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Photo Catalytic Oxidation Degradation of Volatile Organic Compound with Nano-TiO_2/LDPE Composite Film

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***Abstract*—**The photocatalytic activity efficiency of TiO_2 for the degradation of Toluene in photoreactor can be enhanced by nano-TiO_2/LDPE composite film. Since the amount of TiO_2 affected the efficiency of the photocatalytic activity, this work was mainly concentrated on the effort to embed the high amount of TiO_2 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 TiO_2 on the polyethylene matrix. The XRD patterns interpreted that TiO_2 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-TiO_2/LDPE composite film.

I. Introduction

IN the last decade, TiO_2 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 TiO_2 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-tilled 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 compounds adsorbed on the surface of a photocatalyst [1, 2, 3] The Equation can be written as :

$$TiO_2 + h\gamma \rightarrow h^+ + e^- \quad (1)$$

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

Oxidation reaction:

$$h^+ + OH^- \rightarrow OH^- \quad (2)$$

Reduction reaction:

$$e^- + O_{2ads}{}^- \rightarrow O^-_{2ads} \quad (3)$$

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:

$$OH^- + VOC + O_2 \rightarrow nCO_2 + mH_2O \quad (4)$$

The activity of TiO_2 as photocattalyst 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 TiO_2 has been reported recently such as high energy ball milling, polyeurethane 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 TiO_2 leaching during the light irradiation, and allow photocatalytic oxidation to process with acceptable kinetics.

Polymer with TiO_2 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 $(CH_2CH_2)_nH$ [7].

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

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the present paper [8], Toluene was selected as the model VOCs to investigate to capability with nano-TiO_2/LDPE composite film

The purpose of this study, the nano-TiO_2 incorporating polyethylene plastic film (TiO_2/LDPE) with maleic anhydride copolymer has been introduced as a photocatalyst material. The nano-TiO_2 composite LDPE 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 diffraction (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 Toluene in gas phase was investigated.

II. Materials and Method

A. Materials

Titanium dioxide (TiO_2, 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-TiO_2/LDPE Composite Film Preparation

The TiO_2 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-TiO_2 and enhance the compatibility between TiO_2 and LDPE matrix. The nano-TiO_2/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-TiO_2/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-TiO_2/LDPE Film at Various Nano-TiO_2 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 $BaSO_4$ 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-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 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-TiO_2/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-TiO_2/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 (Co-C)/Co *100) ,where C is the concentration of the reactant after irradiation as a function of reaction time and Co 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-TiO_2/LDPE Composite Film SEM Characterization and AFM Images

Surface morphology of TiO_2 is one of the most important factors which affect the efficiency of a photocatalyst. In Fig.1, it was clearly that TiO_2 was deposited and well dispersed in the polyethylene matrix. On the other hand, TiO_2 was rarely spread onto film. The SEM images also reveal that TiO_2 increasing onto the film as increasing dosage of TiO_2. However, 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 in this work, the compatibilizer was cooperated into the nano-TiO_2/LDPE composite matrix.

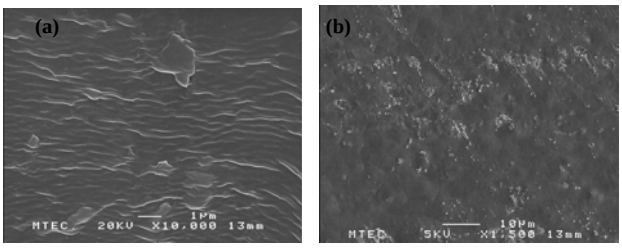

Fig. 1 SEM micrographs (a) LDPE film (b) 15 wt.% nano-TiO_2/LDPE composite film

From the surface analysis of the nano –LDPE TiO_2 Film with the AFM, the 2 –dimension and 3 –dimension of the surface plots (10x10 um^2) were obtained.

The film of nano –LDPE TiO_2 Film from the starting dosage of TiO_2 at 10, 15, 25 and 50% w/w were shown. Moreover, the grains of TiO_2 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 TiO_2 dosage gave lowest surface roughness. Higher of TiO_2 dosage will increase the number of surface roughness intensity. The formation of TiO_2 bigger particle at high TiO_2 dosage (25, 50% w/w) will result the bad distribution and the higher surface roughness were observed. The surface area of the TiO_2 film were shown in Fig. 2.

B. Optical Properties of the Nano-TiO_2/LDPE Composite Films

UV-Vis absorbance spectra of the nano-TiO_2/LDPE composite film at various amounts of nano-TiO_2 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-TiO_2/LDPE composite films had strong absorption.

