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Solid-phase photocatalytic degradation of polystyrene with modified nano-TiO_2 catalyst

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Abstract

A novel photodegradable polystyrene-grafted-TiO_2 (PS-*g*-TiO_2) nanocomposite was prepared by embedding the grafted-TiO_2 into the commercial polystyrene. Solid-phase photocatalytic degradation of the PS-*g*-TiO_2 nanocomposite was carried out in ambient air at room temperature under ultraviolet lamp and/or sunlight irradiation. The properties of composite film were compared with those of the pure PS film by methods such as weight loss measurement, scanning electron microscope (SEM), gel permeation chromatogram (GPC), X-ray photoelectron spectroscopy (XPS), FT-IR spectroscopy, and UV–vis spectroscopy. The results show that the photo-induced degradation of PS-*g*-TiO_2 composite film is significantly higher than that of pure PS film. The weight loss of composite film reached 31.9%, average molecular weight (M_w) of composite film decreased by 53.1%, and the number average molecular weight (M_n) decreased by 73.2% after 396 h of UV-light irradiation. FT-IR analysis and weight loss indicated that the benzene rings in PS-matrix of composite film were cleaved during UV-light irradiation. The photocatalytic degradation mechanism of the films is briefly discussed.

Keywords: Polystyrene; Grafted-TiO_2; Solid-phase photocatalytic degradation

1. Introduction

Polystyrene (PS), an important material in the modern plastic industry, has been used all over the world, due to its excellent physical properties and low-cost. PS and its related plastic products are non-biodegradable in natural environment. The waste PS plastics do not decompose in landfills. A large amount of disposable PS plastic commodities cause serious environmental problems, called ‘‘white pollution’’.

PS nanocomposites are an area of active research because the addition of very small amounts of nanoparticles brings about a large enhancement of the mechanical properties, thermal and fire properties of the polymer [1,2]. But the reports about the photodegradation properties of PS nanocomposites are very few. It is well-known that when photons, with energy greater than the band gap of TiO_2 semiconductor, are absorbed by TiO_2 particles, active electron–hole pairs will be induced and transferred to the TiO_2 surface, where they react with the surface absorbed molecules, and form active radicals, such as $O_2^{\bullet -}$, $HOO^\bullet$ and $HO^\bullet$. These active radicals are able to oxidize the C–H band and lead to the degradation of the organic molecule. TiO_2 photocatalyst has been successfully used to purify water, to degrade the organic pollutants and to kill the bacteria in liquid-phase [3,4]. Photocatalytic degradation of the polymers in TiO_2 aqueous suspension system has been reported [5]. As most of the waste plastics are exposed to the sunlight in open air, it is important to investigate the solid-phase photocatalytic degradation of polymer under the ambient air condition. A few researchers have recently studied the solid-phase photocatalytic degradation of polymer–TiO_2 nanocomposite. Cho

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and Chio [6] have investigated the photocatalytic degradation of PVC films by embedding TiO_2 particles into PVC. Shang et al. [7] have reported the solid-phase photocatalytic degradation of expanded polystyrene (EPS) film with TiO_2. The TiO_2 powder particles used in both of the works are original without any surface treatment.

It is well recognized that a uniform distribution of catalytic material is vital to the photocatalytic efficiency in the heterogeneous photocatalytic reaction. The good dispersion of particles results in a larger interface area between the polymer matrix and catalyst, and a higher photocatalytic activity is expected. Some studies [8–10] showed that the grafted nano-TiO_2 (*g*-TiO_2) particles dispersed excellently in low polarity solvent, with high stability owing to the steric hindrance, while the untreated TiO_2 nanoparticles usually aggregate seriously. When untreated TiO_2 particles were embedded into polymer, they also aggregated and formed floccules of a few micrometers. The existence of agglomerates will decrease the interface area between the polymer and the photocatalyst, resulting in a low efficiency of photocatalytic degradation.

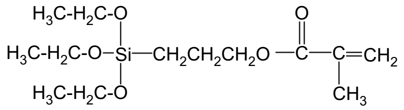
To authors' best knowledge, there is no research in the field of the photodegradable polymer–TiO_2 composite with modified TiO_2 yet. In our recent studies [11,12], TiO_2 nanoparticles were first modified by grafting polymer on its surface (*g*-TiO_2), and then dispersed in the monomer of PS. The PS-*g*-TiO_2 nanocomposite finally formed through polymerization. It has been revealed that the efficiency of photocatalytic degradation of PS-*g*-TiO_2 film is significantly higher than that of PS–TiO_2 (untreated) film.

In this work, an alternative method to prepare PS-*g*-TiO_2 nanocomposite is reported. The *g*-TiO_2 nanoparticles were embedded into commercial PS to prepare a new type of PS-*g*-TiO_2 nanocomposites. The dispersion behavior of *g*-TiO_2 particles and the photocatalytic degradation property of PS-*g*-TiO_2 nanocomposite in the ambient air under the ultraviolet light or sunlight irradiation are reported.

