

Solid-phase photocatalytic degradation of polyethylene plastic under UV and solar light irradiation

Xu Zhao^a, Zongwei Li^a, Yi Chen^b, Liyi Shi^b, Yongfa Zhu^{a,*}

^a Department of Chemistry, Tsinghua University, Beijing 100084, PR China

^b Research Center of Nano-Science and Nano-Technology, Shanghai University, Shanghai 200444, PR China

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Abstract

This paper investigated solid-phase photocatalytic degradation of polyethylene (PE) plastic with TiO₂ in the ambient air under solar and ultraviolet light irradiation. The photodegradation of the composite plastic was compared with that of pure PE through weight loss monitoring, scanning electron microscopic (SEM) analysis, gas chromatography (GC), FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS). PE-TiO₂ composite plastic can be efficiently decomposed and the main products are CO₂ and water. The weight-loss of PE-TiO₂ (1 wt%) film reached 42% under solar irradiation for 300 h. The degradation rate can be controlled by changing the content of TiO₂ nanoparticles in PE plastic. The degradation of composite plastic initiated on PE-TiO₂ interface and then extended into polymer matrix induced by the diffusion of the reactive oxygen species generated on TiO₂ particle surface. The present study demonstrates that the polymer-TiO₂ compositing is a practical and promising way to degrade the plastic waste under solar light without any pollution.

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1. Introduction

As a conventional plastic material, polyethylene (PE) is widely used in food packaging or food service, retail industry and agriculture field. It is almost inevitable that PE will continue to play an essential part in the commodities in spite of its resistance to microbial or enzymatic degradation [1]. This situation leads to the growing problem of pollution. Environmental concerns have promoted the development of degradable plastics. The biodegradable and photodegradable (by introducing chromophores or adding photosensitizer) plastics investigated till now still cannot solve the problem because these plastics have the limitation of long-term degradation and cause an environmental problem by the stabilizers [1–3]. In recent years, thermal or catalytic degradation of plastic wastes into fuel oil has been studied extensively [4,5]. However, this technique requires not only high temperature and cost but also appropriate catalysts to guarantee narrow distribution of hydrocarbons [5].

Heterogeneous photocatalytic oxidation that can occur at moderate conditions has been widely used to deal with aquatic or air pollutants [6,7]. Due to the characteristics such as inexpensiveness, good photo stability, non-toxicity, and high-reactivity, TiO₂ has been generally regarded as the best photocatalyst. Previous studies on TiO₂ photocatalytic degradation of polymers mainly dealt with liquid-phase reactions, such as photocatalytic degradation of poly(vinyl chloride) (PVC) particles in aqueous TiO₂ suspension [8]. However, waste plastics are usually exposed to the solar light in the open air, so the degradation of plastics should be studied in solid-phase under the ambient air. Composition of plastics and TiO₂ presents a new way to decompose solid plastics in an open air. The photocatalytic degradation of PVC-TiO₂ and PS-TiO₂ composite films has been investigated [9–11]. However, increase in degradation efficiency of their composite films and a close investigation of the degradation mechanism is still necessary.

In this paper, PE-TiO₂ composite films were prepared and their photocatalytic degradation under ultraviolet light and solar light in the ambient air was investigated. Photodegradation intermediate products was detected and the mechanism of the solid-phase photocatalytic reaction was proposed.

* Corresponding author. Tel.: +86 10 62783586; fax: +86 10 62787601.
E-mail address: zhuyf@tsinghua.edu.cn (Y. Zhu).

2. Materials and method

2.1. Materials

PE was supplied by Yanshan Petrochemical Company Ltd. The average molecular weight (M_w) was about 100,000. P-25 photocatalyst, the primary particles of which ranged from 20 to 40 nm in diameter with mixed crystalline phases, was provided from Degussa Company [12].

