

# Enhancement of Photocatalytic Degradation of Poly(vinyl chloride) with Perchlorinated Iron (II) Phthalocyanine Modified Nano-TiO<sub>2</sub>

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**ABSTRACT:** A novel photodegradable thin film of poly(vinyl chloride) (PVC) composite was prepared by embedding modified TiO<sub>2</sub> nanoparticles into the commercial PVC. The photocatalyst nanoparticles were modified with perchlorinated iron (II) phthalocyanine (FePcCl<sub>16</sub>) to improve their photocatalytic activity. Solid-phase photocatalytic degradation of the PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> thin film was carried out under ultraviolet (UV) lamp or sunlight irradiation in atmosphere. The properties of composite films were compared with those of pure PVC film and poly(vinyl chloride)-TiO<sub>2</sub> (PVC-TiO<sub>2</sub>) composite films through performing weight loss

monitoring, scanning electron microscope and Fourier-transform infrared spectroscopy. The results indicated that the degradation efficiency of PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> composite film was significantly higher than that of pure PVC film and PVC-TiO<sub>2</sub> composite film under UV or sunlight irradiation. The photocatalytic degradation mechanism was discussed briefly. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1823–1828, 2011

**Key words:** poly(vinyl chloride); FePcCl<sub>16</sub>-TiO<sub>2</sub>; PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> composite film; solid-phase photocatalytic degradation

## INTRODUCTION

Poly(vinyl chloride) (PVC) is widely used as heat shrink membranes, transparent slices, one-off medical products, emulsion gloves, cable insulation, and so on. A massive amount of PVC is now produced globally and is consumed with exceedingly low recovery value. PVC is nondegradable when it is abandoned in the natural environment, which causes serious environment problems. Nowadays disposal of wasted PVC such as landfill, incineration, or recycle is neither economically valuable nor acceptable due to causing more serious air pollution.<sup>1–3</sup> Therefore, studying and developing degradable PVC plastic has an important meaning. There are two kinds of familiar degradable plastic, one is biodegradable plastic and the other is photodegradable plastic. Some biodegradable PVC plastics have been reported.<sup>4–6</sup> But these biodegradable PVC plastics have to include a great quantity of starch (about 30%) to achieve better degradation effect, which

affect the transparency and mechanical performance and do not fit uses for transparent PVC material. Some defects such as overlong degradation cycle, halfway degradation and others in the degradation of biodegradable PVC plastics also limit their expanded applications. Developing photodegradable transparent PVC packing materials will overcome the above weaknesses and achieve significant theory and applications.

The photodegradable mechanism of PVC is generally proposed that the aging proceeds primarily with a radical-type mechanism.<sup>7–9</sup> When a sample is exposed to UV or sunlight, the high energy absorbed by PVC is able to initiate free radicals by the breakage of chemical bonds in PVC molecules, and then activate a series of chemical reactions, such as molecular chains scission and crosslinking, hydrogen chloride elimination to form alkene or polyene linkages. Nano-TiO<sub>2</sub>, as an effective photocatalyst, is used to add into PVC to achieve quick photocatalytic degradation of PVC. The interaction between UV radiation and TiO<sub>2</sub> surface can generate free radicals that might improve the degradation efficiency of polymer such as PVC, polystyrene (PS) or polyethylene (PE).<sup>10–16</sup> Cho and Choi<sup>10</sup> had reported that PVC-TiO<sub>2</sub> nanocomposite could be degraded under UV irradiation. However, its technological application seems limited because of the UV excitation source, which is only 3–5% of the solar beam that can reach the earth.<sup>17</sup> The efficient use of solar light,

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or in other light from the visible region of the spectrum, may appear to be an appealing challenge for developing the future generation of the photodegradation plastics.