2. Experimental

2.1. Materials

Commercial polystyrene (PS) particles were supplied by Zhanjiang Xinzhongmei Chemical Co. Ltd. The average molecular weight (M_w) of PS was determined by gel permeation chromatography (GPC) to be $4.67 \times 10^5\ g\ mol^{-1}$ with the polydispersity (M_w/M_n) being 2.46. TiO_2 powder was Degussa P25 with 70% in anatase phase and 30% in rutile, whose primary particle diameter was in a range of 30–50 nm. The molecular formula of WD-70 silicone coupling agent (Wuhan University Chemical & New Material Co. Ltd.) is as follows:



$$(H_3C\text{-}H_2C\text{-}O)_3Si-CH_2CH_2CH_2O-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2$$

2.2. Preparation of PS-*g*-TiO_2 nanocomposite

The preparation of PS-*g*-TiO_2 composite film consists of two major steps.

(1) The grafting of TiO_2 nanoparticles: 5 mL of WD-70 was dissolved in 125 mL of isopropanol; then 50 g of TiO_2 (dried at 120 °C for 2 h) was dispersed in the solution under ultrasonic vibration for 20 min. This suspension solution was added in a Wolff bottle, stirring at 35 °C for 2 h. Styrene (25 mL), in which 0.2 g of AIBN was dissolved, was added into the Wolff bottle and the mixture was refluxed with stirring at 80 °C for 20 h under nitrogen. After the reaction, the mixture was centrifuged and the grafted-TiO_2 was extracted three times with toluene and dried in vacuum at 110 °C. The grafted-TiO_2 (*g*-TiO_2) should be stored at room temperature in the dark. The structure and graft ratio of the *g*-TiO_2 had been reported elsewhere [10].

(2) The preparation of composite films: the *g*-TiO_2 or untreated TiO_2 (0.15–0.6 g) was suspended in 100 mL trichloromethane by ultrasonic vibration for 20 min, then dissolving PS particles (30 g) in suspension with a continuous intense stirring for 5 h. The TiO_2 catalyst content was 0.5–2.0% relative to the total mass of PS. The mixed solution was spread on the ceramic plate (15 cm × 15 cm), and dried for 48 h in an airtight system to form the PS-*g*-TiO_2 or PS–TiO_2 nanocomposite film. The thickness of these films was measured about 40 μm by a micrometer.

2.3. Photocatalytic degradation and characterization of the films

The photocatalytic degradation was performed under 30 W ultraviolet lamp (ZSZ-D, Changsha Guangming Co. Ltd.) irradiation in the ambient air. The typical surface area of the film samples was around 16 cm^2. The 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.) to be 2.5 mW/cm^2 at primary wavelength (254 nm). The degradation extent of the films was evaluated directly by their weight loss. Each sample was weighed by accurate balance every 24 h during 396 h of irradiation.

The photocatalytic degradation of these films was also investigated under sunlight illumination. The 16 cm^2 samples were placed in the quartz vessel on a terrace in sun-shining condition from the summer to the autumn. The average irradiation time was 5–8 h in 1 day. The average light intensity was approximately 1.5 mW/cm^2 (365 nm) measured using a UV intensity meter (UV-II, Beijing Shida Ltd.). The weight loss was measured every 50 h.

In order to assess the effect of oxygen, the photocatalytic degradation of the films was also carried out under Argon atmosphere. The pure PS and PS-*g*-TiO_2 samples were put into a quartz cell, which was filled with Ar during UV-irradiation.

The light intensity was measured to be 2.5 mW/cm^2 at primary wavelength (254 nm).

UV–vis spectrophotometer (Hitachi UV-3400) and FT-IR spectrophotometer (JA. Transform Nicolet FT-170SX) were used to study the spectrum character of these films before and after the irradiation. The surface morphologies of all samples were observed by scanning electron microscope (SEM, Hitachi X-650). The films were also examined by X-ray photoelectron spectroscopy (XPS, PHI 5300, Al Kα). The average molecular weights of the films were measured by gel permeation chromatogram (GPC, Waters 2690D Separation Module, Waters 2410 Refractive Index Detector) equipped with a PL mixed C ($\times 2$) column. PS standards were used for the M_w calibration. For GPC analysis, all the PS samples were dissolved in trichloromethane ($CHCl_3$), and then filtered through a 0.2 μm PTFE syringe filter in order to remove TiO_2 particles.

