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Application of Nano-TiO_2 /LDPE composite film on photocatalytic oxidation degradation of dichloromethane

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Abstract

This study focused on the photocatalytic destruction of dichloromethane (DCM) in indoor air using the nano-TiO_2 /LDPE composite film as an economical photocatalyst. The nano-TiO_2 was dispersed in a polyethylene matrix to form composite film. The photocatalytic activity of the nano-TiO_2/LDPE composite films was evaluated through the degradation of dichloromethane(DCM) under UV-C irradiance at specific wavelength of 254 nm. The percentage of nano-TiO_2 contents varied from 0, 5, and 10% (wt cat./wt LDPE composite film). The results derived from the kinetic model revealed that the photocatalytic rates of 5 and 10 wt.% nano-TiO_2/ LDPE composite films follow the first order reaction while the rate of the film without TiO_2 followed the zero order reaction. At low concentration of DCM, the rate of photocatalytic degradation of the DCM was slower than that at high DCM concentration. The 10 wt.% of TiO_2 content of the nano-TiO_2/LDPE composite film yielded the highest degradation efficiency of 78%, followed by the removal efficiency of 55% for the 5 wt.% of TiO_2 content of the nano-TiO_2/LDPE composite film. In contrast with the composite film containing nano-TiO_2, the LDPE film without adding nano-TiO_2 expressed the degradation efficiency of 28%.

Key words

Titanium dioxide, Nano-TiO_2/LDPE composite film, Dichloromethane, Photocatalytic degradation

Introduction

Chlorinated volatile organic compounds (VOCs) in indoor air environments has received great attention from many scientists and researchers due to their toxicity and carcinogenicity (Hager *et al*., 2005). Unfortunately, application of traditional method for indoor VOCs treatment seems impractical at low level concentration. For instant, adsorption process, which has been the most commonly used method to treat indoor air contaminants, is practical but ineffective for some types of organic compounds (Jo *et al*., 2004). Recently, photocatalytic oxidation (PCO) has been gaining attention as a possible alternative method for indoor air purification because it promises to clean air more efficiently and effectively (Jacoby *et. al*., 1996). In the PCO reaction, UV light was used to activate the catalyst to generate hydroxyl radicals (OH*) which reacted with organic contaminants. The contaminants were then transformed into less harmful substances. The photocatalyst mainly used in the PCO was titanium dioxide (TiO_2) because of its physical and chemical stability, non-toxicity, lowest cost, and resistance to corrosive. In order to activate TiO_2, it is necessary to supply the light intensity with energy higher than the energy band gap (E_{bg}) of TiO_2. It has been reviewed by numbers of researchers that different forms of TiO_2 such as thin and thick film coating, powder, membrane, and sol-gel have been utilized to make this photocatalyst more efficient

and more applicable (Hung *et al*., 2007; Liu *et al*., 2006; Sonawane *et al*, 2004). Previous studies indicated that the method of photocatalyst production and its physical form were among the most determining parameters influencing the overall photocatalytic efficiency. Recently, TiO_2 film which was prepared via sol-gel processing (Yu *et al*., 2000) and the degradation of organic compounds under UV light has been reported (Naskar *et al*., 1998). In this study, the nano-TiO_2 incorporating in polyethylene plastic film (TiO_2/LDPE) has been newly introduced as a photocatalyst material. This is because the nano-TiO_2/ LDPE composite film was economic and efficient technique for indoor air treatment application.

The characterizations of the nano-TiO_2/LDPE composite films were examined by the X-ray diffractometer (XRD), the UV VIS near-IR spectrophotometer, and the scanning electron microscope (SEM) to observe how homogenizing and well mixing of nano-TiO_2 in the LDPE polymer. In addition, removal efficiencies of dichloromethane (DCM) in gas phase using nano-TiO_2 incorporating in LDPE film as photocatalyst material was investigated.

Materials and Methods

Photocatalyst film and characterization : The TiO_2 powder, A220 (Ishihara Kaisha company), with varying contents, e.g. 0, 5, and 10 wt. %, were incorporated in molten LDPE resins (TPI Polene Co. Ltd.) using the twin screw extruder. Certain amount of polyethylene graft maleic anhydride was added during the compounding process in order to improve the dispersion of the nano-TiO_2 and enhance the compatibility between TiO_2 and LDPE matrix. The nano-TiO_2/LDPE composite films with the thickness of 30μm were obtained from the blown film extrusion technique using the operation temperature in a range of 150°C-180°C (Zhiyong *et al.,* 2007 and Suwannahong *et al*., 2010).

Morphology and optical properties : The microstructure of the nano-TiO_2/LDPE composite film was examined by using the scanning electron microscope (SEM, Model Jx A-840, JEOL, Japan). 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 (Shinde *et al*., 2008).