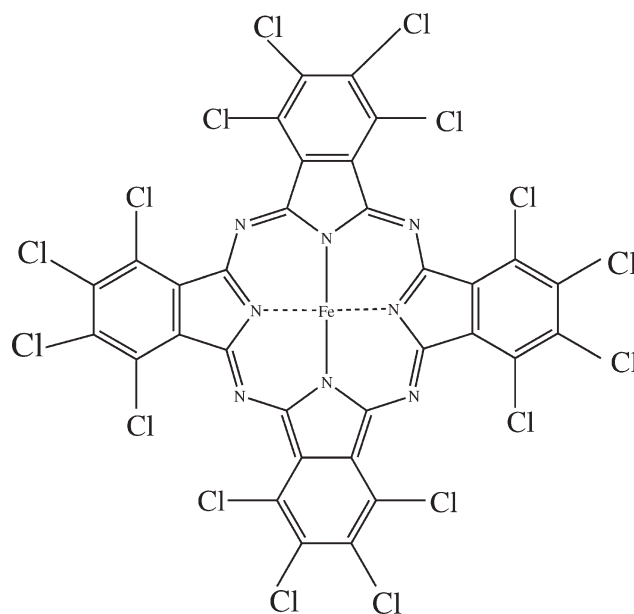
To develop modified  $\text{TiO}_2$  photocatalysts that show a high activity under the visible light irradiation, many methods are carried out such as transition metal ion-implanting,<sup>18–21</sup> nonmetal elements doping,<sup>22–25</sup> and hydrogen peroxide or chelating agent treating.<sup>26,27</sup> Dye modified is considered to be an efficient method to extend its absorption to the visible spectral region due to the cooperative function of photosensitization and  $\text{TiO}_2$  semiconductor in the generation of OH radicals.<sup>28–30</sup> Phthalocyanines themselves or their metal complex compound are one kind of organic functional dye which has absorption in the visible spectral region. What's more, they have a macrocyclic structure and conjugated  $\pi$ -electrons system which can delocalize. It possesses good chemistry stability and excellent photo and hot stability, which make it a promising modified dye.<sup>31</sup> Halogenated metallophthalocyanines as heterogeneous catalysts for the oxidation of cyclohexene has been reported that the active form of the perchlorinated iron (II) phthalocyanine ( $\text{PcFeCl}_{16}$ , See Fig. 1) catalyst was more stable than  $\text{FePc}$  and it was still active even after 4 weeks of continued catalysis.<sup>32</sup> The former research indicated that metal perchlorinated phthalocyanine had the better photocatalytic activity, especially  $\text{FePcCl}_{16}$  is the best photocatalysis in  $\text{MPcCl}_{16}$  ( $M = \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}$ ).<sup>33</sup> In a probe reaction, i.e., Rhodamine B photo-oxidation carried out in the aqueous system, the photocatalytic degradation ratio is 80–90% after 100 min irradiation using  $\text{FePcCl}_{16}$  as the photocatalysis. Owing to the good photocatalytic activity and the absorption of the visible light of  $\text{FePcCl}_{16}$ , it was chosen as the sensitizer of nano- $\text{TiO}_2$  to improve the visible light activity of  $\text{TiO}_2$ .

In this work, a novel PVC- $\text{FePcCl}_{16}$ - $\text{TiO}_2$  photodegradable composite film was prepared using the  $\text{FePcCl}_{16}$ -modified nano- $\text{TiO}_2$  as the photocatalyst to improve the photodegradation efficiency of the composite film under either UV or sunlight irradiation. The photodegrading properties of the composite film were investigated.

## EXPERIMENTAL

### Catalyst preparation and characterization

1.0 g  $\text{TiO}_2$  (Degussa P25) powder was dispersed into 50 mL ethanol by ultrasonic vibration for 20 min to obtain a uniform suspension. Then 50 mL  $\text{FePcCl}_{16}$  (synthesized according to reference 33) ethanol solution was added drop by drop into the above  $\text{TiO}_2$  suspension and the amount of  $\text{FePcCl}_{16}$  was 2 wt %



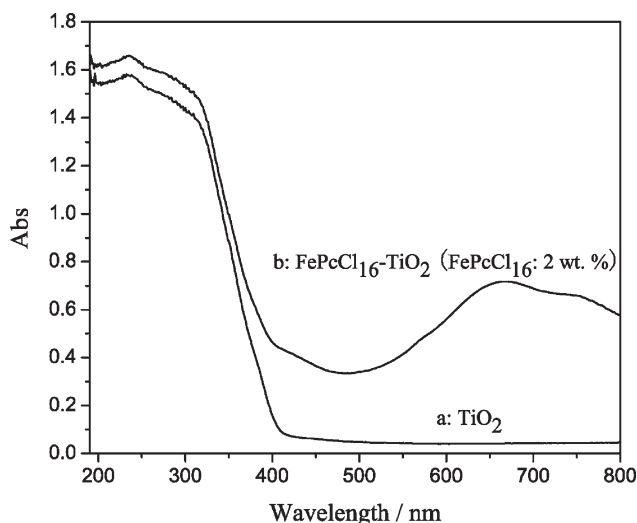
**Figure 1** Molecular structure of perchlorinated iron (II) phthalocyanine ( $\text{FePcCl}_{16}$ ).

of  $\text{TiO}_2$ . The mixed solution was maintained stirring for 2 h at 343 K, then cooled down to room temperature to filtrate. The precipitate was washed several times with distilled water and ethanol, respectively. Then the product was dried at 373 K. Finally, a dark green color  $\text{FePcCl}_{16}$ - $\text{TiO}_2$  photocatalyst was obtained. UV-vis diffuse reflectance spectrum of the as-prepared  $\text{FePcCl}_{16}$ - $\text{TiO}_2$  photocatalyst was recorded on a UV-vis spectrophotometer (VARIAN, Cary 5000).