3. Results

3.1. The dispersion of TiO_2 nanoparticles in PS

The dispersion of TiO_2 nanoparticles in PS was estimated by SEM observation. It could be seen from Fig. 1 that the untreated TiO_2 aggregated seriously in the polymer. However, the *g*-TiO_2 particles demonstrate drastically different morphologies in the polymer matrix. Actually, the grafted nanoparticles disperse so well that it is hard to recognize the individual particles under the same instrumental setting. This result justifies that the grafting treatment of the nanoparticles is an effective method to get the uniform dispersion in nanocomposite materials' preparation.

3.2. Spectroscopic characterization

Fig. 2 shows the UV–vis transmittance spectra of the pure PS film and PS-*g*-TiO_2 composite film (TiO_2: 1%). The transmittance of pure PS film was less affected by UV-irradiation for 1 mW/cm^2 light intensity (Fig. 2b). However, the transmittance of composite film gradually decreased with the irradiation time, as shown in Fig. 2a. Both the presence of catalyst and the whitening of the irradiated composite film influenced the transmittance of the composite films. Because of TiO_2 nanoparticles absorbing the ultraviolet light, the transmittance of PS-*g*-TiO_2 composite film was lower than that of pure PS film. The PS-*g*-TiO_2 composite film was degraded by UV-light to form some cavities in the films (see Fig. 9d) that further scatter light. Thus, the transmittance was reducing with the UV-light irradiation time, implying that the TiO_2 catalyst promotes the photodegradation.

The photocatalytic degradation of PS films was also examined by FT-IR spectroscopy. Fig. 3 shows the FT-IR spectra of the pure PS film and PS-*g*-TiO_2 (TiO_2: 1%) composite films. It can be seen from the spectrum of the original PS-*g*-TiO_2 composite films (Fig. 3a) that the characteristic peaks of phenyl ring are at 1496, 1450, 756, and 701 cm^{-1}, and they are the same as in pure PS [13]. It showed that the IR spectra character

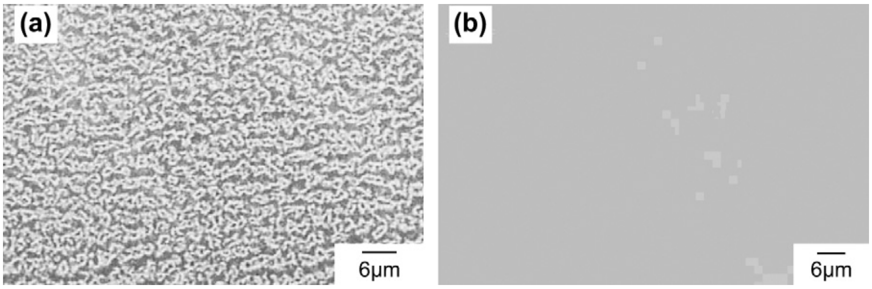


Fig. 1. The photographs amplified 100 times. (a) PS-untreated TiO_2 film, (b) PS-*g*-TiO_2 film (TiO_2: 1%).

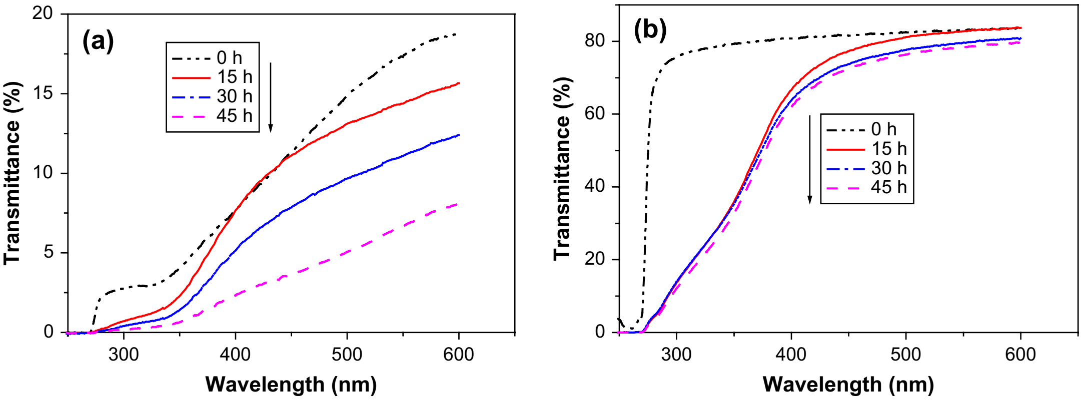


Fig. 2. (a) The UV–vis spectra of PS-*g*-TiO_2 (2%) films under UV-irradiation for 0 h, 15 h, 30 h, and 45 h. (b) The UV–vis spectra of pure PS films under UV-irradiation for 0 h, 15 h, 30 h, and 45 h.

