

Photo Catalytic Oxidation Degradation of Volatile Organic Compound with Nano-TiO₂/LDPE Composite Film

Kowit Suwannahong, Wipada Sanongra, Jittiporn Kruenate, Sarun Phibanchon, Siriuma Jawjit, and Wipawee Khamwichit

Abstract—The photocatalytic activity efficiency of TiO₂ for the degradation of Toluene in photoreactor can be enhanced by nano-TiO₂/LDPE composite film. Since the amount of TiO₂ affected the efficiency of the photocatalytic activity, this work was mainly concentrated on the effort to embed the high amount of TiO₂ in the Polyethylene matrix. The developed photocatalyst was characterized by XRD, UV-Vis spectrophotometer and SEM. The SEM images revealed the high homogeneity of the deposition of TiO₂ on the polyethylene matrix. The XRD patterns interpreted that TiO₂ embedded in the PE matrix exhibited mainly in anatase form. In addition, the photocatalytic results show that the toluene removal efficiencies of 30±5%, 49±4%, 68±5%, 42±6% and 33±5% were obtained when using the catalyst loading at 0%, 10%, 15%, 25% and 50% (wt. cat./wt. film), respectively.

Keywords—Photocatalytic oxidation, Toluene, nano-TiO₂/LDPE composite film.

I. INTRODUCTION

IN the last decade, TiO₂ is one of the most interesting used in photocatalysis process. It has been found to show effective of photocatalytic activity during both oxidation and reduction reactions. Photocatalytic oxidation (PCO) commonly uses semiconductor catalysts as TiO₂ and ultraviolet (UV) light. Under optimal reaction condition, organic pollutions can be completely oxidized to form carbon dioxide, water, etc., as final product. Recently, the interest of its application is to remove volatile organic compounds (VOCs).

An electron in an electron-filled valence band (VB) is excited by photo irradiation to vacant conduction band (CB), leaving a positive hole in the VB. These electrons and positive holes drive reduction and oxidation, respectively, at

Kowit Suwannahong is with the Faculty of Science & Technology, Suan Sunandha Rajabhat Univesity, 1 U-Thong Nok Road, Wachira, Dusit, Bangkok 10300, Thailand.

Wipada Sanongraj is with the Department of Chemical Engineering, Faculty of Engineering, Ubon Ratchathani University, Ubonratchathani 34190, Thailand.

Jittiporn Kruenate is with the National Metal and Materials Technology Center, 114 Thailand Science park, Paholyothin Road, Klong1, Klong Luang, Patumthani 12120, Thailand.

Saran Phibanchon is with the Faculty of Science and Art, Burapha University, Chanthaburi campus, Chanthaburi, 22170, Thailand.

Siriuma Jawjit is with the Institute of Allied Health Sciences and Public Health Walailak University 222 Thaiburi Thasala Nakhon si thammarat 80161, Thailand.

Wipawee Khamwichit is the with Institute of Engineering and Resources Walailak University 222 Thaiburi Thasala Nakhon si thammarat 80161, Thailand (E-Mail:kowit007@gmail.com).

compounds adsorbed on the surface of a photocatalyst [1, 2, 3] The Equation can be written as :



In this reaction, h⁺ and e⁻ are powerful oxidizing and reducing agent, respectively. The oxidation and reduction reaction can be expressed as:

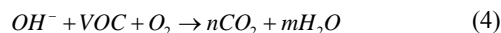
Oxidation reaction:



Reduction reaction:



When Volatile organic compounds are chemically transformed by a PCO device, it is the hydroxyl radical (OH[·]) derived from the oxidation of adsorbed water or adsorbed OH⁻, that is the dominant strong oxidant. It is net reaction with a VOC can be expressed as:



The activity of TiO₂ as photocatalyst is well recognized to depend strongly upon the method of preparation. Currently, the preparation of polymer nanocomposite film its material has been intently considered due to their relatively. Supporting of TiO₂ has been reported recently such as high energy ball milling, polyurethane composite coating, foamed polyethylene sheet and synthetic fabrics. Suitable thin film supports could show properties: withstand reactive oxidative radicals attack during light, maintain long term catalytic stability, preclude TiO₂ leaching during the light irradiation, and allow photocatalytic oxidation to process with acceptable kinetics.

Polymer with TiO₂ composite has been successfully synthesized in difference polymer matrixes such as polyethylene, poly propylene, poly vinylchloride [4, 5, 6]. The commercial use of polyethylene (PE) thin film is due to the single bond presence that make this material stable towards chemical and corrosive agent. This film is a flexible, semi-transparent, low cost commercial product. PE has excellent electrical properties making it widely used as insulator. The low density PE used consists of highly branched low crystalline unit with the formula H (CH₂CH₂)_nH [7].