2.2. Preparation of PE-TiO₂ composite films

PE-TiO₂ composite film samples were cast as follows. The polymer stock solution was prepared by dissolving 1 g of PE in 100 ml cyclohexane at 70 °C under vigorous stirring for 60 min. Then, TiO₂ powder was suspended uniformly in the above 100 ml solution to give 0.02, 0.1 and 1.0 wt% TiO₂ contents with respect to the total mass of PE. An aliquot of 10 ml PE-TiO₂ solution was spread on a glass plate ($R=4$ cm) and first dried for 20 min at 70 °C, then dried for 48 h at room temperature. The thickness of the resulting PE-TiO₂ composite film sample measured 15–20 μ m by SEM. Its weight was ca. 0.1 g.

2.3. Photodegradation and characterization of PE and PE-TiO₂ films

PE-TiO₂ composite and pure PE samples were exposed in solar light under the ambient conditions from 9:00 am to 5:00 pm every sunny day. TiO₂ photocatalyst only absorbs UV light ($\lambda < 387$ nm), thus only UV light takes a role in solar degradation of PE-TiO₂ composite plastic. In order to reveal the photocatalytic degradation behavior and mechanism of PE-TiO₂ plastic, the photo-degradation reaction was conducted under ambient air in a lamp-housing box (40 cm \times 30 cm \times 20 cm) where the temperature during UV-irradiation was maintained around 25 °C. The pure PE and PE-TiO₂ composite samples were irradiated under four 8 W ultraviolet lamps. The primary wavelength of the lamps was 254 nm and the light intensity measured 1.0 mW/cm² at 5 cm away from the lamps. A typical size of the film sample was around 5 cm \times 5 cm. In order to detect the intermediates of PE photocatalytic degradation, the PE photodegradation experiment was performed in a columned quartz reactor. Its diameter and length was ca. 35 and 280 mm, respectively. Its actual volume was ca. 250 ml. At a given time, the air of 0.2 ml was taken from the airproof quartz reactor and analyzed by a gas chromatograph (GC).

The pure PE samples and PE-TiO₂ composite samples before and after being irradiated at different times were all characterized by means of FT-IR, XPS and SEM techniques. IR analysis was carried out on a PE-2000 FT-IR spectrometer. XPS analysis was conducted in a PHI 5300 ESCA system with Al K α radiation. The texture of the samples was examined by using SEM (KYKY 2000). In the experiment, the initial temperature was 40 °C, and then was ramped to the final temperature 100 °C at a rate of 40 K/min. The initial and final times were 1 and 5 min, respectively. The volatile organics were identified individually by standard gases, which were provided by Beijing AP

BAIF Gases Industry Limited. The concentration of CO₂ was measured by GC equipped with a thermal conductivity detector (TCD) using 5A zeolite steel column at 343 K. Its detect limit was ca. 1×10^{-3} mg/l.

3. Results and discussion

3.1. Weight loss

Fig. 1 shows the photoinduced weight loss of pure PE film and PE-TiO₂ composite samples in air under solar and UV irradiation. The weight loss rate was much greater for PE-TiO₂ sample than for the pure PE one. The degradation rate of PE-TiO₂ films increased with TiO₂ concentration. The weight of PE-TiO₂ (1 wt%) sample steadily decreased with solar irradiation and led to the total 42% reduction in 300 h while PE sample showed only 0.39% weight loss under the same experimental conditions. The above weight loss data indicate that the photocatalytic reaction of PE-TiO₂ film led to the bond scission and produced a mass of volatile intermediates.

3.2. Formation of photodegradation products

GC equipped with TCD or FID was used to monitor the amount of carbon dioxide and volatile organics produced during the photolysis process, respectively. Fig. 2 shows variations of the concentration of carbon dioxide with UV-irradiation time. CO₂ concentration for the pure PE sample increased with irradiation time and then leveled off after 5 h irradiation, while that for PE-TiO₂ (1 wt%) sample increased continuously. The amount of CO₂ produced from PE-TiO₂ (1 wt%) sample was always much more than that from the pure PE sample. The formation of CO₂ in the pure PE sample was due to the photolysis. For PE-TiO₂ sample, CO₂ was produced not only from the photolytic degradation but also from the photocatalytic degradation, and the latter was