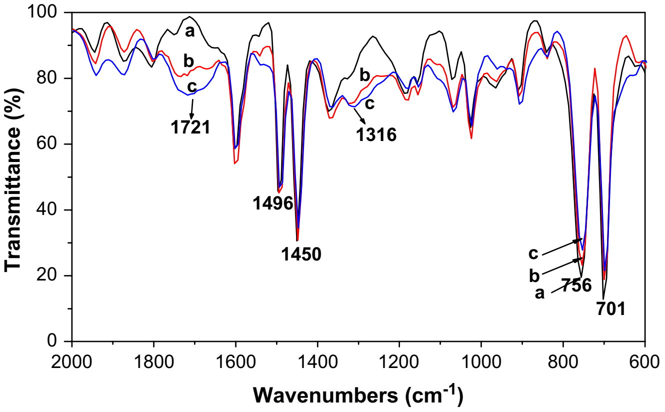


Fig. 3. FT-IR spectra of (a) original PS-*g*-TiO_2 (1%), (b) pure PS irradiated for 45 h, (c) PS-*g*-TiO_2 (1%) irradiated for 45 h.

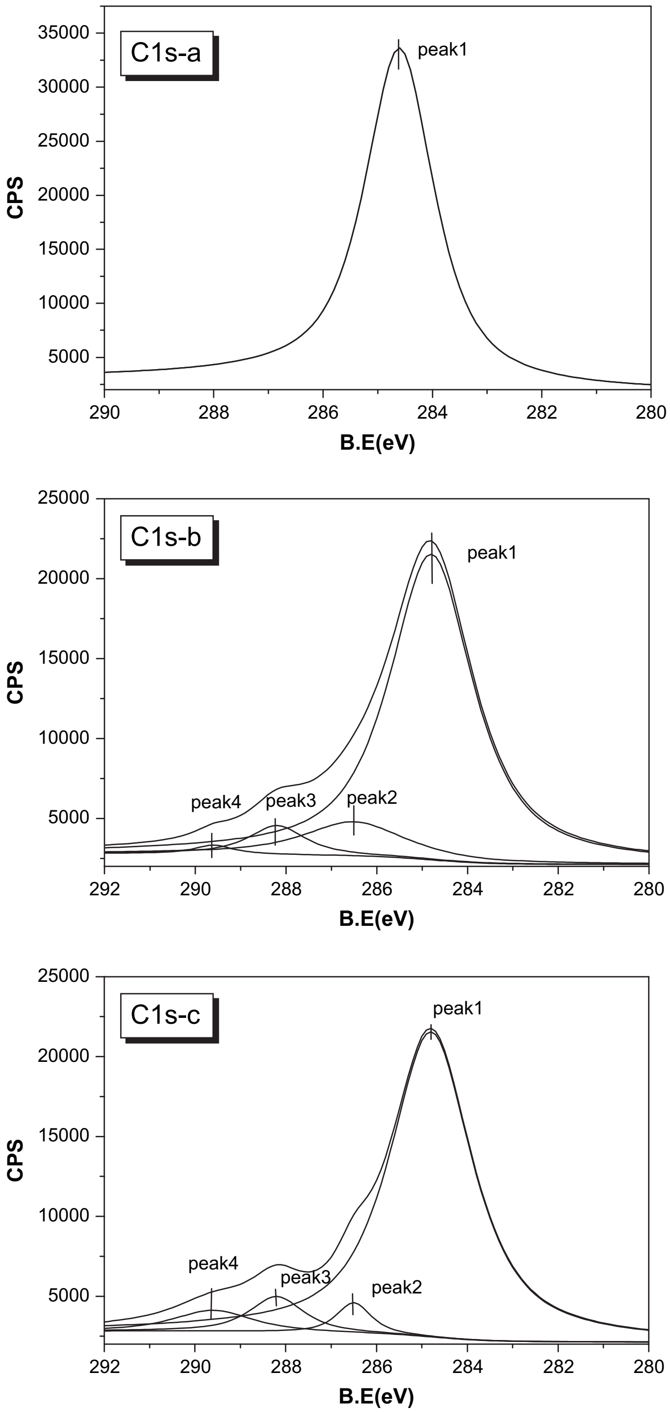


Fig. 4. XPS spectra of C1s. (a) Pure PS film (0 h), (b) pure PS film (50 h), (c) PS-*g*-TiO_2 (TiO_2: 1%) film 50 h.