Toluene is a major indoor and industrial air pollutant, and it was recommended as one of representative indoor VOCs. In

the present paper [8], Toluene was selected as the model VOCs to investigate to capability with nano-TiO₂/LDPE composite film

The purpose of this study, the nano-TiO₂ incorporating polyethylene plastic film (TiO₂/LDPE) with maleic anhydride copolymer has been introduced as a photocatalyst material. The nano-TiO₂ composite LDPE film was economic and efficient technique for indoor air treatment application. The characterizations of the nano-TiO₂/LDPE composite films were examined by the X-ray diffraction (XRD), the UV VIS near-IR spectrophotometer, and the scanning electron microscope (SEM) to observe how homogenizing and well mixing of nano-TiO₂ in the LDPE polymer. In addition, removal efficiencies of Toluene in gas phase was investigated.

II. MATERIALS AND METHOD

A. Materials

Titanium dioxide (TiO₂, A220) with crystalline size ca. 16 nm. was purchased from the Ishihara Sangyo Kaisha company. The commercial grade of LDPE (JJ4324) used in this study was supplied by the TPI Polene Co, Ltd. Melt Flow Index of the resin from the manufacturer was 5.5 g/10 min. The commercial grade of polyethylene graft maleic anhydride (PE-g-Ma, Compolene COLL) was purchased from the BenMayer, Ltd.

B. Photocatalyst Nano-TiO₂/LDPE Composite Film Preparation

The TiO₂ powder, A220, with varying contents, e.g. 0, 10, 15, 25, and 50 %,wt.cat./wt. film, were incorporated in molten LDPE resins 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-TiO₂ and enhance the compatibility between TiO₂ and LDPE matrix. The nano-TiO₂/LDPE composite films with the thickness of 30 micrometers were obtained from the blown film extrusion technique using the operation temperature in a range of 150°C-180°C. All of photocatalyst films are shown in Table I.

C. Photocatalyst Characterization Morphology

The microstructure of the nano-TiO₂/LDPE composite film was examined by using the 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. [9].

TABLE I
PROPERTIES OF THE NANO-TiO₂/LDPE FILM AT VARIOUS
NANO-TiO₂ LOADING

Sample	Nano-TiO ₂ Contents (wt.%)	Average Particle size (nm)	Nano-TiO ₂ /LDPE composite film thickness (μm)
1	0	-	30
2	10	16	30
3	15	16	30
4	25	16	30
5	50	16	30

D. Optical Properties

The Ultraviolet-visible spectra of the photocatalysts were recorded by the UV-VIS spectrophotometer (Lamda 35, Perkin Elmer instrument) that equipped with an integrating sphere. A BaSO₄ dye was used as a reference. The scan ranges from 200 to 1,000 nm. All spectra was monitored in the absorbance mode and acquired under ambient conditions. [9, 10].

E. Atomic Force Microscopy

Microstructural surface morphology of samples was observed by atomic force microscope (AFM). All imaging and lithography were performed in tapping mode on a Asylum research MFP-3D-BIO™ Atomic Force Microscope. with rotated tapping mode etched silicon probes. The rotated tapping mode etched silicon probe is 125mm with a spring constant of 40 N/m developed to measure high-aspect ratio features.

F. X-ray Diffraction (XRD)

The crystalline structures of photocatalysts were determined by X-Ray Diffraction (XRD) technique. XRD patterns were obtained on the X-Ray Diffraction (Model 6000, Shimadzu) using Cu Kα and radiation with a nickle filter. The current and voltage applied were 30 mA and 40 KV, respectively. The scan ranges from 10° to 80° with a scan rate of 2° min⁻¹ [9, 10].

G. 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-TiO₂/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 litres per minute. The gas sample was pumped through the annular region. The reactor was designed to direct flow of incoming air toward the nano-TiO₂/LDPE composite film thereby, enhancing the distribution of the air pollutant onto the catalytic surface of the film.

The photocatalytic degradation of Toluene using the nano-TiO₂/LDPE composite film was conducted in the continuous flow reactor at operating conditions as shown in Table II. The gas sample applied for all experiments was from a compressed

air tube. After the Toluene initial concentration was at steady state, the UV lamp was turned on. This step is necessary for the Toluene 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). 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 [11].

In this paper, the conversion rate was calculated by $(C_0 - C)/C_0 * 100$, where C is the concentration of the reactant after irradiation as a function of reaction time and C_0 is the concentration of the reactant after adsorption equilibrium and before the irradiation in the presence of catalyst.

