Photodegradation study of TiO$_2$-organoclay modified acetate cellulose bioplastic

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Abstract. Biodegradable cellulose acetate films have been synthesized using TiO$_2$ modified organobentonite as nanofiller. The aim of titania addition is to add photocatalyst to the biocomposite, so it has self-photodegradation properties. Organobentonite was prepared from Tapanuli bentonite, previously purification and Na$^+$-exchanged, modified with cationic surfactant hexadecyltrimethylammonium bromide (HDTMABr). The composition of bioplastic cellulose acetate was 7 wt.% organobentonite and certain amount of TiO$_2$ (0 wt.%, 1 wt.%, 3 wt.%, 5 wt.%, 10 wt.% of the total composite weight. Fabrication of nanocomposite film was carried out using acetone as solvent and through solvent casting method. FTIR analysis showed the intercalation with surfactant was successfully carried out, indicated by new absorption band at 2636 cm$^{-1}$ and 2569 cm$^{-1}$. Nanocomposite application in photodegradation test was carried out under direct sunlight irradiation, UV light, and without irradiation for thirty days. It is found that the greater the amount of TiO$_2$ added into the composites, the more weight loss occurred due to photodegradation. Percent weight loss in the UV light irradiation are 4.02%, 13.45%, 18.66%, 22.35%, 27.86%, respectively for (TiO$_2$ 0 wt.%, 1 wt.%, 3 wt.%, 5 wt.%, 10 wt.%). While for bioplastic irradiated by direct sunlight, the weight loss was 2.15%, 8.49%, 13.85%, 14.70%, 15.02%, respectively. In contrast, without irradiation, the weight reduction of bioplastic was insignificant. The results indicate that the addition of TiO$_2$ to the composition of bioplastic has given the ability of self-photodegradation to the composite.

Keywords: bioplastic, biodegradable, nanofiller, organobentonite, self-photo degradation, TiO$_2$

1. Introduction
The use of materials as fabrication of polymer has been increased since some last decades. Plastic becomes popular because it is low cost production and easy to be produced. It also has good tenacity and light of weight. Although it is very helpful in human daily activity, the exceed use of plastic become hazard waste for environment. Plastic wastes need many time to be decomposed naturally by land microbe. This waste quantity increases day by day significantly and become the biggest polluting agent for environment.

Many researches have focused to prevent and minimalize the harmful effect of plastic wastes. One method that can be suggested is by employing photocatalytic reaction. This method is known for eco-friendly technique and the result for degrading organic pollutant is significant. It has been reported that TiO$_2$ is an effective photocatalyst because this molecule is non-toxic, has ability to do photo electric conversion and oxidative capacity, low cost and stable [1].
This present work focused on fabrication of biodegradable cellulose acetate films modified by variation amount of TiO$_2$-organobentonite as nanofiller and then the nanocomposite application in photodegradation test carried out under direct sunlight radiation, UV light, and without irradiation.

Our previous work has successfully prepared biocomposite membrane from acetic cellulose using organobentonite made of hexadecyl trimethyl ammonium bromide (HDTMABr) as well as octadecyl trimethyl ammonium bromide (ODTMABr) surfactants [2, 3]. The bentonite initially has hydrophilic properties. Therefore, in order to be 'compatible' with organic compounds such as polymers, it needs to be modified so that it has organophylic properties [4]. Modification is often done by inserting a cationic surfactant into intergallery of bentonite to produce organobentonite or also named organoclay [5]. Other research showed that nano composite membrane can be synthesized from acetic cellulose–butyric cellulose using organoclay modified with same surfactant [6].

In our work, the organoclay was then modified further with TiO$_2$ anatase in order to add photocatalytic properties to the composite. Generally, TiO$_2$ is added to the bentonite, as a pillar in intergallery of clay [7]. Until now, titanium dioxide still dominate photocatalytic applications. Andhika [8] and Luthfiyah et al. [9] have synthesized nanocomposite using TiO$_2$-bentonite intercalated with hexadecyl trimethyl ammonium bromide (HDTMA-Br) as surfactant in order to increase nano composite cellulose acetic photocatalytic activity.

2. Materials and methods

2.1. Materials
Natural bentonite was supplied from Tapanuli, North Sumatera Utara. It was fractioned, purified and Na-exchanged before being used follow [10]. All other materials in this research were used without further purification, e.g. synthetic plastic, NaOH and NaCl (Merck), hexadecyl trimethyl ammonium bromide (HDTMA-Br), acetic cellulose p.a, acetic acid p.a and silver nitrate p.a. (Sigma Aldrich), and TiO$_2$ P25 Evonik.

2.2. Synthesis of organoclay
Follow previous procedure [9], Na-bentonite was dispersed in distilled water and mixed with hexadecyl trimethyl ammonium bromide (HDTMA-Br) surfactant by 1 CEC. The suspension was stirred at 60°C for about 1 hour. After stirring completed, then suspension was sonicated at 150 ppm about 3 m and decanted. The precipitation was dried at 70°C.