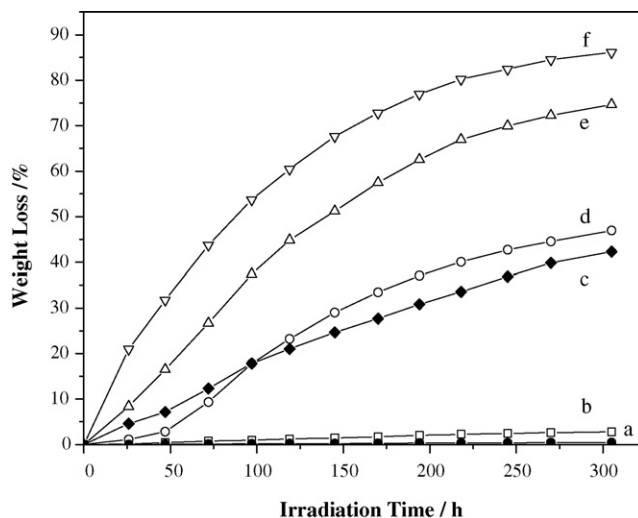


Fig. 1. Weight loss of PE and PE-TiO₂ samples under solar or UV irradiation in air. (a) PE under solar irradiation; (b) PE under UV irradiation; (c) PE-TiO₂ (1 wt%) under solar irradiation; (d) PE-TiO₂ (0.02 wt%) under UV irradiation; (e) PE-TiO₂ (0.1 wt%) under UV irradiation; (f) PE-TiO₂ (1 wt%) under UV irradiation.

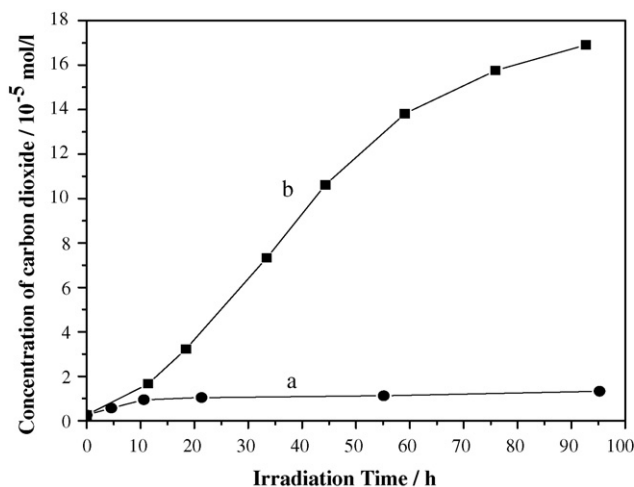


Fig. 2. The variations of concentration of CO_2 for PE (a) and PE-TiO₂ (1 wt%) (b) samples with UV-irradiation time.

more important. The total amount of carbon in CO_2 produced during photodegradation process accounts for 98% of the carbon loss of PE-TiO₂ (1 wt%) sample after 100 h irradiation and GC equipped with TCD failed to detect other volatile organics. It is concluded that CO_2 is the main product of the photocatalytic degradation of PE plastic and the degradation process is environment friendly.

Fig. 3(A) shows the gas chromatogram of the volatile organics. Curve h displays the peaks of the volatile organic products identified by GC. Curves a–g refer to GC peaks of methane, ethene, ethane, propane, acetaldehyde, formaldehyde and acetone standard gases, respectively. It can be seen that peaks 1–7 exhibit the same retention time as that of a–g, respectively. The good consistency of the retention time was independent of the oven temperature. Therefore, the generated volatile organics are methane, ethene, ethane, propane, acetaldehyde, formaldehyde and acetone. Fig. 3(B) compares the total amount of these volatile organics for PE and PE-TiO₂ (1 wt%) samples for the same irradiation time. It is seen that the organics amount for PE-TiO₂ (1 wt%) sample was almost the same as that for the pure PE sample, though the reaction rate of the composite sample was much higher than that of the pure sample. These results indicate that PE-TiO₂ composite sample has the potential for complete photodegradation of PE into CO_2 , while the pure PE sample has little ability for deep decomposition.