TABLE II
OPERATING CONDITIONS FOR TOLUENE
PHOTOCATALYTIC DEGRADATION

Operating conditions	Representative value
Initial Relative Humidity, %	45-55%
Temperature, °C	26-42
Air Flow rate, L min ⁻¹	4
Reactor residence time, s	30
Initial TOLUENE concentration, ppm	6.5 (±5)
UV light source	6-W, UV-C light
UV light intensity, mW cm ⁻²	4
Reactor material	stainless steel
Loading of catalyst film, (wt.% cat/wt. film)	0, 10,15,25, 50
Reaction time, min	300

III. RESULTS AND DISCUSSION

A. Characterization of the Nano-TiO₂/LDPE Composite Film SEM Characterization and AFM Images

Surface morphology of TiO₂ is one of the most important factors which affect the efficiency of a photocatalyst. In Fig.1, it was clearly that TiO₂ was deposited and well dispersed in the polyethylene matrix. On the other hand, TiO₂ was rarely spread onto film. The SEM images also reveal that TiO₂ increasing onto the film as increasing dosage of TiO₂. However, as the amount of the nano-TiO₂ content increases the dispersion ability of the TiO₂ decreases affecting the efficiency of photocatalytic activity. In order to overcome such drawback in this work, the compatibilizer was cooperated into the nano-TiO₂/LDPE composite matrix.

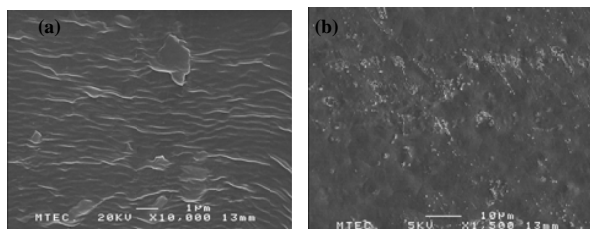


Fig. 1 SEM micrographs (a) LDPE film (b) 15 wt.% nano-TiO₂/LDPE composite film

From the surface analysis of the nano-LDPE TiO₂ Film with the AFM, the 2-dimension and 3-dimension of the surface plots (10x10 µm²) were obtained.

The film of nano-LDPE TiO₂ Film from the starting dosage of TiO₂ at 10, 15, 25 and 50% w/w were shown. Moreover, the grains of TiO₂ were implanted in the film and shape edges were pointed out at various sizes and were scattered throughout the film. The film surface roughness study was shown that the 15% w/w TiO₂ dosage gave lowest surface roughness. Higher of TiO₂ dosage will increase the number of surface roughness intensity. The formation of TiO₂ bigger particle at high TiO₂ dosage (25, 50% w/w) will result the bad distribution and the higher surface roughness were observed. The surface area of the TiO₂ film were shown in Fig. 2.

B. Optical Properties of the Nano-TiO₂/LDPE Composite Films

UV-Vis absorbance spectra of the nano-TiO₂/LDPE composite film at various amounts of nano-TiO₂ are shown in Fig. 3. As can be seen from the spectra, the pure LDPE film rarely absorbed UV light with wavelength lower than 400 nm, while the 10,15,25 wt.% and 50 wt.% nano-TiO₂/LDPE composite films had strong absorption.

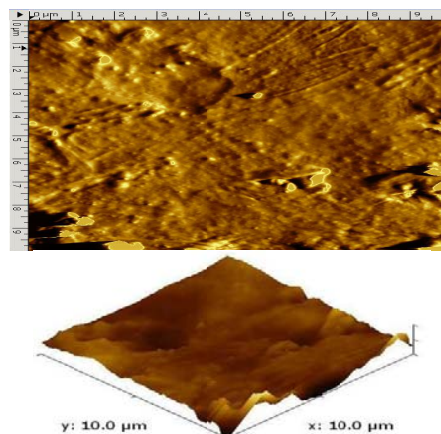


Fig. 2 AFM images of 15% w/w nano-LDPE TiO₂ Film surface image and 3-D image

The 50 wt.% nano-TiO₂/LDPE composite film exhibited the broadest absorption peak followed by the 25,15,10 wt.% nano-TiO₂/LDPE composite film and the pure LDPE film, respectively.