of polymeric matrix was not affected by embedding TiO_2 particles [14]. Upon 45 h UV-light irradiation, the intensity of phenyl ring peaks of pure PS film (Fig. 3b) began to decrease, but the extent was less than what was observed in PS-*g*-TiO_2 composite film after the identical irradiation (Fig. 3c). The larger decrease of an aromatic band at 756 and 701 cm^{-1} can be responsible for the phenyl ring opening reaction in PS [15]. Two new absorption peaks appear in the region of 1721 and 1316 cm^{-1} which are the characteristic absorptions of carbonyl (C=O) group and hydroxyl (OH) group, respectively. It can be seen that the intensities of carbonyl peak in the composite PS increase more intensively than that in pure PS. The formation of the carbonyl groups in the photo-oxidized pure PS has been well documented elsewhere [16,17]. In the composite film, the surface water on TiO_2 reacts with valence band (VB) holes to generate hydroxyl radicals or O_2 molecules react with conduction band (CB) electrons to generate reactive oxygen species; these radicals and species are responsible for most of the oxidizing power of TiO_2 photocatalysts. These hydroxyl radicals and active oxygen species oxidize the C−H bond in polymer chain to form the carbonyl group. The result also shows that the TiO_2 catalyst makes the photodegradation of PS film more effective. The detailed mechanism is being investigated.

3.3. The XPS analysis

Figs. 4 and 5 show the XPS spectra of C1s and O1s of the films before and after 100 h irradiation. According to the peak-fitting result of C1s (Fig. 4a), there is only one peak at 284.8 eV (peak 1) in original PS film, which is assigned to −C−C− or −C−H group of polymer. The irradiated PS and PS-*g*-TiO_2 samples present three new peaks, assigned to C−O group at 286.5 eV (peak 2), C=O group at 288.2 eV (peak 3), and −COO group at 289.6 eV (peak 4) [17]. The presence of C−O peak indicates the existence of alcohols and carboxylic [18]. And the intensity of peak 3 and peak 4 for irradiated PS-*g*-TiO_2 sample is higher than that of irradiated pure PS sample, which indicates that the C−O groups are further oxidized to the C=O or polycarbonate, carboxylic acids and carboxylates in PS-*g*-TiO_2 sample [18,19]. This result confirms that the oxidation rate of composite film is much higher than that of the pure PS film.

The initial PS sample surface (Fig. 5) shows the presence of oxygen at the binding energy of 532.3 eV (peak 1), which is assigned to the impure oxygen groups such as carbonyl and OH [20]. After irradiation for 50 h, a new peak at 533.6 eV (peak 2) appeared on the surface of PS film and PS-*g*-TiO_2 composite film, which belonged to −COO [20]. The intensity