The functional groups in PE were characterized by IR spectroscopy. Fig. 4 compares FT-IR spectra of PE and PE-TiO₂ (1 wt%) samples after UV-irradiated for 100 h with that of the original samples. The peaks at 2923, 2850, 1472 and 719 cm^{-1} correspond to the long alkyl chain. The irradiated PE-TiO₂ samples showed much lower intensity of characteristic alkyl peaks compared with the original PE sample, while the pure PE samples showed little change. These results also indicate that the degradation of PE-TiO₂ samples was much more complete and fast than that of the pure PE samples. In Fig. 4(c), there are three new peaks at 1713, 1631 and 1177 cm^{-1} , which can be assigned to C=O, C=C and C–O stretching vibrations, respectively.

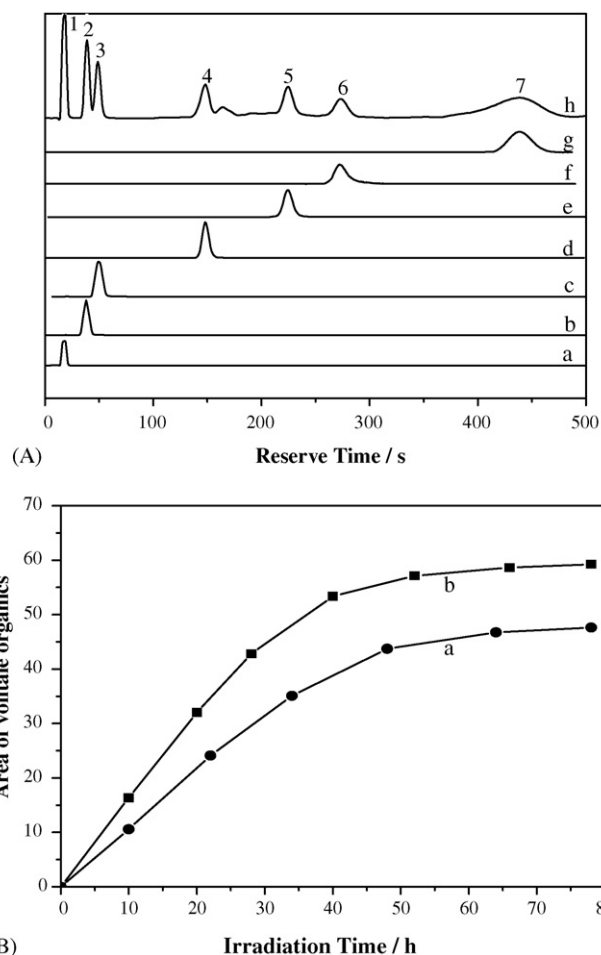


Fig. 3. (A) Curves a–g refer to GC peaks of methane, ethene, ethane, propane, acetaldehyde, formaldehyde and acetone standard gases, respectively; curve h is GC peaks of volatile organics. (B) The total area of volatile organics for PE (a) and PE-TiO₂ (1 wt%) (b) samples with UV-irradiation time.