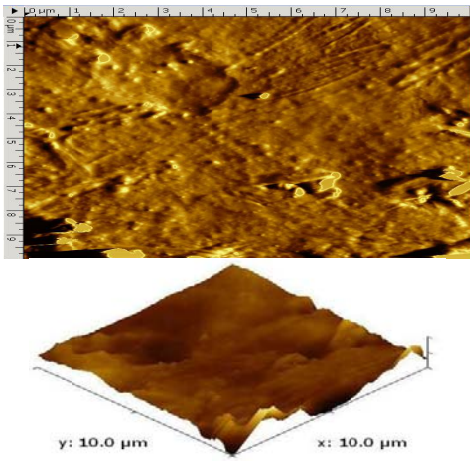

Fig. 2 AFM images of 15% w/w nano –LDPE TiO_2 Film surface image and 3-D image

The 50 wt.% nano-TiO_2/LDPE composite film exhibited the broadest absorption peak followed by the 25,15,10 wt.% nano-TiO_2/LDPE composite film and the pure LDPE film, respectively.

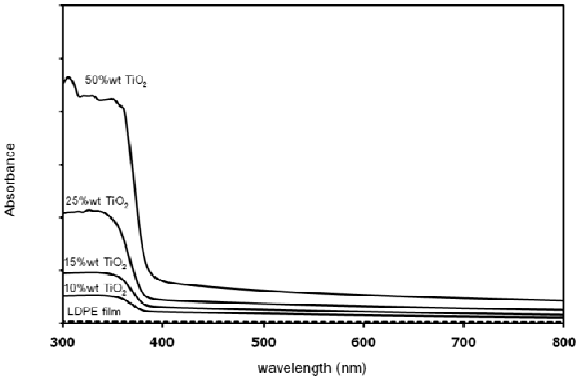

Fig. 3 UV absorbance spectras of the nano-TiO_2/LDPE composite film at various loading of TiO_2

C. X-ray Diffraction Patterns of the Nano-TiO_2/LDPE Composite Films

Fig. 4 displays the XRD patterns of the nano-TiO_2/ LDPE composite film at various loading of TiO_2. The XRD patterns of 0,10,15,25 and 50 wt.% TiO_2/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-TiO_2 [12]. Moreover, the XRD peak of 50wt.% 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 50 wt.% TiO_2/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-TiO_2 contents increase can contribute to the efficiency of photocatalytic degradation of the composite films [13].

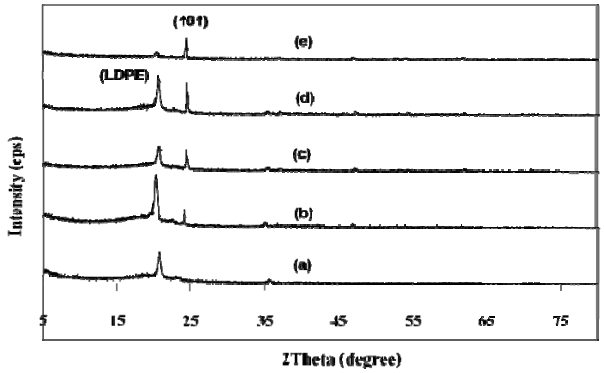

Fig. 4 X-ray diffraction patterns (a) LDPE film, (b) 10 wt.% Nano-TiO_2/LDPE composite film, (c) 15 wt.% Nano-TiO_2/LDPE composite film, and (d) 25 wt.% Nano-TiO_2/LDPE composite film and(e) 50 wt.% Nano-TiO_2/LDPE composite film

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

For Toluene photocatalytic degradation using the LDPE-nano TiO_2 composite film, the loading of TiO_2 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 photocatlytic activity of different TiO_2 on LDPE composite film. Table III shows that the conversion rate of toluene increases and then drops as the TiO_2 loading increases. The highest efficiency of 68% is obtained when the TiO_2 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 TiO_2 cannot provide enough TiO_2 photocatalyst, while a large amount of TiO_2 may lead to a drop in the conversion of Toluene due to the nucleation of TiO_2 on the support, which decreases the amount of TiO_2 surface. From result, the number of particle deposited on surface at different TiO_2 loading is consistent with photocatalytic activity of different TiO_2 loading on LDPE composite film.

TABLE III
TOLUENE CONVERSION, NUMBER OF PARTICLE DEPOSITED ON SURFACE AND TiO_2 LOADING OF THE NANO-TiO_2/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

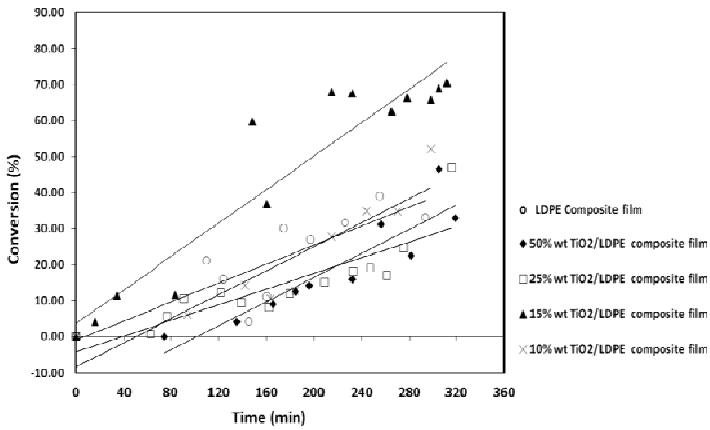

Fig. 5 Dependence of conversion rate at different Percentage of TiO_2

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 dagradation 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.

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