The ultraviolet-visible spectra of the photocatalysts were recorded by the UV-VIS spectrophotometer (Lamda 35, Perkin Elmer instrument, USA) equipped with the integrating sphere. A $BaSO_4$ dye was used as a reference. The scan ranged from 200 to 1,000 nm. All spectra was monitored in the absorbance mode and acquired under ambient conditions. The band gap energy of the nano-TiO_2/LDPE composite film was calculated from absorbance results (Shinde *et al*., 2008). The optical absorbance spectra, the adsorption coefficient and the band gap energy of the nano-TiO_2/ LDPE composite film were evaluated. Briefly, the absorption coefficient was calculated using the following relation, $\alpha = \ln(1/d)/\tau$, where τ is the transmittance and d is the thickness of the film. The thickness of the film was also evaluated from the UV spectrum and the average value corresponded to 260 nm. The band-gap energy was obtained by plotting the optical absorption $(\alpha h\upsilon)^2$ and the photon energy ($h\upsilon$). Then the extrapolation of the linear portion of the curve must be performed to receive the band gap energy (Stamate *et al*., 2005).

X-ray diffraction (XRD) : The crystalline structures of photocatalysts were determined by the XRD technique. XRD patterns were obtained on the X-ray diffractometer (Model 6000, Shimadzu, Japan) using Cu Ká and radiation with a nickle filter. The current and voltage applied were 30 mA and 40 KV, respectively. The scan ranged from 10° to 80° with a scan rate of 2° min^{-1} (Shifu *et al*., 2009)

Photocatalytic oxidation reactor : The photocatalytic oxidation reactor used in this study is an annular closed-system. The reactor is composed of an UV-C lamp with 254 nm wavelength. The UV light intensity was recorded using a digital radiometer equipped with a UV-C sensor. The nano-TiO_2/LDPE composite film was inserted inside the chamber. The humidity and temperature were monitored continuously using the thermo-hygrometer (DT-2 Kingtill). The reactor was connected with the air compressor pump which can be adjusted air flow rate from 0 to 5 l min^{-1}. The gas sample was pumped through the annular region. The reactor was designed to direct flow of incoming air toward the nano-TiO_2/LDPE composite film thereby, enhancing the distribution of the air pollutant onto the catalytic surface of the film.

The photocatalytic degradation of DCM using the nano-TiO_2/LDPE composite film was conducted in the continuous flow reactor at operating conditions as described by Suwannahong *et al*. (2010). The gas sample applied for all experiments was from a compressed air tube. After the DCM initial concentration was at steady state, the UV-C lamp was turned on. This step is necessary for the DCM in order to reach the adsorption equilibrium. The quantitative analysis of pollutant was made with the gas chromatograph (GC) equipped with a flam ionization detector (FID, model 5890, Hewlett Packard, USA). The gas sample with the volume of 1 ml was collected from the reactor using a gas syringe and was then injected into the GC-FID with a capillary column CP sil 8. The injector temperature was set at about 250°C and the initial column temperature was set at about 50°C and was increased to 110°C at a rate of 40°C min^{-1} (Hung *et al*., 2007). Since there was only one contaminant in this study, a single site Langmuir-Hinshelwood (L-H) model was introduced to evaluate photocatalytic rates (Obee *et al*., 1996; Obuchi *et al*., 1999, and Coronado *et al*., 2003).

Results and Discussion

Surface morphology of TiO_2 is one of the most important factors which can affect the efficiency of photocatalyst. In spite of readily agglomerating on the LDPE film, the TiO_2 was found to be deposited and well dispersed in the polyethylene matrix as seen in Fig.1. The SEM images also reveal that number of lump of TiO_2

