High translucent of polymeric membrane reinforced by nanocellulose from oil palm empty fruit bunches

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Abstract. Polymeric membranes have gained high interest since they provide great potential to be used as functional products in energy, electronics and remediation applications. In this study, cellulose nanocrystals (CNCs) and TEMPO-oxidized cellulose nanofibrils (TOCNs) extracted from oil palm empty fruit bunches (OPEFB) cross-linked with poly(methyl vinyl ether co-maleic acid)/PMVEMA and poly(ethylene glycol)/(PEG) by insitu polymerization to produce polymeric membranes. Characterization of resultant polymeric membranes was employed by microscopic observation to evaluate membrane morphology. UV-Vis analysis and mechanical testing were conducted to observe the effect of nanocellulose addition towards membrane translucent and mechanical properties. Results indicated that the presence of nanocellulose improved membrane translucent and mechanical properties by only 5 weight (wt)% of addition. CNCs addition has higher translucent improvement on polymeric membrane compared to TOCNs. However, TOCNs addition has higher improvement in mechanical properties than CNCs. Polymeric membrane reinforced by nanocellulose has potential utilization for thin film-based composite.

1. Introduction
Currently, the fabrication and applications of nanocelluloses (NC) have increasingly gained interest in polymer nanocomposites owing to the growing environmental risks of petroleum based products [1]. Compared to cellulose substrates in larger scale, much smaller NC have higher mechanical strength, better optical transparency, and smoother surface. These properties combined with their low cost, light weight, flexibility, and environmental friendliness, make NC are promising candidates for fabrication of novel composites [2]. Existing literatures have indicated that the addition of NC in lower amount increased mechanical properties, but up to certain level (higher concentration), NC addition causes development of weaker section in polymer/NC composite, increase brittleness and causing fracture [3,4]. The utilization of NC in polymers matrix is not only to improve mechanical properties but also to improve antibiofouling, thermal and high gas barrier properties [5-8]. However, utilization of NC from oil palm empty fruit bunches (OPEFB) as reinforcing agent is still limited to be explored.
Previous study investigated the use of NC as reinforcing fillers in poly(methyl vinyl ether co-maleic acid)/PMVEMA and poly(ethylene glycol)/PEG matrix in high concentration (25-75 wt%) [9,10]. In addition, high amount of NC addition drive NC aggregation due to the presence of hydroxy groups on their surface. Meanwhile, the addition of NC did not follow linear pattern of “the more the better”. When the higher amount of nanocellulose applied, the thermal stability and elongation at break of the composite films were reduced, and the tensile force remained unchanged or even weakened after reaching maximum value [11]. Therefore, in this study cellulose nanocrystals (CNCs) and TEMPO-oxidized cellulose nanofibrils (TOCNs) extracted from oil palm empty fruit bunches (OPEFB) waste cross-linked with poly(methyl vinyl ether co-maleic acid)/PMVEMA and poly(ethylene glycol)/PEG by insitu polymerization to produce polymeric membrane by 5 wt% addition of nanocelluloses. Characteristic of resultant membrane was observed by microscopic, physical and mechanical properties analyses.

2. Materials and Methods

2.1. Materials
Poly (methyl vinyl ether maleic acid)/PMVEMA, Mw 1,980,000 (Sigma Aldrich, USA) (Mw 1,980.000) and PEG (Wako Pure Chemical Industries, Osaka, Japan) (Mw 20,000) were used in this study. Hydrochloric acid 0,1 M was used to obtain the solution in pH 2. The water used in this study was purified with an Arium Ultrapure Water System (Sartorius Co., Ltd., Tokyo, Japan). Bleached kraft pulp of oil palm empty fruit bunches (OPEFB) was kindly supplied from Biomaterial Research Institute, Indonesian Institute of Sciences (Bogor, Indonesia) and used as raw materials to produce CNC and TOCNs as described in our previous studies [12,13]. CNCs and TOCNs of OPEFB were denoted as CO and TO, respectively. The CO used in this study has crystallinity index (65%), aspect ratio 23±18. The TO used in this study was TO has crystallinity index 55%, aspect ratio 41±14.

2.2. Methods
A 6.7:1 mass ratio of PMVEMA:PEG (1.5 g) was added in 40 mL of deionized water (DI) preheated at 68°C and acidified with HCl 0.1 M to reach pH 2. At first, PMVEMA was poured into the heated and acidified DI to get it dissolved completely, then followed by PEG and 5 wt% NC of OPEFB addition. The 5 wt% addition of NC in PMVEMA-PEG matrix was chosen because the addition of NC OPEFB below 6% to the PVA considerably results enhancements in tensile strength and modulus as reported by Asad and co-authors [14].

The sample denoted as P100, CO5 and TO5 for sample with PMVEMA and PEG only, PMVEMA and PEG with the addition 5 wt% of CNCs and TOCNs of OPEFB, respectively. Solution was continuously stirred to get all components mixed completely. Then solution was homogenized by electrical homogenizer for 2-3 min, poured into teflon Petri dish, cured at 135°C for 5 minutes and dried at 40°C for 3-4 days. The dried films/membranes were peeled off carefully and characterized.