### Composite films preparation and characterization

The preparation of PVC- $\text{FePcCl}_{16}$ - $\text{TiO}_2$  composite film was cast as follows: 5 g PVC was dissolved in 60 mL tetrahydrofuran (THF) under vigorous stirring for 2 h to obtain the uniform PVC solution. At the same time, 0.05 g  $\text{FePcCl}_{16}$ - $\text{TiO}_2$  powder was dispersed uniformly into 10 mL THF by ultrasonic vibration for 20 min. Then the suspension was added to PVC solution to give  $\text{FePcCl}_{16}$ - $\text{TiO}_2$  to PVC ratio of 1.0 wt %. The mixed solution was maintained stirring for 6 h. The composite film was prepared by spreading the viscous solution on a slide glass surface (10 cm  $\times$  10 cm) and dried in airtight system for 48 h at room temperature. The pure PVC film and PVC- $\text{TiO}_2$  film were also prepared in a similar procedure to compare the photocatalytic activity. The thickness of these films was measured to be about 20–30  $\mu\text{m}$  by a micrometer.

The pure PVC and composite films were irradiated under 30W ultraviolet lamp (ZSZ-D, Changsha Guangming Co. Ltd.) in the ambient air. The typical surface area of samples was around 16  $\text{cm}^2$ . The



**Figure 2** UV-vis diffuse reflectance spectra of two kinds of catalyst (a:  $\text{TiO}_2$ ; b:  $\text{FePcCl}_{16}\text{-TiO}_2$ ).

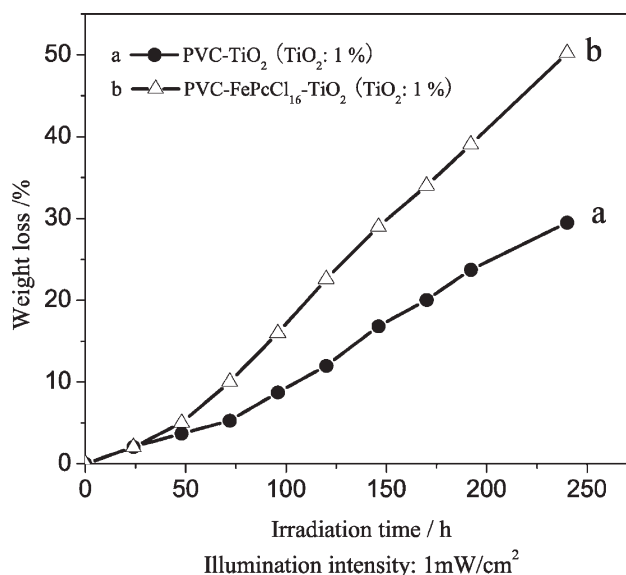
samples were placed 15 cm away from the lamp, where the light intensity was measured using a UV intensity meter (UV-I, Beijing Shida Ltd.) at primary wavelength (254 nm). The degradation extent of the films was evaluated directly by their weight loss. The photocatalytic degradation of these films was also investigated under sunlight illumination. The 16  $\text{cm}^2$  samples were placed in the quartz vessel on a terrace in sun-shining condition in July, Wuhan city, China. The average exposure time was 8–10 h in one day. The average overall light irradiation intensity was measured using a radiometer (FZ-A, Beijing Shida Ltd).

Fourier-transform infrared (FTIR) spectrophotometer (JA. Transform Nicolet FT-170SX) was used to study the spectrum character of these films before and after irradiation. The surface morphologies of all the films were observed by scanning electron microscope (SEM, Netherlands FEI company, Quanta 200).

