Bio-nanocomposite of polyvinyl alcohol/Tapanuli organoclay-intercalated surfactant HDTMA-Br: synthesis, tensile and degradation tests

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Abstract. Currently, the development of plastics that can be easily decomposed is attracting attention, especially for the conversion of polymer-based materials such as modified polyvinyl alcohol (PVA) into composites. Bio-nanocomposites were prepared using the solvent casting method of PVA and organoclay as the matrix and nanofiller, respectively. In this study, the characteristics and mechanical properties of the PVA/hexadecyltrimethylammonium bromide (C16)-intercalated organoclay nanocomposite were examined. This study was carried out in two stages, i.e., the interactions between organoclay and C16 and the synthesis and characterization of the PVA/organoclay-C16 nanocomposites. Intercalation was verified from the shift of the X-ray Diffraction (XRD) peak from $2\theta = 6^\circ$ to $4.9^\circ$ of bentonite and organoclay, with a shift in the basal spacing from 15.1 to 19.7 Å. The highest tensile strength of 58.02 MPa was observed for pristine PVA, and the lowest tensile strength of 41.33 MPa was observed for the PVA/organoclay–7% C16 nanocomposite. The highest water vapor transmission rate of 0.35 g/m$^2$/h was observed for the PVA/organoclay–7% C16 nanocomposite, and the lowest value of 0.62 g/m$^2$/h was observed for pure PVA. PVA/organoclay–3% C16 exhibited the optimum, as well as the least, decomposition properties, and PVA exhibited natural decomposition.

1. Introduction
Polyvinyl alcohol (PVA) is a commercial polymer that is easily obtained, which has become one of the popular polymer materials for conversion into bioplastic materials because of its transparency and high biodegradability, as well as high Young’s modulus and excellent mechanical resistance. For manufacturing applications of composites, a PVA hydrogel matrix is used to appropriately disperse the filler because of its semi-crystallinity and hydrophilicity, as well as facile bonding with organic materials [1]. PVA is biodegradable and can easily decompose in the environment because it can produce wastes in the form of H2O and CO2, which are required by microorganisms such as Acinetobacter, Escherichia coli, Pseudomonas, Saccharomyces, and Lipomyces [2].

In this study, a PVA matrix was used because of its better mechanical resistance and a fairly good decomposition ability, which is expected for the formation of a plastic nanocomposite that utilizes a new approach compared to the mechanical nature of the formed nanocomposite.

2. Experimental method
First, the preparation and characterization of Tapanuli organoclay with HDTMA-Br (OCT-C16) were carried out, followed by the synthesis and characterization of the PVA/organoclay nanocomposite (PVA/OCT-C16). Step by step the process of sample synthesizes is presented in the diagram in figure 1.
3. Results and Discussion

Figure 2 shows the X-ray Diffraction (XRD) spectra at $2\theta = 2^\circ$–$10^\circ$ for natural bentonite and organoclay. There is a change in the shape of the XRD spectra and a shift in $2\theta$ position on the organoclay after several processes from the initial bentonite material. The XRD data showed a typical peak for bentonite at $2\theta = 5^\circ$ and $9^\circ$. Furthermore, from the XRD spectrum of organoclay, the peak slightly shifted to the left from $2\theta = 6^\circ$ to $4^\circ$ and $9^\circ$, which was in accordance with the results obtained previously [3,4]. Further analysis using High Score software can detect changes in basal spacing from 15.1 Å for natural bentonite to 19.7 Å for organoclay. This is related to the addition of a surfactant.

The XRD patterns of the PVA/OCT-C16 nanocomposite are shown in figure 3. Characteristic XRD peaks of PVA were observed, i.e., $2\theta = 6^\circ$, $18^\circ$, $22.5^\circ$, and $41.2^\circ$. 

![Figure 1. Research framework](image)

![Figure 2. XRD spectra of bentonite and organoclay](image)
The Fourier Transform Infrared (FTIR) spectra of Tapanuli natural bentonite and Tapanuli organoclay are shown in figure 4. An absorption band was observed at 450–500 cm⁻¹, corresponding to the Si–O–Si deformation. Another absorption band was observed at 1600 cm⁻¹, corresponding to the O–H vibrations, and absorption bands were observed at 3200–3600 cm⁻¹, corresponding to the absorptions related to the H₂O and OH groups (i.e., H₂O vibrations, H₂O, and OH strains).