2.2.1. Membrane characterization
Optical transmittance (T%) was observed using UV-Vis spectrophotometer UH5300 (Hitachi, Tokyo, Japan) at 250-800 nm wavelength. Surface analysis was observed using Atomic Force Microscopy (AFM) in mode Scanning Probe Microscope/Dimension Icon with Scan Asyst function, the results were analyzed by NanoScope Analysis Version 1.80. Color analysis of membranes was measured using handy colorimeter NR-3000 (Nippon Denshoku Industries Co., Ltd., Tokyo, Japan). A white standard color plate (L = 97.75, a = −0.49 and b = 1.96) was used as a background for color measurements. Hunter color (L, a, and b) values were averaged from three readings from each sample. Color values were
expressed as $L^*$ (whiteness or brightness/darkness), $a^*$ (redness/greenness), and $b^*$ (yellowness/blueness) [15]. The total color difference ($\Delta E$) was calculated as follows:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$  \hspace{1cm} (1)

Tensile tests were observed using Material Testing Instruments (STA-1225, ORIENTEC Co., Ltd., Tokyo, Japan) equipped with a 100 N load cell. Sample specimens were prepared by cutting the film sheets into 40-50 x 10 mm strips. Measurement was conducted at 10% min$^{-1}$ strain rate in 20 mm span length [16]. The sample were kept at 50% humidity for 2-3 days before testing. Sample thickness were measured using Digital Micrometer (Mitutoyo Corp., Kawasaki, Japan); length and width of films was measured using TACKLife Digital Caliper DC01 (Shenzen Take Tools. Co.Ltd., Guangdong, China).

3. Results and Discussion

3.1. Optical Transmittance

Optical transmittance (T%) of PMVEMA-PEG membrane only (P100) was 70% at 550 nm. Meanwhile, a light transmittance of membrane with the addition of 5 wt% nanocelluloses (CNCs and TOCNs), denoted as CO5 and TO5 were 90% and 78%, respectively. Polymeric membranes of PMVEMA-PEG by nanocellulose addition had higher light transmittance compared to the control in the order of T% of CO5 was higher than TO5 (Figure 1).

![Figure 1. Light transmittance of control membrane (PMVEMA-PEG only/P100) and membranes with the 5% wt addition of nanocellulose in PMVEMA-PEG matrices (CO5 and TO5)](image)

The high light transmittance may indicate that nanocellulose had high dispersibility in the water. It was in agreement with the previous study which stated that the rod-like CNC OPEFB which produced by HCl hydrolysis revealed long term nanodispersibility and showed clear birefringence [12].
interference near infrared region indicates high smoothness on the film surface and the uniformity of film thickness [17]. Nanocellulose fibers orientation in PMVEMA-PEG matrices also influence the optical transmittance. Component rearrangement in the film matrix during the film drying, which defines its internal and surface structure, has an important role in the film optical properties [18]. The optical images of resultant membranes as described in Figure 2.

3.2. Surface analysis

Surface morphology of obtained PMVEMA-PEG-NC membranes were observed using Atomic Force Microscopy (AFM) (Figure 3). Microscopy images of AFM showed that the nanocelluloses have been well dispersed in PMVEMA-PEG matrices. These images were clearly showed the presence of NC in lower amount (5 wt%) of addition compared to the previous study conducted by Goetz and co-authors which used higher amount of NC about 25-75% [9]. The fibrous appearance of TOCNs from OPEFB was easier to be observed than the rod-like appearance of CNC OPEFB.

![Figure 3. Surface analysis of polymeric membranes made from PMVEMA-PEG only (left) and by the presence of 5% wt of CNCs (CO5) (middle) and TOCNs (TO5) (right)](image)

3.3. Color analysis

Color analysis was employed by calculating the color differentiation. It can be calculated by total color difference (TCD), denoted as ΔE, using equation (1). In this study, color differentiation referred to the color coordinate system developed by Commission Internationale de l’Eclairage’s (CIE) L*a*b*. Results of TCD as described on Table 1.

Table 1. Color differentiation of obtained films of nanocellulose in PMVEMA-PEG matrices

| Sample | $(\Delta L^*)^2$ | $(\Delta a^*)^2$ | $(\Delta b^*)^2$ | $\Delta E$/TCD (to P100) |
|--------|----------------|----------------|----------------|-------------------------|
| P100   | 88.86          | -0.55          | 18.61          | n.d                    |
| CO5    | 90.58          | 0.24           | 4.03           | 14.70                   |
| TO5    | 90.59          | 0.56           | 3.77           | 14.99                   |

Remarks: n.d = not determined

Differences in perceivable color can be classified as very distinct (TCD > 3), distinct (1.5 < TCD < 3), and small differences (TCD < 1.5). Therefore, based on TCD values, the color differences among the obtained membranes were very distinct [15,19]. According to Rheddy and co-author, the TCD increased linierly with increase of nanocelluloses content [20]. However, the addition of nanocellulose increased the brightness and reduced the yellowish of PMVEMA-PEG membrane (Table 1).
3.4. Tensile tests

Mechanical properties of obtained membranes can be interpreted from tensile stress-strain curves (Figure 4).

![Figure 4. Tensile test curves](image)

Tensile strength of PMVEMA-PEG membrane (P100) was lower than the membranes with the nanocellulose addition (CO5 and TO5). However, the strain of membrane reduced by the presence of nanocelluloses. Previous study reported the use of PMVEMA-PEG film in ratio 1:1 with low concentration of PMVEMA (5%) showed relatively low stress about 31 MPa and Young Modulus about 9 MPa [21]. Nanocellulose of OPEFB which was prepared by TEMPO-mediated oxidation (TO) revealed higher reinforcing effect than nanocellulose prepared by acid hydrolysis (CO). Formation of the reactive carboxyl groups on its surface due the mediated oxidation of OH groups is expected to increase the interactions with the polymeric matrix at the interfacial region, therefore TOCN had been examined as interfacial strengthener in continuous fiber-reinforced polymer composite [22].

4. Conclusion

The presence of nanocelluloses in PMVEMA-PEG membrane increased the light transmittance and mechanical properties by 5 wt% of addition. Nanocellulose in form of TOCNs gave higher improvement in mechanical properties but lower in optical transmittance improvement compared to CNCs. The presence both of TOCNs and CNCs improved the brightness of polymeric membranes.

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