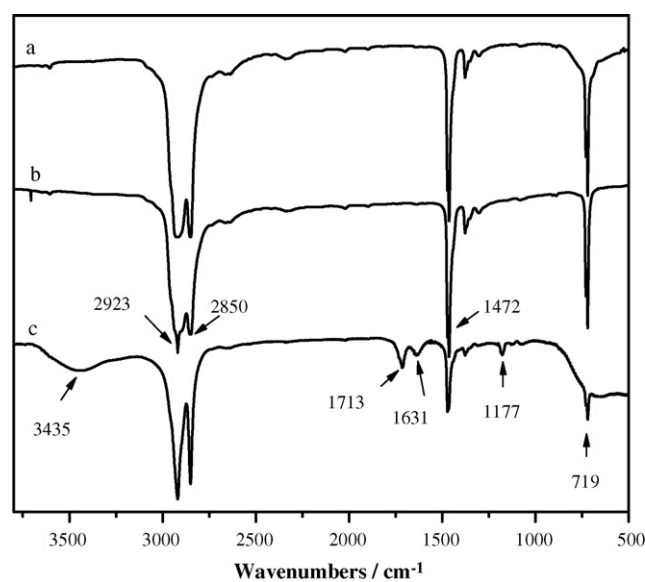


Fig. 4. FT-IR spectra of PE samples before irradiation (a), PE sample UV-irradiated for 100 h (b) and PE-TiO₂ (1 wt%) sample UV-irradiated for 100 h (c).

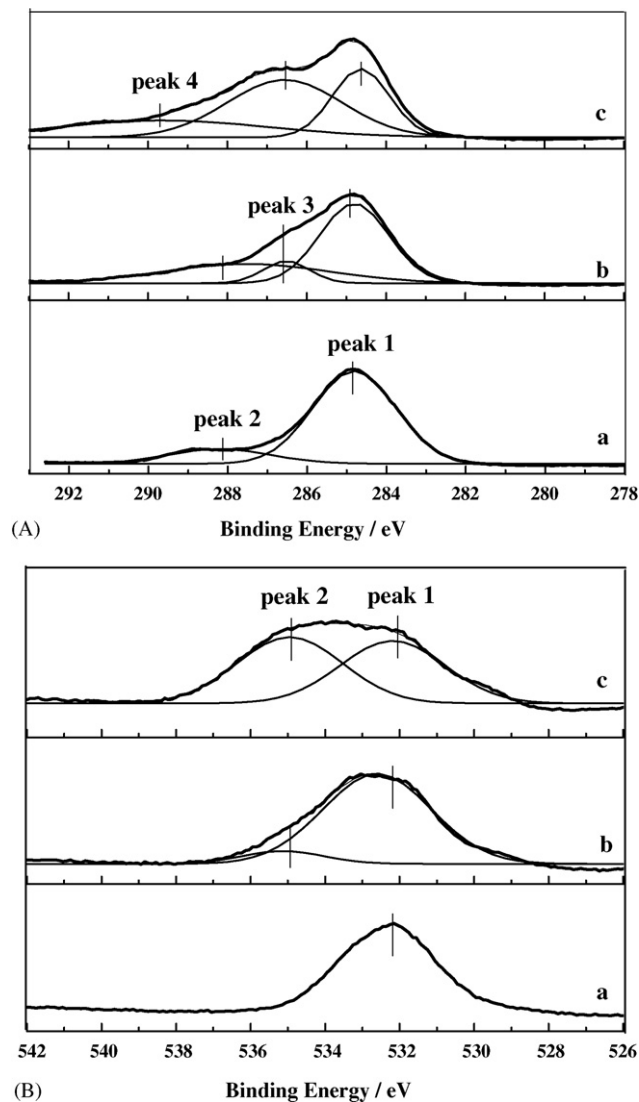


Fig. 5. High-resolution XPS spectra of C_{1s} (A) and O_{1s} (B) of PE sample before irradiation (a), PE sample UV-irradiated for 100 h (b) and PE-TiO₂ (1 wt%) sample UV-irradiated for 100 h (c).

Fig. 5(A) and (B) present XPS spectra of C_{1s} and O_{1s} of PE and PE-TiO₂ (1 wt%) samples after 100 h UV-irradiation as well as that of the original samples. In Fig. 5(A), C_{1s} spectra of the original PE sample consist of peaks at 284.6 (peak 1) and 288.2 eV (peak 2), corresponding to $-C-C-$ group of polymers and the carboxyl group of impurities. The irradiated PE and PE-TiO₂ samples present a new peak at 286.4 eV (peak 3), which is an indication of the existence of $-C-O$ group, implying the presence of alcohols, ethers, and carboxylic acids [13]. The proportion of peak 3 for the irradiated PE-TiO₂ sample (47.4%) is higher than that of the irradiated PE sample (9.8%), implying the reaction rate of the composite sample was much higher than that of the pure PE sample. The extended peak at 289.6 eV (peak 4) for the irradiated composite sample can be estimated to be further oxidation products including $-COO-$ or $-C=O$ group, indicating the presence of carboxylic acids, carboxylates, ketones and aldehydes [13,14]. In Fig. 5(B), O_{1s} peak of the original PE sample is 532.1 eV (peak 1), which is