The FTIR spectra of the PVA/OCT-C16 nanocomposite are shown in figure 5. Absorption was divided into several functional groups namely, 3200–3400 and 1310–1400 cm⁻¹, corresponding to the vibration of the “polymeric” O–H group and flexibility of the O–H group. The band corresponding to the asymmetric stretching vibration of the methyl (CH₃) group was observed at 2900 cm⁻¹. The absorption band observed at 1660 cm⁻¹ corresponded to the C=O stretching vibrations of PVA, and the band observed at 840–950 cm⁻¹ corresponded to the CH₂ stretching band. An absorption band observed at 1100 cm⁻¹ corresponded to the C–O stretching band, with the acetyl group comprising a major part of PVA; these data were not considerably different from that reported previously [5].
The water vapor transmission rate of pure PVA was 0.62 g/m²/h, and that of PVA/OCT–7% C16 nanocomposite was 0.35 g/m²/h (figure 6). The water vapor transmission rate decreased to 42%. Hence, organoclay can limit the transmission rate of H₂O, possibly because bentonite can easily absorb water or molecules that enter into the PVA/OCT-C16 membrane, which are mostly captured by organoclay.

The tensile test results of the PVA/OCT-C16 nanocomposite are shown in figure 7a. The PVA/OCT–7% C16 nanocomposite exhibited the lowest tensile strength of 41.33 MPa, and the total tensile strength of pure PVA was 58.02 MPa, leading to a decreased tensile strength of 40 %. Mondal et al. [6] have reported a tensile strength of 53 MPa, and that for a nanocomposite is ~50 MPa. The strain test results for the PVA/OCT-C16 nanocomposite are shown in figure 7b. The nature of the strain can be described by the increase in the polymer length: If the polymer is pulled or if a load is provided to break the polymer or if organoclay is added into the PVA matrix as a nanofiller to make a nanocomposite be easily broken. A lower strain was observed for the PVA/OCT– 7%C16 nanocomposite, which could only grow to an average length of 238% of the initial length, and an average increase in the length by 452% of the initial length was observed for PVA.
Figure 7. (a) tensile test and (b) strain test results of the PVA/OCT-C16 nanocomposites

Figure 8. Comparison of the results obtained from the burial test of the PVA/OCT-C16 nanocomposites in ( ) 15, (■) 20, (■■) 30, (■■■) 40, ( ) 50 and (■■■) 60 days

Mass measurements for the plastic decomposition of the PVA/OCT-C16 nanocomposite for 15, 20, 30, 40, 50 and 60 days are shown in figure 8. Pure PVA exhibited the lowest mass loss, and PVA/OCT-3% C16 exhibited a missing mass value of the most excellent decomposition results.

Optical microscopy observations for the decomposition of pure PVA plastic, 3% PVA/OCT-C16 nanocomposite, and PVA/OCT-7% C16 nanocomposite for 20, 40 and 60 days are shown in figure 9. From the figure, the decomposition on sectional plastic PVA/OCT-C16 nanocomposite was revealed by several black spots, corresponding to the entry of soil into the plastic membrane PVA/OCT-C16 nanocomposite, although it was repeatedly washed with distilled water. The entry of soil into the sectional plastic PVA/OCT-C16 nanocomposite was related to the moisture and soil pressure; hence, the change in the lattice structure of the plastic becomes more tenuous, which can be observed in the visible accretion sectional area of the plastic PVA/OCT-C16 nanocomposite when it was directly exposed to the soil or the hole sample boards with a diameter of ~2 cm. Furthermore, water entered into the soil will make the nanocomposite dominated by PVA polymer to decomposed.
4. Conclusions
In this study, the addition of organoclay as a nanofiller into PVA matrix led to the decrease in the mechanical tensile strength and tensile strain by 40% on the PVA nanocomposite/OCT-7% C16 compared to pristine PVA. Hence, the addition of organoclay as a reinforcement material in the PVA matrix is not suitable. In addition, the addition of the organoclay as a nanofiller in the PVA matrix led to the decrease in the water transmission rate to 42% for the plastic PVA/OCT-C16 nanocomposite compared to the PVA nanocomposite/OCT-7% C16. Plastic PVA/OCT-C16 nanocomposite was easily decomposed, with a high concentration of organoclay as the nanofiller, and decomposition and degradation appeared even more clearly, as well as the increased reduction in the mass of plastic PVA/OCT-C16 nanocomposite. Thus, in other applications, the combination of the organoclay and PVA nanocomposite can be used as products with low mass, such as a pack of clothes, food wrappers, and other food products.

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