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Reinforcement of Carrageenan/Starch Based Bio-Composite by Beads-Milled Chitosan

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ABSTRACT
Carrageenan/corn starch bio-composites is an important biodegradable composite as a substitute for conventional plastic and known as an environmentally friendly material. However, Carrageenan/corn starch bio-composite has poor mechanical properties. This paper reports the effect of chitosan NPs filler concentration on the properties of carrageenan/corn starch bio-composites. Chitosan suspension was prepared by beads mill method and characterized using PSA, SEM and FTIR. The performance of the obtained films was investigated on their mechanical, optical, thermal and transport properties. The result showed that the increased of additional of chitosan NPs caused improved on the tensile strength, WVTR, WPV, and temperature degradation of the bio-composite, but reduced their transparency. It is concluded that additional chitosan NPs able to reinforce carrageenan/corn starch bio-composites film.
Keywords: *beads mill, chitosan, composite, suspension*

1. INTRODUCTION

Plastic is the most predominant type of marine fragments found in our ocean. Microplastics formed from fragmented plastic waste which size less than five millimetres in length create massive problem to environment [1]. If ingested, microplastics can block the gastrointestinal tracts of organisms and act as antifeedant to the organism mean that organism feel they don't need to eat, leading to starvation [2]. In addition, contaminated microplastics with many toxic chemicals with high concentration of toxins may also cause massive living organism death [1-3]. Therefore, alternatives biodegradable composite material from renewable resources is very crucial such as an engineering of bio-composite with acceptable characteristics and properties satisfied the requirement of various application of plastics, such as food packaging [1, 4]. The suitable bioplastic properties need to be improved includes their mechanical and water absorption properties [4-7].

Carrageenan and corn starch are renewable bioresources as an alternative film [5-6]. However, this material has yet suitable for the application and need to improve their mechanical and water absorption properties [6]. Usually, proper filler added to enhance their properties. Chitosan is natural filler which is potential candidate applicable to improve the properties of carrageenan/starch bio-composite film [5]. It is also important for massive application that chitosan, carrageenan and corn scratch are abundant in nature. Therefore, in this study, we investigate the application of chitosan as filler in carrageenan/corn starch bio-composite matrix to enhance mechanical and water absorption properties with various chitosan concentrations.

2. MATERIALS AND METHOD

2.1. Materials

Chitosan from crab shell with the degree of deacetylation higher than 80% was purchase from PT. Biotech Surindo, Indonesia. Carrageenan, corn starch, glycerol and tripolyphosphate (TPP) were purchase from Brataco, Co., Ltd. (Bandung, Indonesia). These chemicals used in this experiment were industrial grade and used as obtained without further purification. The acetic acid (99.9%, 1N) was purchased from Merck. Distilled water was used for all sample preparation.

2.2. Preparation of Chitosan Suspension: Beads mill Method

The chitosan nanaoparticles (NPs) were prepared by ionic gelation method using tripolyphosphate (TPP) [8]. First, chitosan powder was milled into size mesh (- 200), then 200 grams of this chitosan powder was dissolved in 100 ml of 1% acetic acid solution (1N) and stirred up to 24 h. The 20 grams of TPP was dissolved into 20 ml distilled water. The TPP solution dropped wise into chitosan solution and precipitated particles as suspension was obtained. The obtained suspension subjected for bead milling process for two hours to obtain well-dispersed

suspension of chitosan NPs in water. A schematic representation of the beads milling apparatus is shown elsewhere [9]. It consists of impeller motor, impeller, dispersing chamber, cooling chamber, cooling water inlet and outlet. The dispersing chamber is containing yttrium stabilized zirconia beads as grinder in the size ranging from 0.08 to 0.12 mm.

2.2. Preparation of Bio-composite Film

The bio-composite film was obtained by adding various amount of chitosan suspension into carrageenan/ corn starch solutions which was prepared separately as follows. Carrageenan was mixed with water (2:100 wt.%) using magnetic stirrer at temperature of 90-100^{o}C for 30 minutes. Whereas the corn starch was prepared by mixed with water (1:100 wt.%) at 60-70^{o}C. These two solutions were mixed with fixed ratio of carrageenan and starch 2:1. A glycerol (1 wt. % of water) was add into the carrageenan/corn starch solution.