## RESULTS AND DISCUSSION

### Spectroscopy properties of $\text{FePcCl}_{16}\text{-TiO}_2$ photocatalyst

Figure 2 displays the UV-vis diffuse reflectance spectra of  $\text{FePcCl}_{16}\text{-TiO}_2$  ( $\text{FePcCl}_{16}$ : 2 wt %) composite powder and blank  $\text{TiO}_2$  powder, respectively. It is observed that blank  $\text{TiO}_2$  only adsorb UV light and has no absorption in visible region beyond 400 nm. However,  $\text{FePcCl}_{16}\text{-TiO}_2$  composite exhibits remarkable absorbance in visible region beyond 400 nm. Especially, there is an absorbance peak centering at 650 nm, which exhibits the characteristic absorption of  $\text{FePcCl}_{16}$ . It indicates that  $\text{FePcCl}_{16}\text{-TiO}_2$  powder can adsorb the visible light more effectively than blank  $\text{TiO}_2$  and  $\text{FePcCl}_{16}\text{-TiO}_2$  powder has more



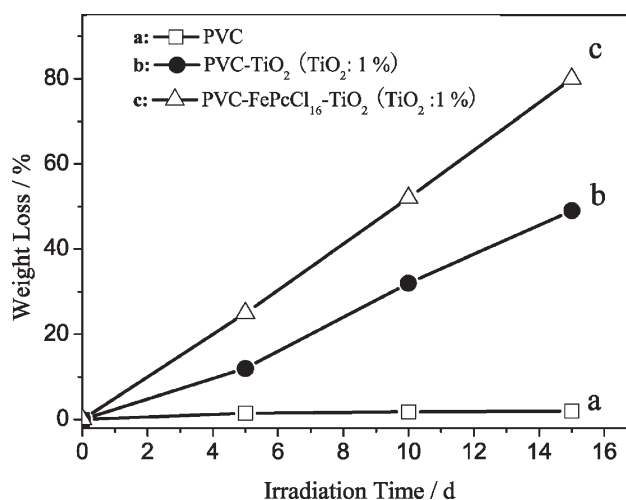
**Figure 3** Weight loss of the composite films under UV light irradiation with  $1 \text{ mW}/\text{cm}^2$  light intensities (a:  $\text{PVC-TiO}_2$  film; b:  $\text{PVC-FePcCl}_{16}\text{-TiO}_2$  film).

extensive applying foreground in photocatalytic degradation aspect.

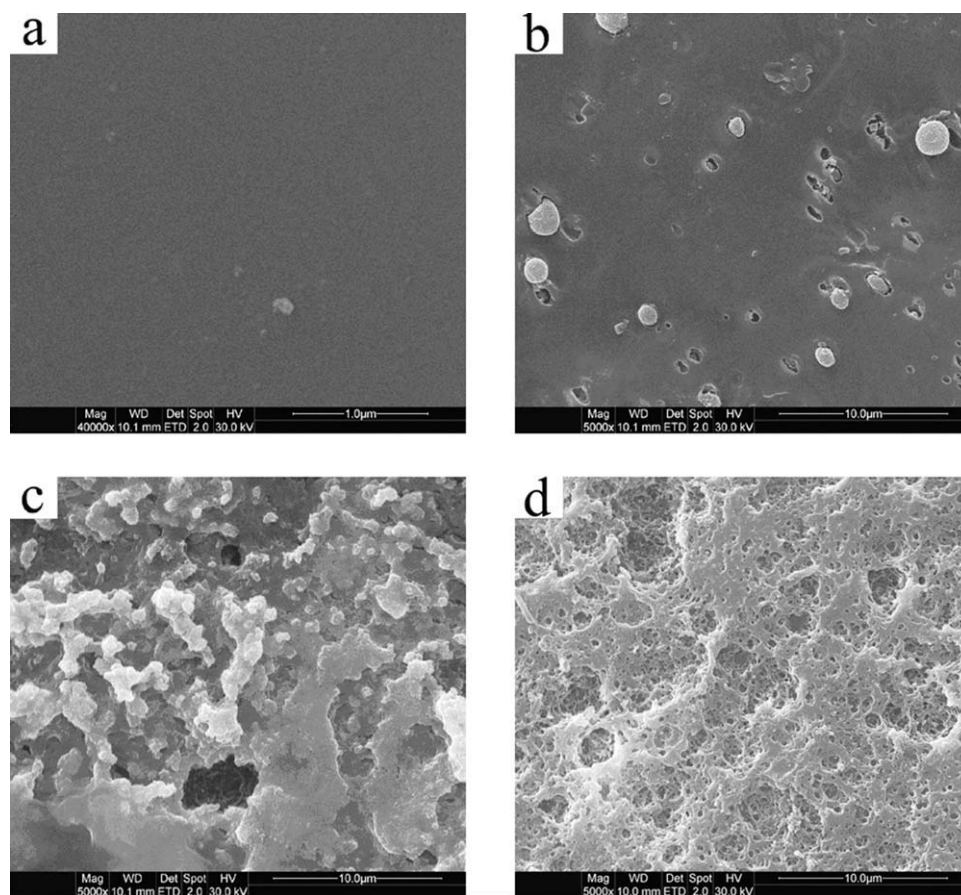
### Weight loss analysis of the film under UV or sunlight irradiation

