticization effect of nanoclay in biopolymer film.
3.3. Thermal properties
The reinforcement of nanoclays in SRC composite film showed overall enhanced thermal stability of the films, this is reflected from the mass losses of samples during heating in TGA thermograms (see Figure 3a). Moreover, among the three different nanoclays used, the hydrophilic bentonite clay showed to increase the thermal stability of SRC film higher than those of other nanoclays by slightly shifting decomposition peak to higher temperature during the second stage of decomposition (see Figure 3b). From the dTGA curve (see Figure 3b), we can see a three major decomposition process of the SRC composite film during heating. The first stage decomposition occurred at temperature of ca. 90 °C that was attributed to evaporation of water and low-weight volatile compounds from the SRC composite film, it was followed by the second decomposition stage at temperature of ca. 205 °C corresponded to volatilization of plasticizer (glycerol) and middle-weight volatile compounds. At heating temperature above 260 °C, the third decomposition stage took place ascribed to the decomposition of main carrageenan polymer structure [6].

3.4. Fourier Transform Infrared (FTIR)
The chemical bonds and functional groups of the composite films were analyzed by observing any distinguish stretching or peaks in the FTIR spectra compared to the control SRC film as presented in Figure 4. In general, all the spectra recorded from each film formulations exhibited very similar
pattern, which shows a typical spectra of SRC film reported by Sedayu, Cran and Bigger [15]. This similarity can be caused by neglected small amount of nanoclay included in SRC film matrix, or it may also be an indicator of good miscibility or compatibility of nanoclay within the SRC polymer.

However, some minor changes are found in stretching bands at 1424 cm\(^{-1}\) corresponded to symmetric CH2 bending vibration [20], which was increased after the nanoclays reinforcement. Increasing of –CH2– alkyl groups may have correlation with the increasing of crystalline region in SRC polymer structure after nanoclay inclusion [21], and it is also in corresponded to the increased stiffness (EM) of the reinforced films (see Fig. 1).

4. Conclusion
Reinforcement of different types of nanoclays into SRC polymer matrix in general enhanced the barrier and thermal properties of the composite films. The SRC film was more compatible with hydrophilic nanoclay facilitating greater clay particles dispersion within the polymer matrix that subsequently resulting in higher tensile and thermal properties in compared with hydrophobic nanoclays. These results suggest a potential development of carrageenan-based plastic for wide applications, including for alternatif food packaging material.

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