Chitosan suspension with various amount (0, 5, 10, 15 and 20 wt.% of all ingredients) were added into carrageenan /corn starch solution and stirred at 65^{o}C for 1 h. The mixture was then poured into a plastic mould and dried in a drying oven at 50^{o}C for 4 hours.

2.3 Characterization

The size distribution of chitosan suspension was examined by Particle Size Analyser (PSA, Beckman Coulter LS 13 320. The morphology of chitosan particles before and after beads mill was characterized by SEM Hitachi SU 3500 measurements. The Fourier transform infrared (FTIR) analysis of suspension before and after milling were examined by using Shimadzu prestige 21 in the wavenumber range of 400-4000 cm^{-1} with KBr as a beam splitter. Film thickness was measured by a digital micrometre (Insize) with an accuracy of 0.001 mm. The mean thickness of each film was determined from an average of 5 random positions on the film samples. Surface morphology of the bio-composite films were observed by SEM Hitachi SU 3500. Water vapor permeability (WVP) tests of bio-composite films were conducted according to ASTM E96-80 [10]. Wettability of different bio-composite film was investigated via contact angle measurements performed using sessile drop method at 27^{o}C (± 1^{o}C) using laboratory-built device. Contact angle measurements of film was carried out using deionized water, formamide and n-hexadecane as the probe liquids. Critical surface tension values (γ_c) was calculated using Fox-Zisman approximation [11] by inserting the measured contact angles of deionized water, formamide and n-hexane. The light transmission value and transmittance and its transparency value of bio-composite film at λ=550nm were measured using UV–visible spectrophotometer (Cary 60 UV-Vis). Tensile strength and elongation were measured by tensile tester Testometric M350-10AT. The thermal degradation of bio-composite films was recorded using thermo gravimetric analyzer (TA Instruments). In this thermal degradation test, the sample is heated from room temperature to 500ºC in a nitrogen atmosphere with a flow rate of 25 mL/min. The heating rate is 10ºC/ minute.

III. RESULTS AND DISCUSSION

3.1. PSA Chitosan Suspension

The chitosan NPs suspension was obtained from precipitation of chitosan solution by adding TPP drop wised. Figure 1a shows the bimodal size distribution of chitosan NPs obtained from precipitation. This result indicate that primary size of precipitated chitosan was partially agglomerated. However, after beads milling process for 2 hours the chitosan particles successfully dispersed to their primary size indicated by single and very sharp particles size distribution with mean size of 184 nm (Figure 1b).

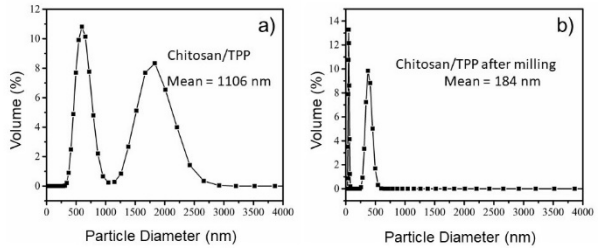

Figure 1. PSA analysis of chitosan suspension, (a) before milling and (b) after milling

Figure 2 shows the SEM images of the chitosan suspension before and after beads mill. It was clearly showed that the obtained morphology of chitosan was agglomerated with flaky-fibrous (Figure 2a). After beads milling, the particles were disintegrated into their primary size of flaky-fibrous Chitosan NPs as shown in Figure 2b.