The photoinduced weight loss curves of the composite films under UV irradiation in the air are shown in Figure 3. The weight loss of  $\text{PVC-FePcCl}_{16}\text{-TiO}_2$  film steadily enhanced with the increase of irradiation time and reached 50% after 240 h irradiation under UV light intensity for  $1 \text{ mW}/\text{cm}^2$ . While that of  $\text{PVC-TiO}_2$  film was only 30% under the identical experimental condition.

Figure 4 shows the weight loss curve of different films under the sunlight exposure directly. The



**Figure 4** Weight loss of pure PVC and composite films under sunlight irradiation [(a)  $\text{PVC}$  film; (b)  $\text{PVC-TiO}_2$  film; (c)  $\text{PVC-FePcCl}_{16}\text{-TiO}_2$  film].



**Figure 5** SEM images of polymer films before and after irradiation with  $1 \text{ mW/cm}^2$  UV light intensity (a) PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film before irradiation; (b) pure PVC film after irradiation for 240 h; (c) PVC-TiO<sub>2</sub> film after irradiation for 240 h; (d) PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film after irradiation for 240 h.

sunlight irradiation experiment is carried out in July, Wuhan city, China. The average overall light irradiation intensity of sunlight was  $\sim 4.2 \text{ mW/cm}^2$ . The weight loss rate of PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> composite film is much higher than that of pure PVC film and PVC-TiO<sub>2</sub> film. The weight of pure PVC film had almost no change under sunlight exposure. This result is well agreed with the fact that pure PVC is nondegradable in natural environment. The weight loss rate of PVC-TiO<sub>2</sub> film was only 49%, while that of the PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film was 81% after 15 days irradiation. Compared with the PVC-TiO<sub>2</sub> film, the weight loss rate of the PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film increased 80%. The results indicated that the photocatalytic degradation efficiency of PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film is much higher than pure PVC and PVC-TiO<sub>2</sub> film under UV or sunlight irradiation.

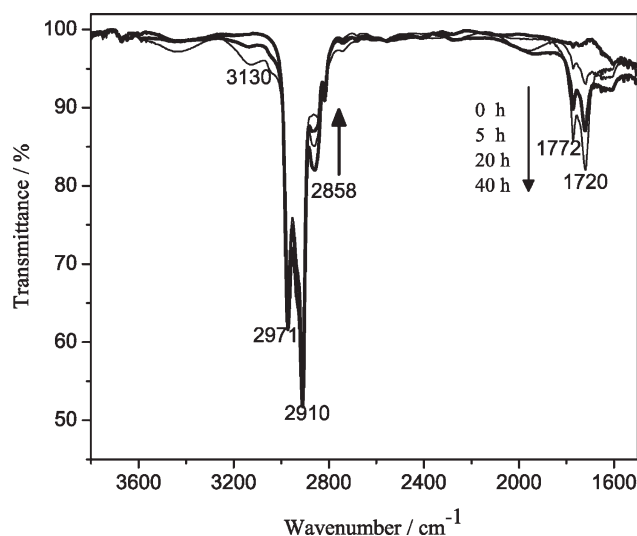
### Surface morphology of films

SEM was carried out to observe the surface morphology of films before and after UV light irradiation for 240 h. The surface of PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> composite film before irradiation is smooth except

some nanoparticles aggregations as shown in Figure 5(a). The PVC film had few changes but some surface cavities appearance after 240 h UV-irradiation [Fig. 5(b)]. The smooth surface of PVC-TiO<sub>2</sub> film had been segmental broken and dense cavities could be seen in surface under zoomed in 5000 times [Fig. 5(c)]. However, the surface of PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film had been severely broken under the identical condition [Fig. 5(d)]. There were big area cavities. The SEM results indicated that PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film had the biggest degradation extent among the three kinds of film under the identical irradiation condition.

