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Removal of VOCs by photocatalytic oxidation using nano-TiO_2/PLA biocomposite

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Abstract

Poly (lactic acid) or PLA has been challenging as one of the most recognizable biopolymer for more than a decade since it has been readily fabricated as biocomposite film. In the present study, biocomposite film, which composed of PLA and nano-TiO_2 particles, were used as a carrier to modify volatile organic compound (VOCs) removal efficiency by photocatalytic oxidation, using the nano-TiO_2/PLA biocomposite film as a photocatalyst. Since the amount of nano-TiO_2 affected the efficiency of photocatalytic activity, the present study mainly focused at the effort to embed high amount of nano-TiO_2 in PLA matrix. Therefore, the developed nano-TiO_2/PLA biocomposite films were characterized for physical properties by Scanning Electron Microscope(SEM),UV-VIS spectrophotometer, and X-ray diffractometer (XRD). The SEM images revealed the presence of high homogeneity of the deposition of nano-TiO_2 on PLA matrix. The XRD patterns interpreted that the nano-TiO_2 embedded in PLA matrix exhibited mainly in anatase form. In addition, photodegradation results showed that DCM removal efficiencies were 41.2%, 63.4% and 49.1% when using the nano-TiO_2/PLA biocomposite films loading at $TiO_2$5.0%, 10.0% and 15.0%wt.cat./wt.film., respectively. The present study emphasises the use of Nato-TiO_2/PLA as promising photo catalyst for degradation of VOC.

Key words

Photocatalytic oxidation, Dichloromethane, Nano-TiO_2/PLA biocomposite film

Introduction

Titaniumdioxide (TiO_2) has been recognized as one of the most interesting semiconductor used in photocatalytic oxidation process. It has been found to be rather effective material of photocatalytic activity during both oxidation and reduction reactions. Photocatalytic oxidation (PCO) commonly uses TiO_2 and ultraviolet (UV) light as semiconductor catalysts. Under optimal reaction condition, organic pollutant scan be completely oxidized to form carbon dioxide and water as final product. Recently, interest of its application was to remove volatile organic compounds (VOCs). An electron in an electron-tilled valence band (VB) is excited by photo irradiation to vacant conduction band (CB), leaving a positive hole in the VB. These electrons and their positive holes drive reduction and oxidation respectively, at compounds adsorbed on the surface of a photocatalyst. The activity of TiO_2 as photocatalyst depends strongly upon the method of preparation (Zhong *et al*., 2010).

Many researchers have investigated widely the techniques for incorporating TiO_2 into the polymer matrix. Those are polyurethane composite coating, foamed polyethylene sheet and synthetic fabrics (Barkoula *et al*., 2010). However, suitable thin film supports show reasonable properties: withstand reactive oxidative radicals attack during light, maintain long term catalytic stability, precluded TiO_2 leaching during light irradiation, and allow photo catalytic oxidation to process for environmental application also. Generally, polymeric substrates TiO_2 technique has been successfully used as photocatalyst with different types of petroleum polymer matrixes such as polyethylene, poly

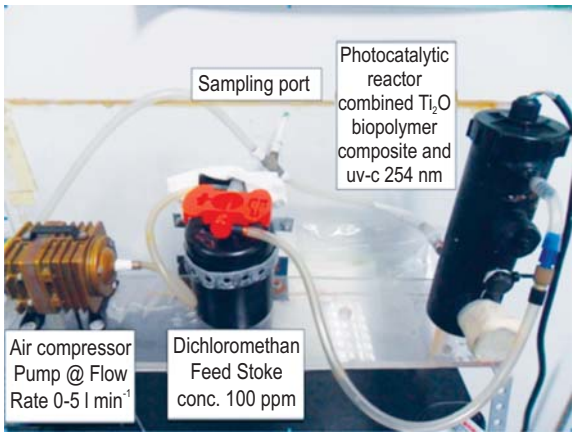

Fig. 1 : Photocatalytic oxidation reactor system

propylene, polyvinylchloride because polymeric substrates are cost effective materials with good mechanical properties and light weight. Unfortunately, the durable property of petroleum polymer materials can cause growing problem of waste disposal of petroleum plastics in the land fill (Avella *et al.*, 2001). Therefore, an alternative way that can overcome such serious environmental problem due to non-decomposable plastic has to be innovated newly and petroleum polymers have to be replaced by

Table 1 : Operation conditions of experiment

Operating conditions	Representative value
Temperature (°C)	26-42
Gas flow rate ($L.min^{-1}$)	2.0
Reactor residence time (s)	60.0
Initial DCM concentration (ppm)	100.0
UV light source	9.0 W, UV-C light
UV light intensity ($mW.cm^{-2}$)	4.0
Reactor material	stainless steel
Dosages of TiO_2 (% wt.cat/wt. film)	5.0, 10.0 and 15.0
Irradiation time (min)	400

environmental friendly, biodegradable polymers.(Grommen and Verstraete., 2002)