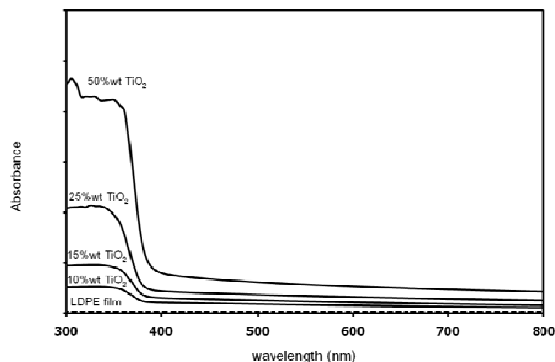


Fig. 3 UV absorbance spectras of the nano-TiO₂/LDPE composite film at various loading of TiO₂

C. X-ray Diffraction Patterns of the Nano-TiO₂/LDPE Composite Films

Fig. 4 displays the XRD patterns of the nano-TiO₂/LDPE composite film at various loading of TiO₂. The XRD patterns of 0,10,15,25 and 50 wt.% TiO₂/LDPE composite films show the clear sharp peaks indicating the anatase phase. The XRD patterns also reveal that the anatase peaks (101) obviously increased with the amount of nano-TiO₂ [12]. Moreover, the XRD peak of 50wt.% nano-TiO₂/LDPE composite film exhibited a similar intensity as that of the TiO₂ powder in anatase form. Consequently, the XRD pattern of 50 wt.% TiO₂/LDPE composite film shows the strongest sharp peak of anatase phase. The XRD patterns revealed that an increase in the intensity of the anatase peak as the nano-TiO₂ contents increase can contribute to the efficiency of photocatalytic degradation of the composite films [13].

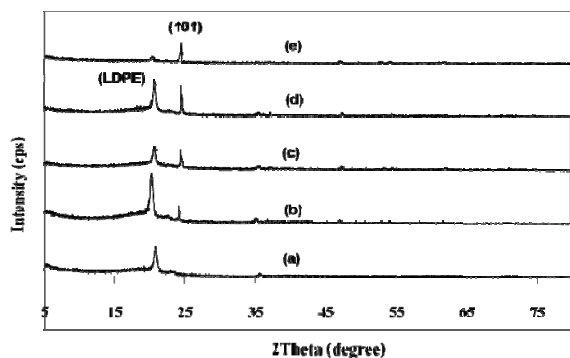


Fig. 4 X-ray diffraction patterns (a) LDPE film, (b) 10 wt.% Nano-TiO₂/LDPE composite film, (c) 15 wt.% Nano-TiO₂/LDPE composite film, and (d) 25 wt.% Nano-TiO₂/LDPE composite film and (e) 50 wt.% Nano-TiO₂/LDPE composite film

D. Photocatalytic Activity at Different of Nano-TiO₂/LDPE Composite Films Loading

For Toluene photocatalytic degradation using the LDPE-nano TiO₂ composite film, the loading of TiO₂ was varied from 0%, 10%, 15%, 25%, and 50% (wt cat./wt film). The photocatalytic activity catalyst not only depends on properties of loading properties, but also on the amount of compound loaded. This study investigated the photocatalytic activity of

different TiO₂ on LDPE composite film. Table III shows that the conversion rate of toluene increases and then drops as the TiO₂ loading increases. The highest efficiency of 68% is obtained when the TiO₂ loading is 15%, then the photodegradation efficiency drop slightly at 50% as shown in Fig 5. It is suggested that a low number of particle deposited on surface of TiO₂ cannot provide enough TiO₂ photocatalyst, while a large amount of TiO₂ may lead to a drop in the conversion of Toluene due to the nucleation of TiO₂ on the support, which decreases the amount of TiO₂ surface. From result, the number of particle deposited on surface at different TiO₂ loading is consistent with photocatalytic activity of different TiO₂ loading on LDPE composite film.

TABLE III
TOLUENE CONVERSION, NUMBER OF PARTICLE DEPOSITED ON SURFACE AND TiO₂ LOADING OF THE NANO-TiO₂/LDPE FILM AFTER REACTION 300 MIN

Sample	Nano-TiO ₂ loading (wt.%)	Surface area (m ² /g)	Conversion rate (%)
1	10	14.87	49
2	15	37.65	68
3	25	15.55	42
4	50	13.32	33