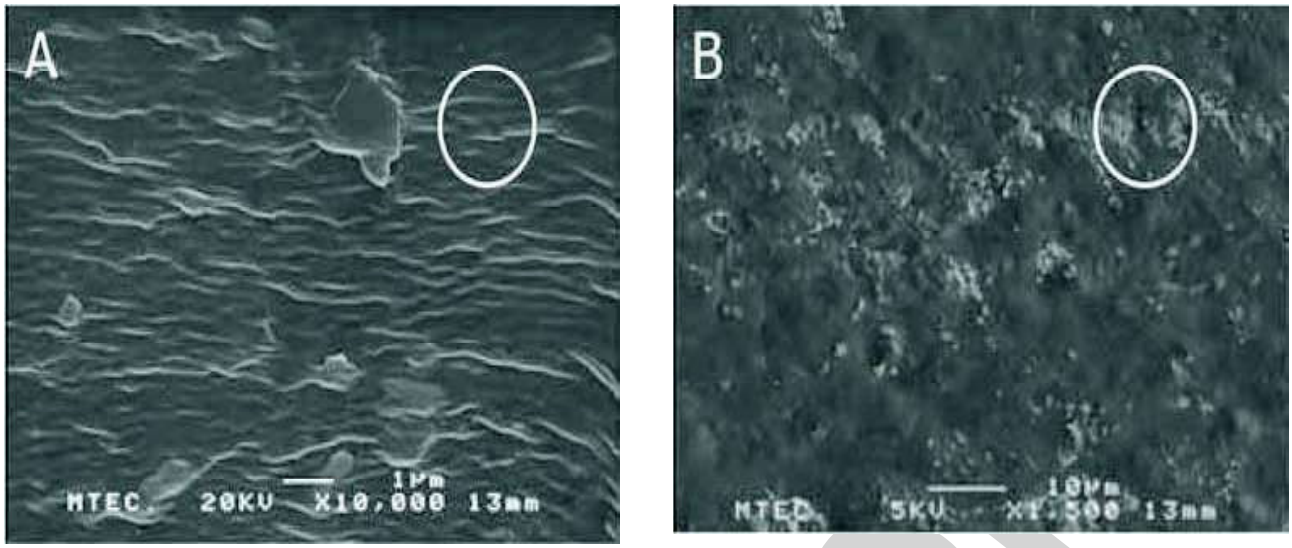

Fig. 1: SEM micrographs (A) LDPE film (B) 10 wt.% nano-TiO_2/LDPE composite film

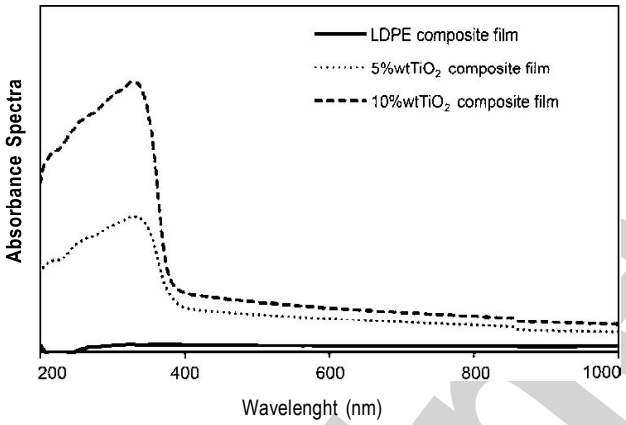

Fig. 2: UV absorbance spectra of the nano-TiO_2/LDPE composite film at various TiO_2 contents.

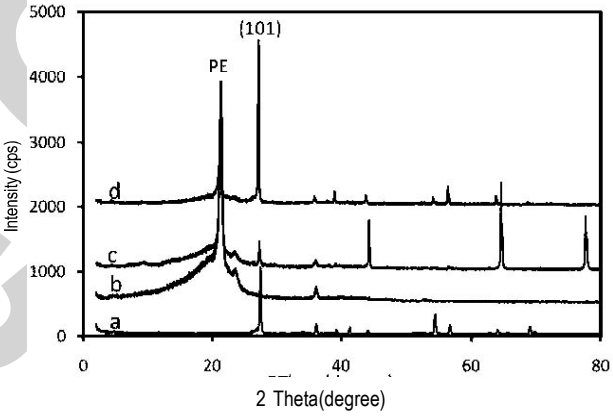

Fig. 3: X-ray diffraction patterns (a) nano-TiO_2 powder, (b) LDPE film, (c) 5 wt.% nano-TiO_2/LDPE composite film, and (d) 10 wt.% nano-TiO_2/LDPE composite film

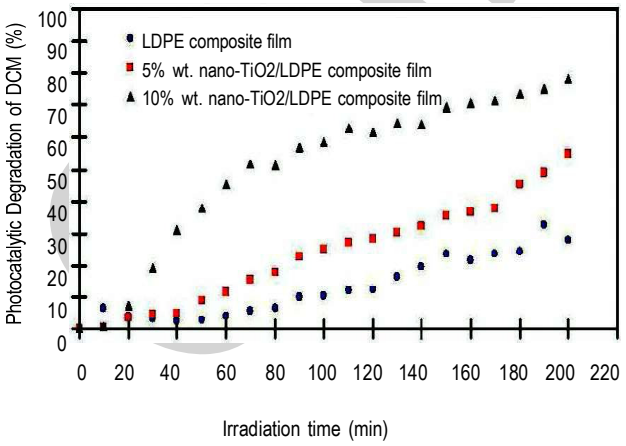

Fig. 4: PCO degradation of DCM at different dosages of TiO_2

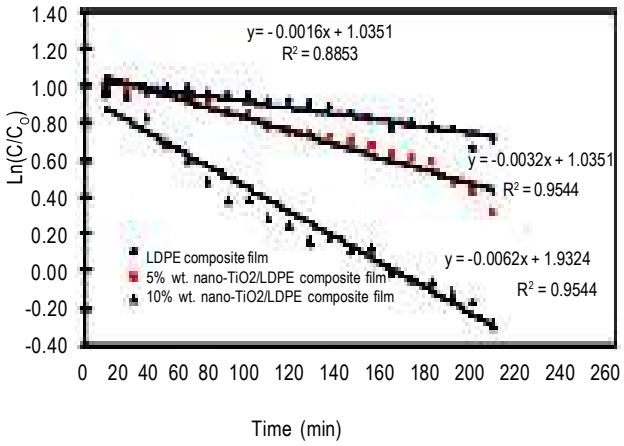

Fig. 5: Correlation between $\ln(C/C_o)$ and time at different percentages of TiO_2