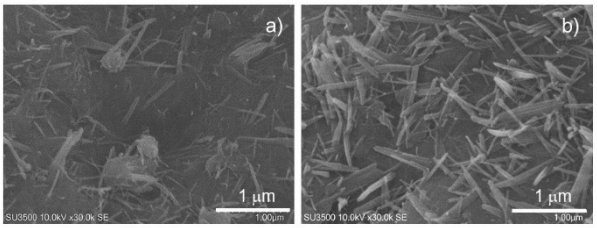

Figure 2. SEM images of chitosan suspension, (a) before milling and (b) after milling

Figure 3 shows the FTIR spectra of chitosan particles aim to know the formation of chitosan with TPP and also to see the effect of beads milling functional group of bio-composite. The indication of bond/stretch in the material identified was shown in Table 1. This result indicates that broad peak of chitosan at 3200-3400 cm^{-1} corresponding with O-H stretching. This peak still appears even though it has been mixed with TPP and treat by beads milling. Others bond/stretching indicated chitosan appear at 2873 cm^{-1} (C-H stretching), 1658 cm^{-1} (C=O stretching), 1318

cm^{-1} (C-N stretching), and 1157 cm^{-1} (C-O-C glycosidic bond).

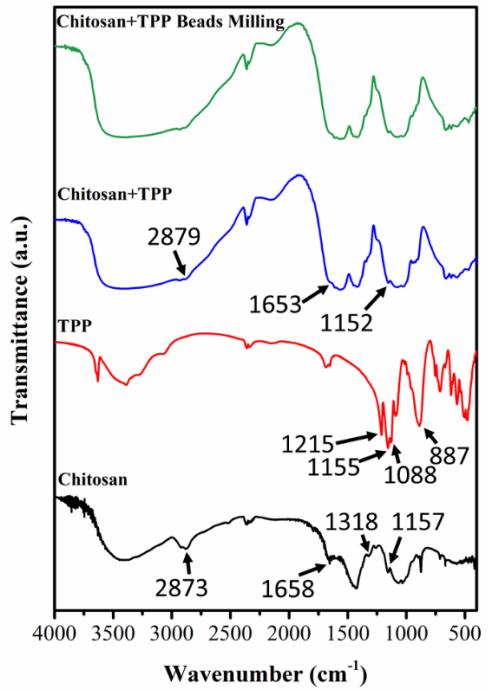

Figure 3. FTIR spectra of initial chitosan suspension and after beads milling

Table 1. Bond/Stretch Indication of Materials

Wave Number (cm^{-1})	Bond/Stretching
Chitosan	
3200-3400	O-H stretching
2873	C-H stretching
1658	C=O stretching
1318	C-N stretching
1157	C-O-C (glycosidic bond)
TPP	
1215	P=O stretching
1155	Sym-asym PO_2 Group
1088 and 887	Sym-asym PO_3 group
Chitosan + TPP	
Broad 3400	O-H stretching
2879	C-H Stretching
1653	C=O stretching
1152	C-O overlapped P-O

Strong peaks indicated of TPP bond/stretching were appear at 1215 cm^{-1} (P=O stretching), 1155 cm^{-1} (sym-asym PO2 Group), 1088 cm^{-1} and 887 cm^{-1} (sym-asym PO3 group) respectively.

Incorporation chitosan with TPP peaks indicated at 2879 cm^{-1} (C-H stretching), at 1653 cm^{-1} (C=O stretching), and 1152 cm^{-1} (C-O overlapped P-O). Beads milling processed did not modify the functional group of bio-composite.

3.2. Film Thickness & Surface Morphology

Figure 4 shows the film thickness of the bio-composite with vary in chitosan concentration. This result showed that additional chitosan Nps as filler in bio-composite increased their thickness significantly compare to the film without filler.

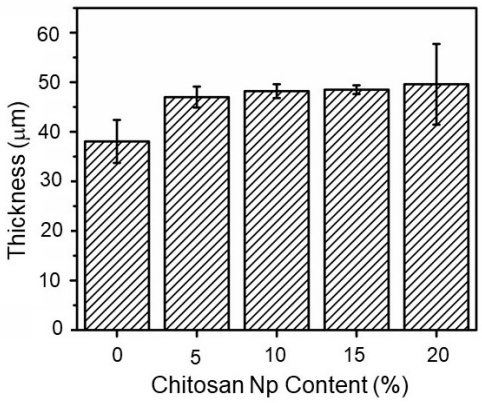

Figure 4. The influence of chitosan Np content on the thickness of bio-composite film

However, the increased on the thickness was not significantly differ among variation of the filler concentration.