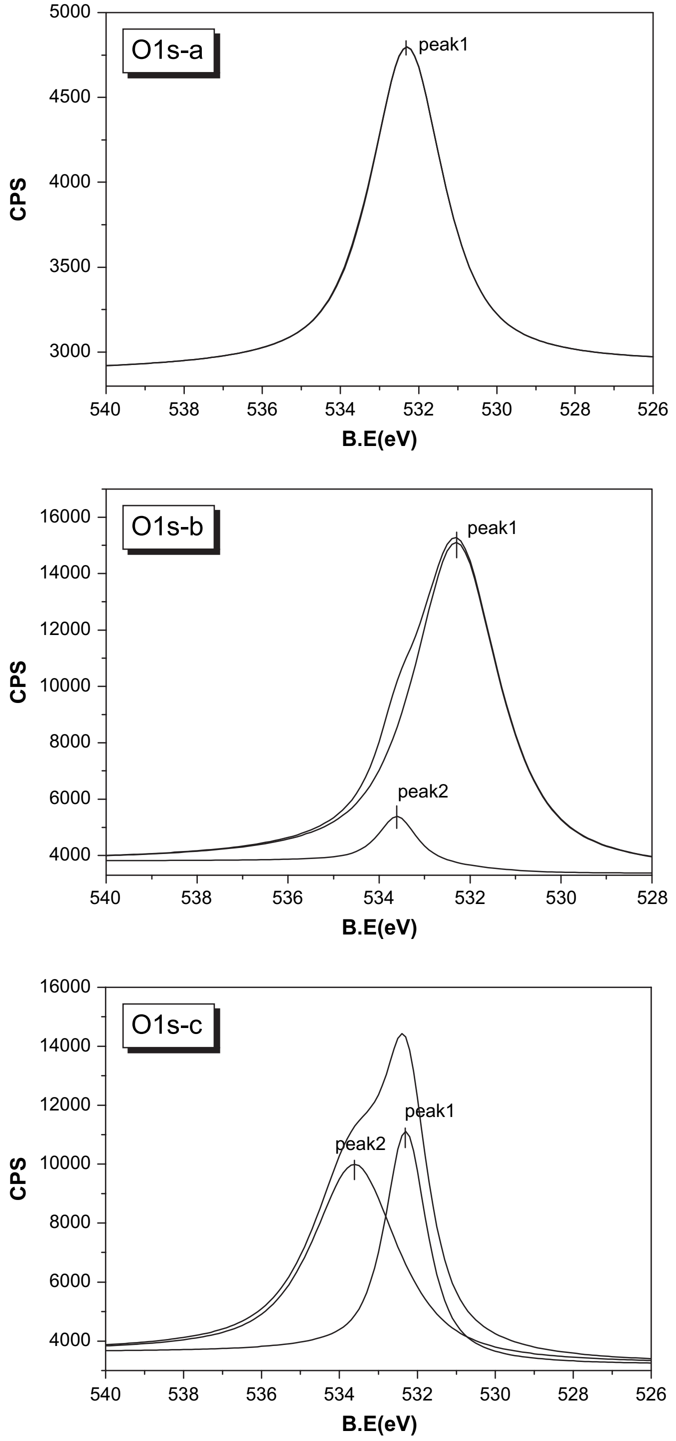


Fig. 5. XPS spectra of O1s. (a) Pure PS film 0 h, (b) pure PS film 50 h, (c) PS-*g*-TiO_2 (TiO_2: 1%, 50 h) film.

of peak 2 of PS-*g*-TiO_2 sample (62.6%, Fig. 5c) is much higher than that of pure PS film (5.9%, Fig. 5b), indicating that these species are generated much faster and in large number on the surface of composite film than on that of pure PS film. XPS results showed the C–O groups were further oxidized to the C=O or –COO. Then these C=O or –COO groups were changed into volatile CO_2, which was speculated from the result of weight loss.

3.4. Weight loss and the decrease of molecular weight

Fig. 6 shows the photodegradation weight loss curves of the pure PS film and PS-*g*-TiO_2 composite films under ultraviolet lamp for 2.5 mW/cm^2 light intensity at 254 nm in the air. The weight loss of the composite films increased gradually with the increasing *g*-TiO_2 concentration in composite films from 0.5% to 2%. When TiO_2 content was 2%, the weight loss rate of PS-*g*-TiO_2 film increased steadily with the increasing irradiation time and reached 31.9% after 396 h irradiation in the air, while that of pure PS film showed only 10.3% under the identical experimental condition.

Fig. 7 shows the weight loss curve of different films under the sunlight illumination. The weight loss rate of composite film is much higher than that of pure film. The weight loss reached 18.9% after 300 h irradiation, while that of the pure PS film was only 0.53%. The pure PS film had almost no change in sunlight irradiation. This result repeats the fact that the pure PS is non-photodegradable in natural environment. But the composite film was indeed photodegradable with evident efficiency under sunlight beam in natural environment.

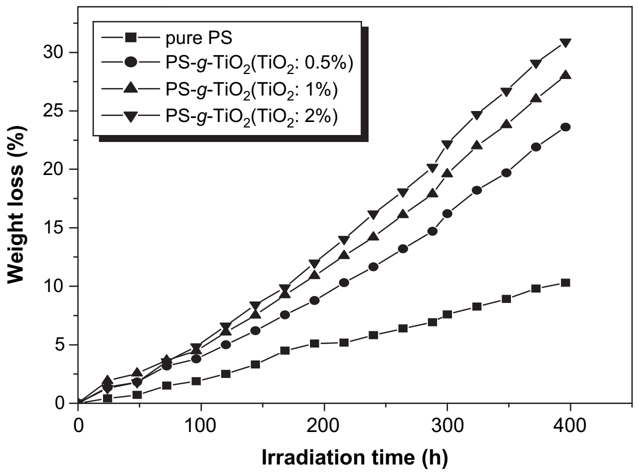


Fig. 6. Weight loss of pure PS and PS-*g*-TiO_2 films under UV-light irradiation (2.5 mW/cm^2, 254 nm).

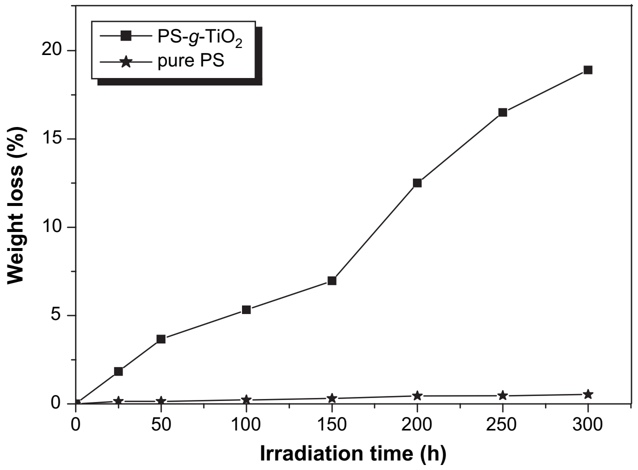


Fig. 7. Weight loss of pure PS and PS-*g*-TiO_2 (TiO_2: 1%) films under sunlight irradiation.

Fig. 8 displays the photo-induced weight loss of the polymer films under the Argon atmosphere and air. The weight loss in Argon was much less than that in air, not only for the pure PS film but also for the PS-*g*-TiO_2 (TiO_2: 2%) composite films. Further, the weight loss of PS-*g*-TiO_2 film shows no difference with the pure PS under Argon atmosphere. This is the proof that oxygen plays the key role in photocatalytic reaction and photolysis reaction of PS films.