assigned to typical oxygen groups such as carbonyl and OH [9]. For the irradiated PE and PE-TiO₂ samples, a new peak at 534.8 eV (peak 2) appears, which can be attributed to $-OCO_2-$ or carboxylic acids. The proportion of peak 2 increased from 8.8% to 52.3%, indicating that these species were produced much more on the surface of the composite sample than on the pure PE sample. XPS results are in agreement with those of IR. These results suggest the formation of the carbonyl and carboxyl groups on the surface of the irradiated PE-TiO₂ samples.

3.3. Texture of samples after photodegradation

The texture of irradiated polymer samples was examined by using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM images (which are not shown) revealed that the main TiO₂ particles in composite films were aggregated up to the size of 0.1–0.5 μm . Fig. 6(A), (C) and (D) show the texture of PE-TiO₂ (1 wt%) composite films that were UV-irradiated for 0, 20, and 100 h in air, respectively. After 20 h irradiation, there were some cavities 2–3 μm in size and 1–2 μm in depth on the surface of the film. The formation of these cavities was induced by the escape of volatile products from PE matrix. After 100 h irradiation, the surfaces of the composite film were almost completely decomposed. The size and depth of the cavities were increased to 6–8 μm and 10 μm , respectively. Fig. 6(B) shows the texture of pure PE film that was irradiated for 100 h in air. In accordance with the weight loss data shown in Fig. 1, the surface of the pure PE film showed little sign of degradation. SEM images suggested that the degradation of PE matrix started from PE-TiO₂ interface and led to the formation of cavities around TiO₂ particle aggregates. It is implied that the active oxygen species generated on TiO₂ surface diffuse to etch out the polymer matrix.

3.4. Effect of content of TiO₂ on degradation rate

It is seen from Fig. 1 that the degradation rate of composite films was not in direct proportion to TiO₂ concentration. The rate increase when it was increased from 0.1 to 1 wt% was much less than when it was increased from 0.02 to 0.1 wt%. Fig. 7 shows the texture of PE-TiO₂ composite films after 50 h UV-irradiation. The hole density of composite films (1.00 wt%, 0.10 wt%, 0.02 wt%) is estimated to be 2.5×10^{-2} , 1×10^{-2} , $2 \times 10^{-3} \mu\text{m}^{-2}$, respectively. The hole number density of 0.10 and 0.02 wt% composite films is in proportion to the content of TiO₂, while the hole density of 1 wt% composite film is only 2.5 times that of the 0.1 wt% composite film. These data indicate that the aggregation of TiO₂ in the composite film (1 wt%) was much more serious than that of the films (0.1 and 0.02 wt%). Only TiO₂ on the surface of agglomerates is photocatalytically active and the aggregation decreased the interface area between the polymer and TiO₂. Thus, the photo-degradation efficiency of the composite film was decreased.