2.3. Synthesis of TiO$_2$-organoclay
TiO$_2$ with variation of weight 1%, 3%, 5% and 10% and 7% organoclay from total composite was dispersed into 25 mL acetone. The suspension was stirred at temperature of 60°C for about 1 hour, follow by sonication [10].

2.4. Fabrication of TiO$_2$-organoclay/acetic cellulose composite
TiO$_2$-organoclay that has been dispersed into acetone was added into acetic cellulose with certain weight. The suspension then was stirred at room temperature for 1 h. After stirring was completed, the suspension was sonicated for 2 m. Then, suspension was poured into bio-plastic molder. Suspension was dried at 40°C. The Films that have been formed, were stored in poly propylene bag for further characterization.

2.5. Photo degradation test
The as-prepared of TiO$_2$-organoclay/ acetic cellulose was irradiated using UV light, direct sun light and without irradiation for 30 days. Each irradiation was performed 6 h a day for 5 days. UV light used in this research has wavelength range 280-320 nm and 8 W power. The distance between sample and UV light source was about 17 cm. Irradiation process took place at room temperature. Sample weighing was performed once in five days. The same treatment was carried out on the experiments with direct sun light (at 9.00 am until 15.00 pm) and without irradiation.
3. Results and discussion

3.1. Preparation of TiO$_2$-organoclay/acetic cellulose composite
An addition of organobentonite nanofiller will strengthen the acetic cellulose plastic but its colour become dark brown, as can be seen in figure 1a.

The gradual addition of TiO$_2$ to acetic cellulose (through the organobentonite nanofiller) somehow has whitened the composite (figure 1a). It was expected that the TiO$_2$ addition into acetic cellulose composite would give self-photodegradation activity to the composite.

The modification of bentonite with surfactants was aimed to change the nature of the properties of the aluminasilicate from hydrophilic to organophilic character. It is reported that this action is a strategic step to create a mineral that can absorb or react with organic pollutants [11]. The change of structure property can be observed in infrared spectra displayed in figure 2. The decrease of stretching band assigned for hydrogen bonded silanol group at 3600-3500 cm$^{-1}$ and the bending peak for water molecules at 1620 cm$^{-1}$ altogether with the presence of symmetric and asymmetric peaks of –CH$_n$ at 2850-2950 cm$^{-1}$ are evidence of the transformation.

3.2. Photodegradation test on as-prepared composite
The photodegradation test was focused on three irradiation sources, i.e. direct sunlight, UV light and without irradiation.

![Figure 1. Nanocomposites, (a) before irradiation, and (b) after irradiation.](image)

![Figure 2. FTIR spectra of raw and modified bentonites.](image)
Shorter UV light with wavelength less than 280 nm can degrade acetic cellulose through photochemical reaction. But, its ability is limited because there are not enough chromophore groups available to adsorb the UV light [11]. Self-photodegradation ability can be increased by adding a certain amount of TiO$_2$ to the composite. Photo-degradation activity of TiO$_2$ will damage the surface of the composite. Combination of photo process and biodegradation may increase total degradation process of composite. Besides, degradation rate is also affected by physical design of acetic cellulose and by the environmental condition [11].

The three different irradiation processes were performed in order to know the effect of environmental conditions to the self-degradation of the composites. The results can be seen in figure 3, 4 and 5. Figure 3 shows that the as-prepared and TiO$_2$-added organobentonite-acetic cellulose composites retained their weights when being kept in the dark room without irradiation. While the commercial available plastic only lost insignificant weight (~1.4%) after 6 week. From figure 4 to 5, it can be seen that there are differences in pattern on lighting using direct sun light and UV light. Irradiation using UV light results in more linear graphic and more weight loss than using direct sun light. This is caused by consistency of intensity used. The use of UV light is more stable and more consistent than direct sunlight which is affected by environmental condition. Furthermore, direct sunlight has wavelength range 409-435 nm (UV A), which has energy lower than the energy of UV light used in this research (UV B, 280-320 nm).

The variation of weight of TiO$_2$ added into composite was then studied in order to know the decrement of composite weight. It is found that the greater the amount of TiO$_2$ added into the composites, the more weight loss occurred due to photodegradation. This is because there is no TiO$_2$ as photocatalyst agent.

As comparison, the synthetic plastic was also tested. The result is decrement of weight of synthetic plastic is more than the acetic cellulose composites with and without TiO$_2$ except with direct sunlight as
shown in figure 4 and 5. The evidence of weight loss and damage in the composites after irradiation for 30 days are shown in figure 1b. The plastics somehow look darker and more fragile after the treatment.

4. Conclusions
Increasing amount of TiO$_2$ photocatalyst agent into composite can increase the decrement of weight of composite with irradiation. Irradiation using direct sunlight is affected by light intensity. In contrast, without irradiation, the weight reduction of bioplastic was insignificant. The results indicate that the addition of TiO$_2$ to the composition of organobentonite modified acetic cellulose plastic has given the ability of self-photodegradation to the composite.

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