Molecular weight of the PS was almost unchanged by embedding TiO_2 particles [7]. The photocatalytic degradation of the PS films is accompanied by reducing the PS molecular weight, which is measured by GPC (as shown in Table 1). After irradiation of 396 h, the average molecular weight (M_w) of the two samples decreased. The M_w of the composite film decreased 53.1%, M_n decreased 73.2%, and the polydispersity (M_w/M_n) was increased from 2.46 to 4.28. While M_w of pure PS film reduced only 18.3%, M_n reduced 19.3%. The polydispersity was increased little (from 2.46 to 2.49).

3.5. Morphology of samples after photodegradation

Fig. 9 displays the morphology of PS-*g*-TiO_2 (TiO_2: 2%) films and pure PS film irradiated for 0 h and 200 h in air, respectively. Both the surface of PS-*g*-TiO_2 composite film and pure film are smooth before irradiation (Fig. 9a and b). After irradiation of 200 h (1 mW/cm^2), the composite film was obviously decomposed (Fig. 9d). The big cavities formed not only on the surface but also inside the film, with the chalking phenomenon taking place. On the other hand, the pure PS film changed only little after 200 h irradiation (Fig. 9c).

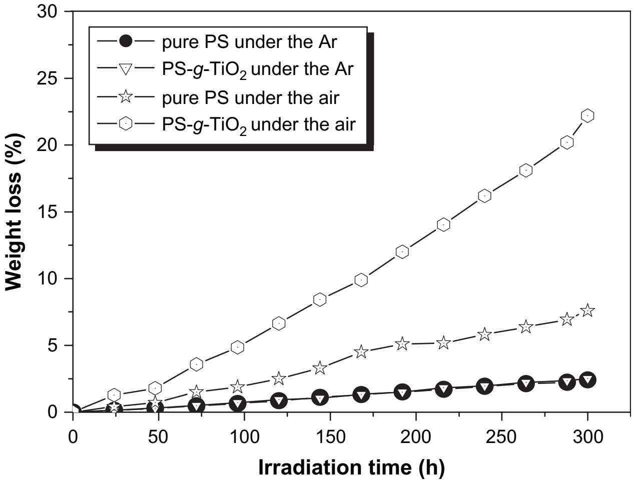


Fig. 8. Weight loss of pure PS and PS-*g*-TiO_2 films (TiO_2: 2%) under the air and Ar atmosphere.

Table 1
The variation of molecular weight of polymer films with irradiation time

Sample	Irradiation time (h)	M_n/g mol^{-1}	M_w/g mol^{-1}	Polydispersity
Pure PS	0	189,796	467,084	2.46
Pure PS	396	153,172	381,787	2.49
PS-*g*-TiO_2 (TiO_2: 2%)	396	51,183	218,912	4.28

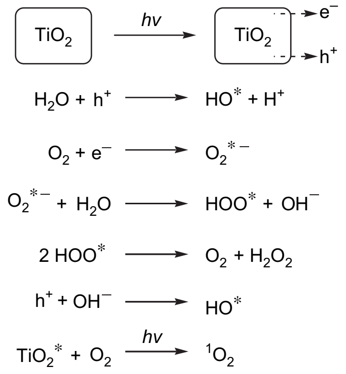
4. Discussion

The PS polymer photodegradation, which is an essential process of bond scission in the backbone of polymer matrix, has long been believed to proceed via both direct photolytic and photocatalytic reactions [21]. In details, there may be two different scenarios in simple PS films and in TiO_2 catalyst-embedded composite films.

For the pure PS film, its photolysis and oxidation reactions had been studied extensively [22,23]. It is generally accepted that the photolysis reaction takes place where the benzene ring in polystyrene molecule is stimulated by absorbing UV light with wavelength less than 280 nm, and forms the macromolecule radicals. These radicals then undergo chain scission, branching cross-linking, and oxidation reaction.

The initiation in the photocatalytic degradation of composite film is quite different. The degradation of PS-*g*-TiO_2 composite film is caused by both the direct photolytic reaction of PS and the photocatalytic reactions of PS on the surface of TiO_2. TiO_2 is stimulated by absorbing UV light to generate various active oxygen species such as $O_2^{\bullet -}$, $HOO^\bullet$ and $HO^\bullet$. These active oxygen species attack the polymer chains, which lead to the irregular bond scission. Although we do not know what the main oxidizing species are, the reaction of O_2 with conduction band electrons is the key step in this solid-phase system according to the experimental result in Argon atmosphere and air.