In the present study, a plant-based biodegradable polymer as PLA was used as bio-supporter for TiO_2 photocatalyst because this plant based biopolymer possesses superior properties with relatively high melting point, crystallinity and stiffness as compared to other biopolymers (Plackett *et al.*, 2003 and Saha *et al.*, 2003). Dichloromethane (DCM) is a major indoor and industrial air pollutant, and it is recommended as one of representative indoor VOCs.

The present study focused on developing nano-TiO_2 incorporating polyethylene (TiO_2/PLA) modified with maleic

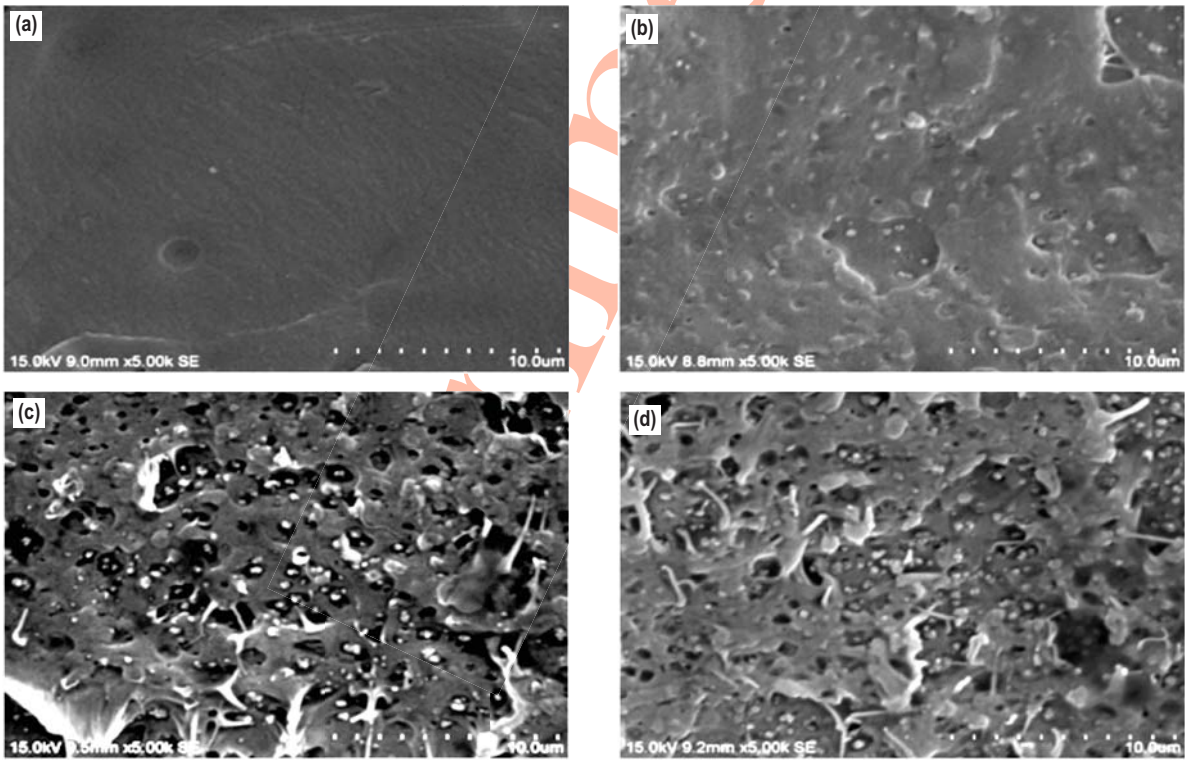

Fig. 2 : SEM micrographs (a) PLA film and (b), (c), (d) 5.0, 10.0, 15.0 % wt. nano-TiO_2/PLA biocomposite film

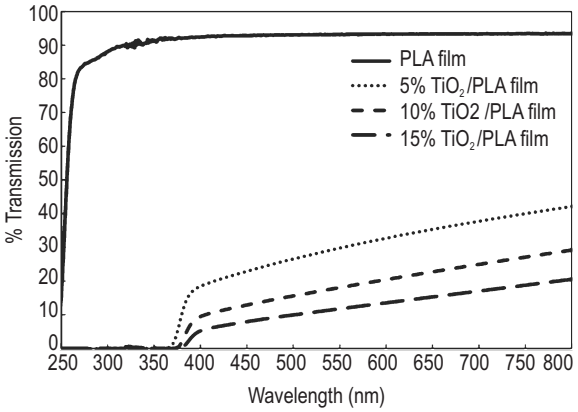

Fig. 3 : UV-VIS transmission spectra of nano-TiO_2/PLA biocomposite films at various dosages of TiO_2