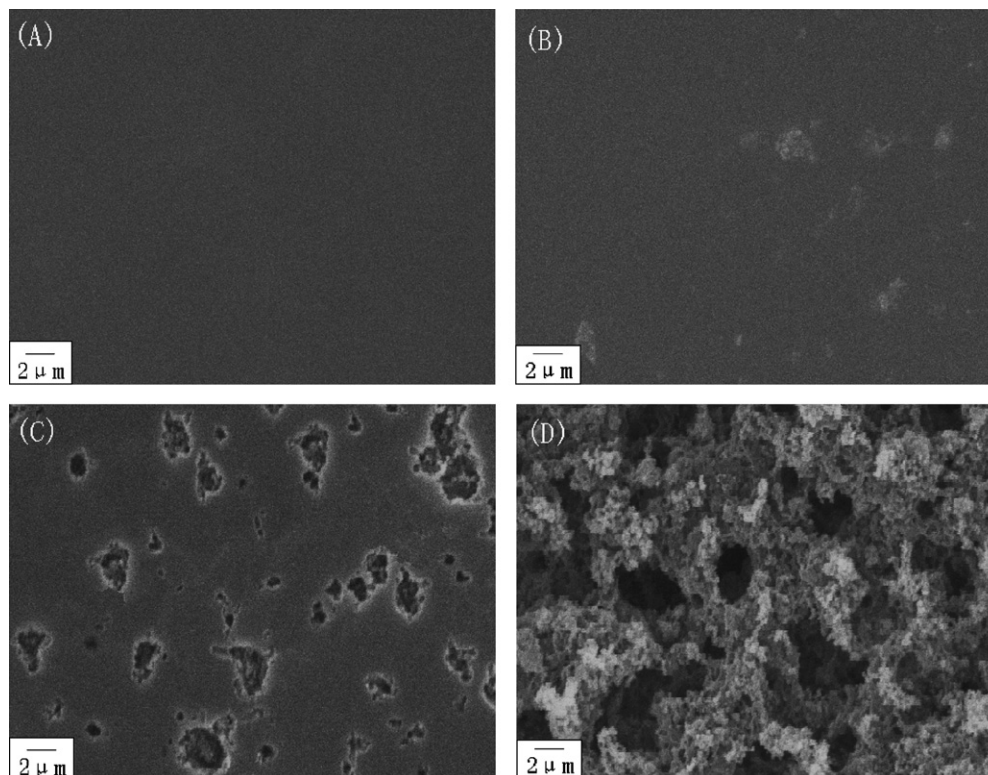
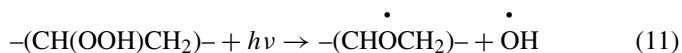
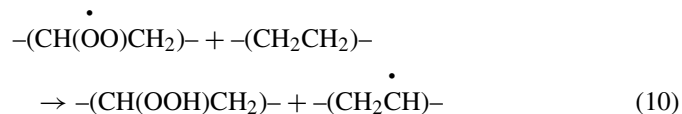


Fig. 6. SEM images of the pure PE or PE-TiO₂ (1 wt%) composite films. (A) PE-TiO₂ (1 wt%) sample before irradiation; (B) PE sample UV-irradiated for 100 h; (C) PE-TiO₂ (1 wt%) sample UV-irradiated for 20 h; (D) PE-TiO₂ (1 wt%) sample UV-irradiated for 100 h.

3.5. Photocatalytic degradation mechanism of PE-TiO₂ composite films

The photolytic degradation of pure PE has been extensively studied [15–18]. The reaction of PE under ultraviolet irradiation occurred via direct absorption of photons by PE macromolecule to create exciton states, and then undergo chain scission, branching cross-linking and oxidation reactions. The composite sample showed higher photo-degradation reactivity than the pure PE sample. For the composite sample, the photocatalytic degradation was the main reaction, which was quite different from the photolytic degradation of the pure PE sample. The photocatalytic reaction mechanism of PE-TiO₂ can be written as follows. TiO₂ particles that absorb UV light ($\lambda < 387$ nm) generate mobile electrons and holes in the conduction and valence bands, respectively (Eq. (1)) [19]. Subsequent reactions with O₂ lead to the formation of several active oxygen species such as HO•, O₂•⁻, and HO₂• (Eqs. (2)–(7)), of which HO• is the most important oxidant in photocatalytic oxidation [20]. The active oxygen species described above initiate the degradation reaction by attacking neighboring polymer chains (Eq. (8)). The degradation process spatially extends into the polymer matrix through the diffusion of the reactive oxygen species. Once the carbon-centered radicals are introduced in the polymer chain, their successive reactions lead to the chain cleavage with the oxygen incorporation and species containing carbonyl and carboxyl groups are produced (Eqs. (9)–(12)). These intermediates can be further photocatalyti-

cally oxidized to CO₂ and H₂O by the aid of reactive oxygen species.