Figure 5 showed the SEM images of film vary in filler concentration chitosan NPs. This result showed that additional chitosan content changed their surface roughness.

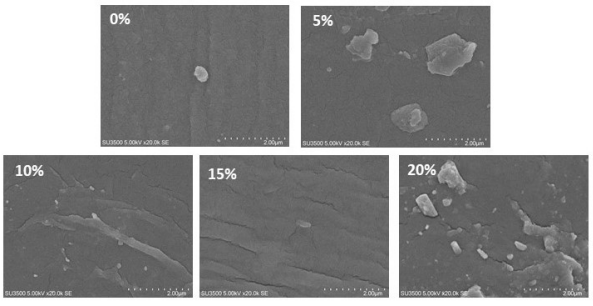

Figure 5. The SEM images on the influence of chitosan NPs content on the roughness of bio-composite film

Figure 6 showed that the effect of chitosan NPs content on the WVTR and WVP of bio-composite film. The WVP and WVTR of the film with 5 wt.% chitosan

NPs were relatively similar indicated that the film did not hold the water vapour. However, for the chitosan NPs content of 10 -20 wt.%, the WVP and WVTR were significantly differ indicated that higher water vapour holding capacity in the film compare to the initial condition.

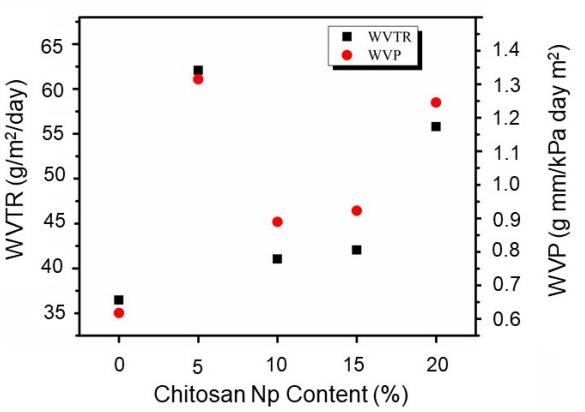

Figure 6. The influence of chitosan NPs content on WVTR and WVP of bio-composite film

Figure 7 shows that the obtained film were hydrophobic where higher value compare to the initial film without chitosan. The additional of chitosan suspension reduced the transparency of the film, but up to 20 vol %, the film remain transparent (Figure 8). This result also clearly indicated in the visual images comparison with various chitosan concentration in Figure 9.

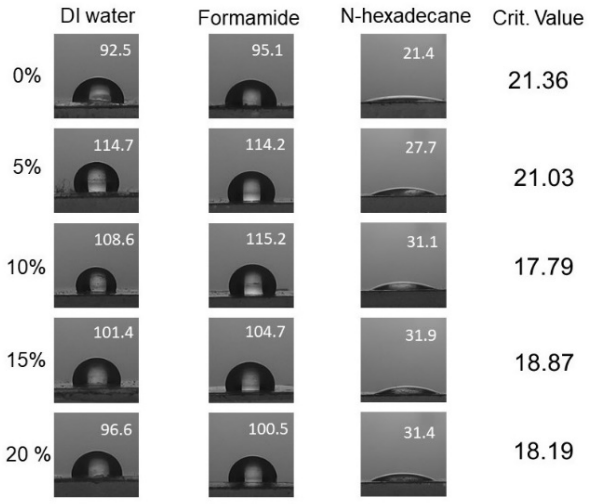

Figure 7. The influence of NPs content on wettability of the bio-composite film

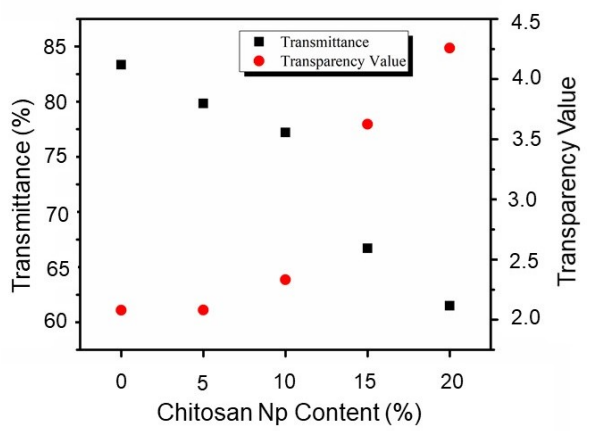

Figure 8. The influence of Np content on the transmittance and its transparency value of bio-composite film at λ=550 nm