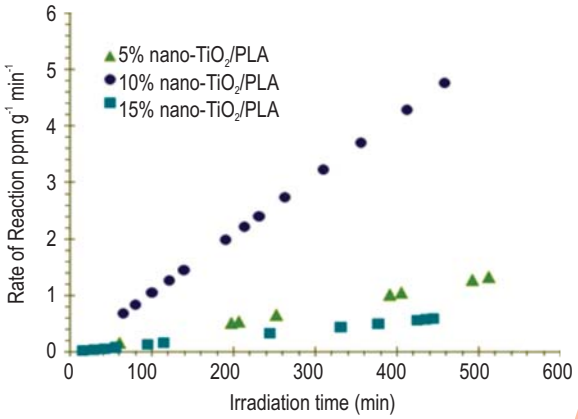

Fig. 5 : Rate of photocatalytic oxidation of gaseous DCM at different TiO_2 dosages (initial acetone concentrations of 100 ppm, UV light intensity of 4 $mW.cm^{-2}$, flow rate of 2.0 l min^{-1})

anhydride copolymer for use as photocatalyst material. The characterization of nano-TiO_2/PLA biocomposite films were examined by scanning electron microscope, UV-VIS spectrophotometer and X-ray diffractometer (XRD) to observe the dispersability and mixing efficiency of nano-TiO_2 in the PLA matrix. In addition, removal efficiency of dichloromethane (DCM) in gas phase was also investigated.

Materials and Methods

Nano-TiO_2/PLA biocomposite film preparations and characterization : Nano-TiO_2 powder, A220, (Ishihara kaisha) complex with varying contents of 5.0, 10.0, and 15.0 wt% were incorporated with maleic anhydride copolymer in molten PLA resins (Nature Works LLC) using the twin-screw extruder. The nano-TiO_2/PLA biocomposite films with thickness of 30 μm were obtained from the blown film extrusion technique using operation temperature in the range of 100C-160 ºC (Suwannahong*et al.*, 2012).

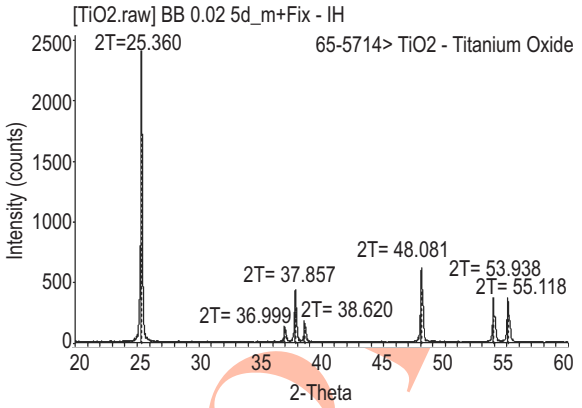

Fig. 4 : X-ray diffraction patterns of 10.0% wt cat wt^{-1} film nano-TiO_2/PLA biocomposite film

Table 2 : Calculated results from the absorbance of nano-TiO_2/PLA biocomposite film at various dosages of TiO_2

Dosages of nano-TiO_2 (%wt/wt)	Energy band gap (eV)
5.0% nano-TiO_2/PLAbiocomposite film	3.26
10.0% nano-TiO_2/PLAbiocomposite film	3.21
15.0% nano-TiO_2/PLAbiocomposite film	3.15

Morphology : The images of nano-TiO_2/PLA biocomposite films were examined by scanning electron microscope (SEM, Model Jx A-840, JEOL). In order to prevent the charge build-up during SEM observation, samples were coated with gold, which was used for ion sputter target. The sputter rate and time were set for 10 nm min^{-1} and 3 min, respectively. The gold film thickness was approximately 30 nm (Shifu *et al.*, 2009)

Optical property : UV-VIS spectra of nano-TiO_2/PLA biocomposite films were recorded by UV-VIS-NIR spectrophotometer (Lamda 950, Perkin Elmer instrument) equipped with an integrating sphere. The scan ranged from 200 to 800 nm. All spectra were monitored in the transmission mode and acquired under ambient conditions. The band gap energy of nano-TiO_2/PLA biocomposite films was calculated from the absorbance results (Shifu *et al.*, 2009).