### FTIR spectroscopic characterization

The photocatalytic degradation of PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> (TiO<sub>2</sub>: 1 wt %) film was also examined by FTIR spectroscopy. Figure 6 displays the FTIR spectra of the composite film before and after irradiation for 5, 20, and 40 h. In comparison with the film before irradiation, there are two new absorption peaks appearing in the region of  $1772$  and  $1720 \text{ cm}^{-1}$  after irradiation, which are attributed to the characteristic



**Figure 6** FTIR spectra of PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> (TiO<sub>2</sub>: 1 wt %) composite film before and after irradiation for 5, 20, and 40 h.

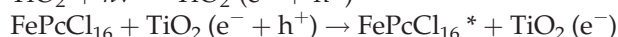
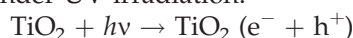
absorption of carbonyl (C=O) group. The intensity of absorption peaks strengthens with irradiation time increasing, which indicates that the polymer is oxidized successively. The vibrational peak of hydroxyl (O-H) group at 3130 cm<sup>-1</sup> is observed until PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> composite film is irradiation for 40 h. Generally, the vibrational peaks of C-H group in PVC appear in the range of 3000–2800 cm<sup>-1</sup>. The intensity of C-H absorption peaks decreases step by step with the increase of irradiation time, which indicates that the C-H bond is being broken. The changes of absorption peaks in FTIR spectrum prove that the photocatalytic degradation of PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film is an oxidizing process.

### Mechanism discussion

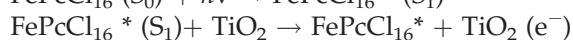
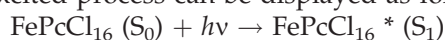
The photodegradation mechanism of PVC film has been extensively studied. But there are few reports about the solid phase photocatalytic degradation mechanism of PVC-TiO<sub>2</sub> composite. It is not only the photolytic reaction of PVC but also the photocatalytic reaction of PVC on the surface of TiO<sub>2</sub>. When TiO<sub>2</sub> particles absorb light with energy higher than 3.2 eV, they can generate electron/hole pairs in conduction band (CB) and valence band (VB), respectively. The electrons can be captured by adsorbed oxygen molecules to form  $\cdot\text{O}_2^-$ . At the same time, photogenerated holes are trapped by water adsorbed on the surface to produce  $\cdot\text{OH}$ . The  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  are two very important reactive oxygen species for photocatalytic degradation of PVC. The above-mentioned active radicals initiate solid-phase photocatalytic degradation of PVC-TiO<sub>2</sub> composite film by

attacking neighboring polymer chains to form carbon-centered radicals such as  $-(\text{CH}_2\cdot\text{CCl})-$  and  $-(\cdot\text{CHCHCl})-$ . Their successive reactions produce hydroxyl derivatives and carbonyls intermediates, resulting in polymer chain cleaved and CO<sub>2</sub> evolution.

Without the electron and hole scavengers, most of them recombine with each other within a few nanoseconds. If the scavengers or surface defects are present, electron-hole recombination can be prevented and the subsequent reactions caused by electrons and holes may be dramatically enhanced. When PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film is irradiated under UV light, TiO<sub>2</sub> is excited to generate electron/hole pairs. A hole injection from the valance band of TiO<sub>2</sub> to the ground state of FePcCl<sub>16</sub> is permitted at the interface between TiO<sub>2</sub> and FePcCl<sub>16</sub>, which efficiently separates electron and hole and prevents the electron-hole recombination. This is probably the primary reason why PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film can degrade more effectively than PVC-TiO<sub>2</sub> film even if under UV irradiation.



When PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film is irradiated under visible light, FePcCl<sub>16</sub> is firstly excited to generate an electron in its excited singlet state and a hole in its ground stated. Then the electron is injected into the conduction band of TiO<sub>2</sub> and a series of oxidation-reduction reactions take place. The possible light excited process can be displayed as follow:



The FePcCl<sub>16</sub>-modified TiO<sub>2</sub> extends the light absorption to the visible spectral region. This is the major reason why PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> composite film has higher efficiency under the sunlight irradiation.

### CONCLUSIONS

TiO<sub>2</sub> modified with FePcCl<sub>16</sub> extends its adsorption region to the visible light and observably improves its photocatalytic activity. Compared with pure PVC film and PVC-TiO<sub>2</sub> film, PVC-FePcCl<sub>16</sub>-TiO<sub>2</sub> film has much higher photodegradation efficiency not only under sunlight irradiation but also under UV-irradiation. It is a novel way to produce the practical photodegradable plastics.

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