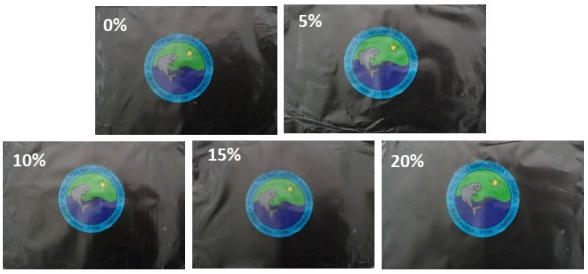

Figure 9. The influence of chitosan NPs content on the visual of bio-composite film

Figure 10 shows the effect of chitosan NPs on the mechanical properties of the film. This result indicated that additional of chitosan NPs increased the tensile strength of the film but lowering the elongation to break.

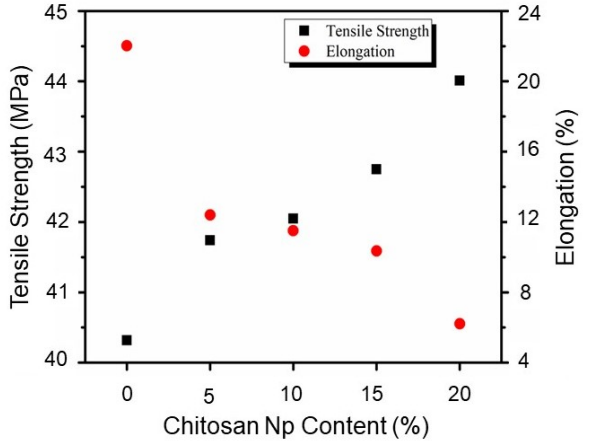

Figure 10. The influence of NPs content on the tensile strength and elongation

Figure 11 shows the TGA spectra of the film vary in chitosan NPs content. The curve at 200°C shifted to the higher temperature upon increased in chitosan NPs content indicated that the temperature degradation of bio-composite film improved.

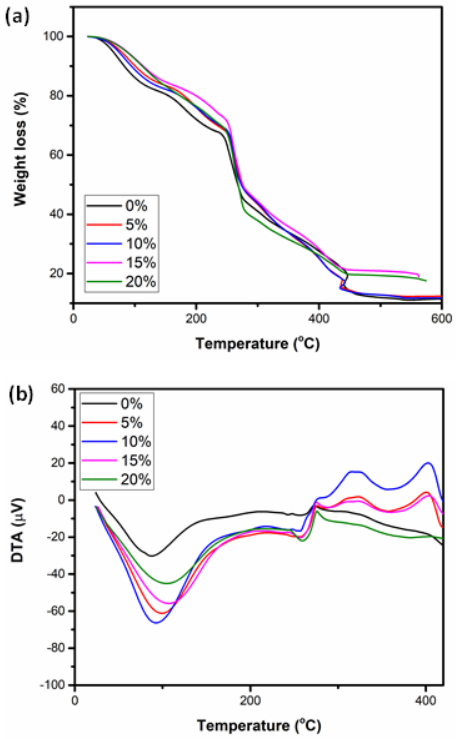

Figure 11. The degradation of film after additional chitosan NPs

IV. CONCLUSION

It was concluded that additional chitosan NPs as filler in the bio-composite improved their mechanical properties, thermal degradation properties, but decreased the transparency of the film. However, considering the application of the bio-composite film has an acceptable transparency.

ACKNOWLEDGMENT

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