X-ray diffraction (XRD) : The patterns of TiO_2 were recorded by XRD technique. XRD patterns were obtained on X-Ray Diffraction (TTRAXIII, Rigaku) using Cu Kα and radiation (=1.5404 Å). The current and voltage applied were 300 mA and 50 KV, respectively. The scan ranged from 20° to 60° with a scan rate of 5° min^{-1}. (Shifu*et al.*, 2009; Ao*et al.*, 2008)

Removal efficiency of photocatalytic oxidation of VOCs : The photoreactor was an annular closed-system. The photoreactor composed of an UV-C lamp with 254 nm wavelength as shown in Fig. 1. The TiO_2 coated nano-TiO_2/PLA biocomposite film was inserted inside the chamber. The reactor was designed to direct

the flow of incoming air towards the nano-TiO_2/PLA biocomposite film. Moreover, DCM gas phase was distributed onto the photocatalyst surface in photoreactor. The operation condition is shown in Table 1. DCM composed of volatile organic compound (Suwannahong*et al.*, 2012). After initial DCM concentration was at a steady state concentration, UV lamp was turned on. The quantitative analysis of DCM was determined by gas chromatograph equipped with flam ionization detector (FID, model GC2010, Shimadzu).

Results and Discussion

The PLA surface clearly exhibited uniform and smooth surface area as shown in Fig. 2(a). The surface morphology of TiO_2 is one of the most important factors, which can affect the efficiency of photocatalyst. In addition, it was observed that TiO_2 was totally deposited and dispersed in the PLA matrix. Fig. 2(b), 2(c) and 2(d) showed that surface morphology of PLA biocomposite films with nano-TiO_2varied in contents of 5.0, 10.0, and 15.0 %wt. cat./wt. film. The micrograph of SEM demonstrated a spherical shape of the TiO_2 particles. The diameter of the particles was less than 0.5 µm. The SEM images also revealed that higher the amount of TiO_2, more the agglomerations and good dispersion of TiO_2. The amount of nano-TiO_2 contents increased the active reactant contact area, thus enhancing photocatalytic degradation for VOCs.In order to overcome such drawback in the present study, the compatibilizer was necessarily cooperated into nano-TiO_2/PLA biocomposite matrix (Kreetachat *et al.*,2013).

To study the optical response of nano-TiO_2/PLA biocomposite film at various amount of nano-TiO_2, their UV–vis absorption spectra were measured, and the results are shown in Fig. 3. As could be seen from the spectra, the virgin PLA film transmitted UV-VIS light in range of 250-800 nm, while 5.0, 10.0 and 15.0 %wt. nano-TiO_2/PLA biocomposite films exhibited UV light absorption with wavelength lower than 400 nm. The absorption spectra determined band gap energy (E_g) of nano-TiO_2/PLA biocomposite films in Table 2. The results obtained in this study is in agreement with other works (Suwannahong *et al.*, 2012).

Fig. 4 was displayed XRD pattern of TiO_2 particles, which showed peak 2 at 25.36, 37.86, 48.08, and 55.12, that matched with plane as (101), (103), (004), (112) and (211), respectively. These XRD result corresponded to anatase phase of TiO_2. The (101) peak position indicated the dominant structure of TiO_2-anatase structure. Moreover, typical diffraction peaks representing rutile structure or brookite structure are not detected in the XRD pattern. The TiO_2-anatase form is well known as the most suitable structure of photocatalyst (Mohammadi *et al.*, 2008).

For DCM photocatalytic degradation using PLA-nano TiO_2 biocomposite film, the dosages of TiO_2 varied from 5.0, 10.0 and 15.0% wt cat wt^{-1} film. The photocatalytic degradation of catalyst not only depends on loading quality, but also on the amount of compound loaded. Photocatlytic degradation of different concentrations of TiO_2 on PLA composite film was studied. Fig. 5 shows that the conversion rate of DCM increased and then rapidly droped as TiO_2dosage further increased. The highest photodegradation efficiency of 63.4% was obtained when TiO_2 loading was at 10.0% wt., then photo degradation efficiency dropped slightly to15.0% wt. This was suggested by the lower content of TiO_2 that was unable to provide enough TiO_2 photocatalyst, while higher amount of TiO_2 might lead to a drop in the conversion of DCM due to nucleation of TiO_2 on the support which decreased of the amount of TiO_2 surface. The rate of reaction result was in agreement with the previous studies of Hung *et al.* (2007).

To summarize, the nano-TiO_2 incorporating in PLA with maleic anhydride copolymer for use as photocatalyst was the improved active site of surface area of the nano-TiO_2/PLA biocomposites film and coating TiO_2 interface. Nano-TiO_2/PLA biocomposites material was highly promising photocatalyst for degradation of volatile organic compound such as dichloro-methane at trace level concentrations.

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