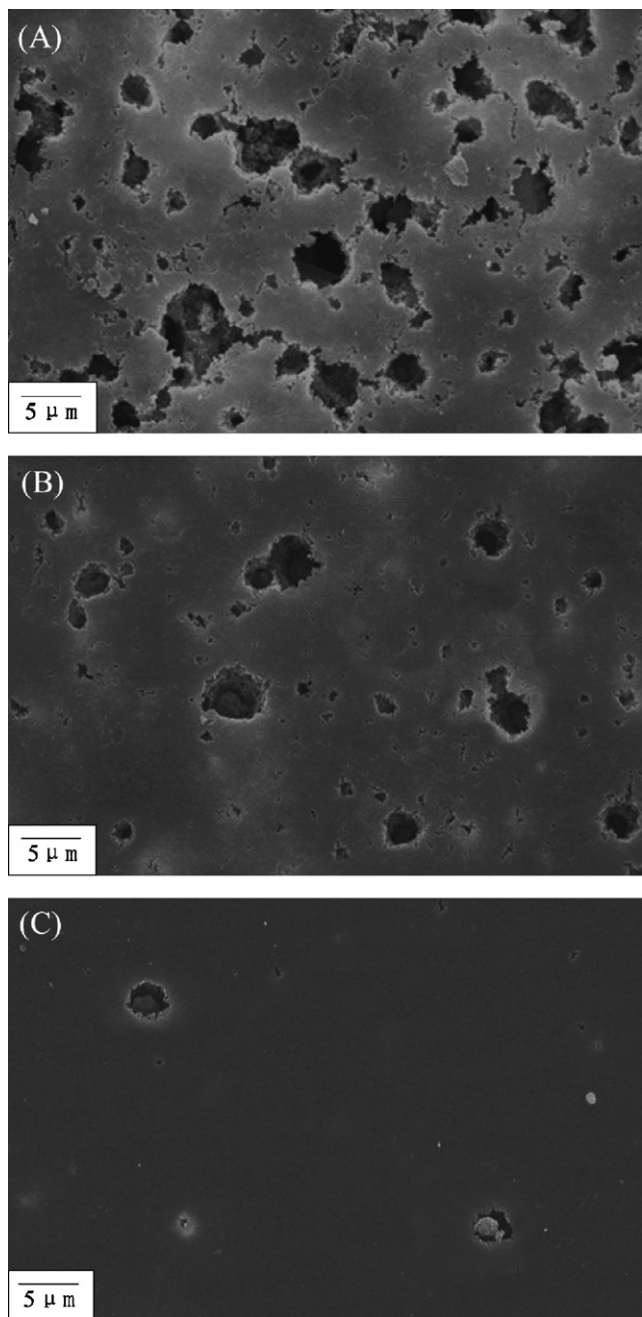
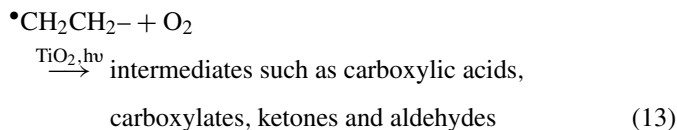


Fig. 7. SEM images of PE-TiO₂ composite films UV-irradiated for 50 h. (A) PE-TiO₂ (1 wt%); (B) PE-TiO₂ (0.1 wt%); (C) PE-TiO₂ (0.02 wt%).



4. Conclusions

In summary, the photocatalytic degradation process of PE-TiO₂ composite films was much faster and more complete than the simple photolysis of pure PE films under UV and solar light irradiation. The main products of PE-TiO₂ composite films via photocatalytic degradation process are CO₂ and H₂O. Their degradation rate can be controlled by changing the content of TiO₂ nanoparticles in the composite films. The development of this kind of composite polymer can lead to an eco-friendly disposal of polymer wastes.

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