Table- 1: Band gap energy of the nano-TiO_2/LDPE composite film at various amounts of TiO_2.

nano-TiO_2 contents (wt.%)	Band gap energy (E_g, eV)
0	2.93
5	3.13
10	3.21

Table- 2: Simplified Langmuir-Hinshelwood form, $\ln(C/C_o) = -kKt = -K't$, at different dosages of TiO_2.

Dosage of TiO_2	Simplified Langmuir Hinshelwood form	K'(min^{-1})	R^2
LDPE Composite film	-0.0016t + 1.0351	-0.0016	0.8853
5 % wt TiO_2 / LDPE composite film	-0.0032t + 1.0727	-0.0032	0.9544
10 % wt TiO_2 / LDPE composite film	-0.0062t + 0.9324	-0.0062	0.9629

increased as increase in dosage of TiO_2. Moreover, as the amount of the nano-TiO_2 content increases the dispersion ability of the TiO_2 decreases affecting the efficiency of photocatalytic activity. In order to overcome such drawback, the compatibilizer was added into the nano-TiO_2/LDPE composite matrix.

As seen from the spectra in Fig.2, virgin LDPE film rarely absorbed UV light with wavelength lower than 400 nm, while the 5 and 10 wt.% nano-TiO_2/LDPE composite films showed strong absorption. The 10 wt.% nano-TiO_2/LDPE composite film exhibited the broadest absorption peak followed by the 5 wt.% nano-TiO_2/LDPE composite film and the virgin LDPE film, respectively.

The band gap energy of the nano-TiO_2/LDPE composite films was estimated using the equation described by Ishu *et al*. (2006). The values of the calculated band gap energy of the nano-TiO_2/LDPE film at various dosages of TiO_2 are summarized in Table 1. The band gap energy of the 10 wt.% nano-TiO_2/LDPE film was approximately 3.2 eV, which was in a good agreement with other results (Andronic *et al*., 2007).

The XRD patterns of both 5 wt.% and 10 wt.% TiO_2/LDPE composite films show clear sharp peaks indicating the anatase phase. The XRD patterns also reveal that the anatase peaks (101) obviously increased with the amount of nano-TiO_2 (Jiang *et al*., 2009). Moreover, the XRD peak of 10 wt.% nano-TiO_2/LDPE composite film exhibited a similar intensity as that of the TiO_2 powder in anatase form. Consequently, the XRD pattern of 10 wt.% TiO_2/LDPE composite film shows the strongest sharp peak of anatase phase as shown in Fig.3. The XRD patterns also revealed an increase in the intensity of the anatase peak as increasing the nano-TiO_2 contents which will enhance the efficiency of photocatalytic degradation of the TiO_2/LDPE composite films.

For DCM photocatalytic degradation using the nano TiO_2/LDPE composite film, the dosages of TiO_2 were varied from 0, 5, and 10% (wt cat./wt film) as shown in Fig.4. The nano-TiO_2/LDPE composite film at 10 wt.% TiO_2 yielded the highest degradation efficiency (78%), followed by the removal efficiency of 55% of the nano-TiO_2/LDPE composite film at 5 wt.% TiO_2. While the virgin LDPE film expressed the degradation efficiency of 28%.

Fig.5 shows the correlation between $\ln(C/C_o)$ at different dosages of TiO_2 using the same initial concentration of dichloromethane and illumination time. The plots indicate that the slopes of fitted straight line using the least square method followed the first order kinetic for the 5 wt.% and 10 wt.% nano-TiO_2 composite films whereas the reaction of the 0 wt.% nano-TiO_2 /LDPE composite film appears to be close toward zero order. The Simplified Langmuir-Hinshelwood form, $\ln(C/C_o) = -kKt = -K't$, at different dosages of TiO_2 are displayed in Table 2.

From the experimental point of view, the lower the initial DCM concentration, the more difficult adsorption on the photocatalyst surface of the DCM. The obtained result leaded to lower adsorption constant rates of photocatalyst because the photooxidation rate was controlled by the catalyst surface in photochemical reaction (Bouanimba *et al*., 2011).

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