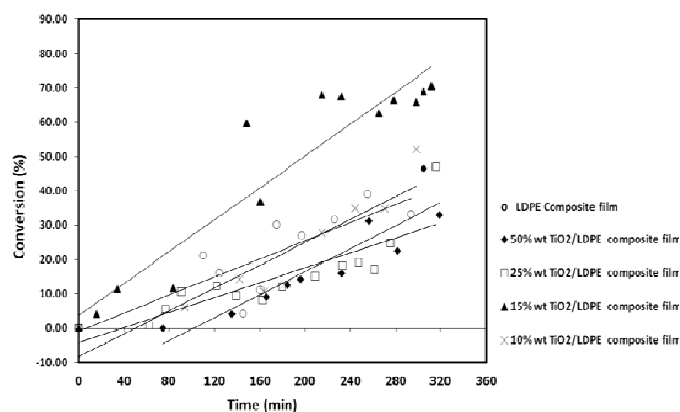


Fig. 5 Dependence of conversion rate at different Percentage of TiO₂

III. CONCLUSION

This work has demonstrated that nano-TiO₂/LDPE composite film can be prepared by blown film extrusion technique. The SEM results revealed depositions of TiO₂ on the thin film. From the UV transmittance and absorbance results, the pure LDPE film rarely absorbed UV light with wavelength lower than 400 nm., while the 10, 15, 25 wt.% and 50 wt.% nano-TiO₂/LDPE composite films had strong absorption. The results of XRD examination showed that the TiO₂ on the thin film has the major structure in anatase form. For Toluene photocatalytic degradation using the nano-TiO₂/LDPE composite film, the conversion of 30±5%, 49±4%, 68±5%, 49±6% and 33±5% were obtained when using the catalyst loading of 0%, 10%, 15%, 25% and 50% (wt cat./wt film), respectively.

ACKNOWLEDGMENT

Kowit Suwannahong would like to express his gratitude to Suan Sunandha Rajabhat University for their financial support and for providing with an opportunity to carry out this project.

REFERENCES

- [1] L. Andronic and A. Duta: "TiO₂ thin films for dyes photodegradation. Thin solid films", **515**, 6294-6297 (2007).
- [2] H.P. Chen and H. Jenq: "Kinetics of photocatalytic oxidation of trace organic compounds over titanium dioxide. Environmental International", **24**, 871-879 (1998).
- [3] J. Chen, D. Okis, W. Rulkens and H. Bruing: "Kinetic processes of photocatalytic mineralization of alcohol on metalized Titanium dioxide". Wat. Res., **33**, 1173-1180 (1999).
- [4] J.M. Coronado, M. Zorn, I. Tejedor and M. Anderson: "Photocatalytic oxidation of Ketones in the gas phase over TiO₂ thin films": A Kinetic study on the influence of water vapor. App. Cat. B: Env., **43**, 329-344 (2003).
- [5] C. Feiyan, O.S. Pehkoenn and B.M. Ray: "Kinetics and mechanism of UV-photodegradation of chlorinated organic in the gas phase". Wat, Res., **36**, 4203-4214 (2002).
- [6] H. Habibi and M. Nasr-Esfahani: "Preparation, characterization and photocatalytic activity of a novel nanostructure composite film derived from nanopowder TiO₂ and sol-gel process using organic dispersant". Dyes and pigments, **75**, 714-722 (2007).
- [7] S. Hager, R. Bauer and G. Kudielka: "Photocatalytic oxidation of gaseous chlorinated organic over titanium dioxide". Chemosphere, **41**, 1219-1225 (2000).
- [8] L. Hongmin, L. Zhiwei, Y. Xiaojiang and W. Feng: "Kinetic analysis of photocatalytic oxidation of gas-phase formaldehyde over titanium dioxide". Chemospher, **60**, 630-635 (2005).
- [9] W. Hung, S. Fu, J. Iseng, H. Chu and T. Ko: "Study on photocatalytic degradation of gas dichloromethane using pure and iron ion-doped TiO₂ prepared by the sol-gel method". Chemosphere, **66**, 2142-2151 (2007).
- [10] O. Ibhaddon, A. Arabatzis, P. Falaras and D. Isoukleris: "The design and photoreaction kinetic modeling of a gas-phase titanium foam pack bed reactor". Chemical engineering J., **133**, 317-323 (2007).
- [11] K.W. Jo and K. Park: "Heterogeneous photocatalysis of aromatic and chlorinated volatile organic compounds (VOCs) for non-occupational indoor air application". Chemosphere, **57**, 555-565 (2004).
- [12] F. Jiang, Zhen Z., Z. Xu and S. Zgeng: "Preparation and characterization of SiO₂-pillared H₂Ti₄O₉ and its photocatalytic activity for methylene blue degradation". J. of Hazard. Mater., **164**, 1250-1256 (2009).
- [13] Jacoby, W. A., Blake, D. M., Fennell, J. A., Boulter, J. E., Vargo, L. M., George, M. C. and Dolberg S. K. J. of Air & Waste Management Association, **46**, 891-898 (1996).