Lots of researches reported [3,24] the catalytic mechanism of TiO_2 semiconductor and the main process as follows:



The active radicals described above initiate the solid-phase photocatalytic degradation of PS-*g*-TiO_2 composite film by attacking neighboring polymer chains and forming carbon-centered radicals such as $-(CH_2{}^\bullet CPh)-$ and $-({}^\bullet CHCHPh)-$. Their successive reactions with $O_2^{\bullet -}$, $HOO^\bullet$ and $HO^\bullet$ cause hydroxyl derivatives and carbonyl intermediates, result in the chain cleavage. Finally, volatile species, such as carbon dioxide are evolved.

The weight percentage of benzene ring in the polystyrene molecule is about 74%, and the weight loss of PS-*g*-TiO_2 composite film reaches 32% after 396 h irradiation. FT-IR analysis proves that the characteristic peaks' intensity of benzene ring decreased for composite film with 45 h UV-light illumination. The experimental observations suggested that some benzene rings were cleaved. According to Ref. [21], benzene rings

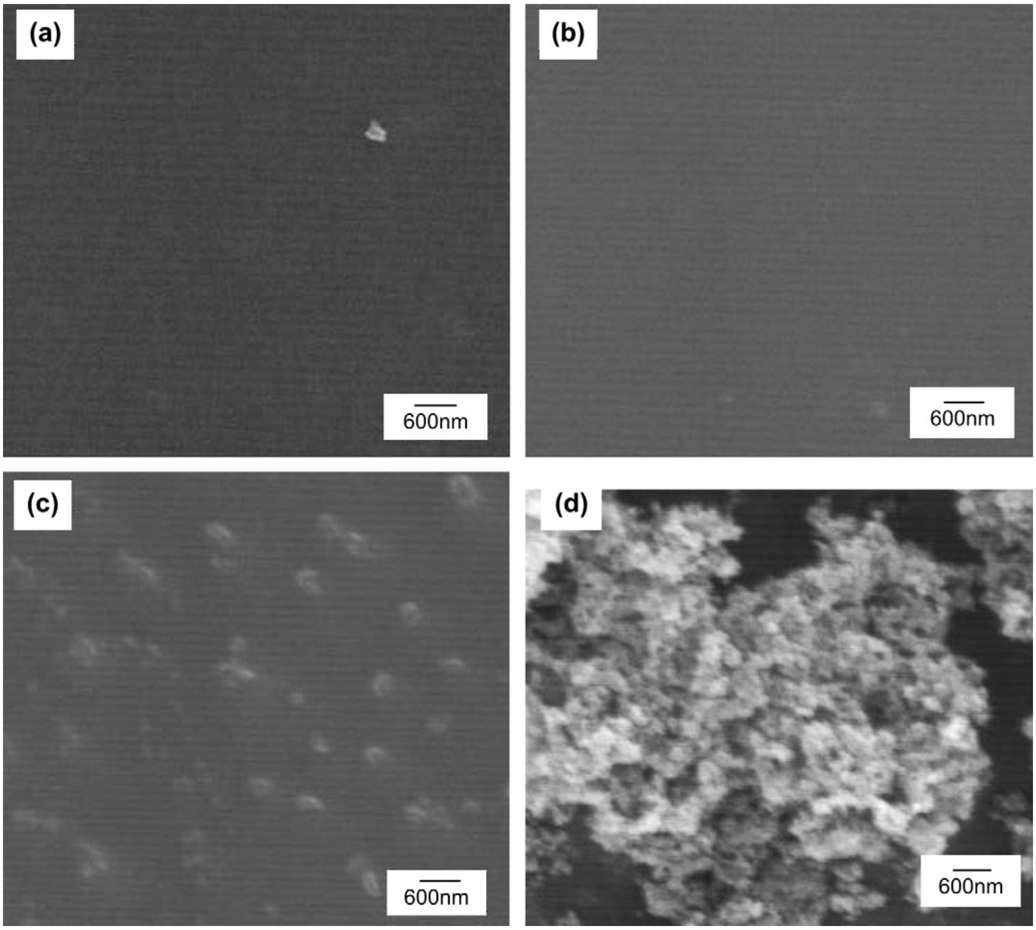


Fig. 9. SEM images of: (a) pure film (0 h), (b) composite film (TiO_2: 1%, 0 h), (c) pure film (200 h), (d) composite film (TiO_2: 1%, 200 h).

were probably oxidized to aldehydes as shown in Fig. 10. Aldehydes can be further photocatalytically oxidized to CO_2 and H_2O with the aid of active oxygen species. The formation of carbonyl intermediates and cleavage of benzene rings in the PS polymer lead to the further degradation of PS.

With this initial photocatalytic degradation, the biological degradation is possible to be applied in this case to degrade furthermore the remnant of the polystyrene composite film [25,26]. In this sense, the photocatalytic degradation of PS-*g*-TiO_2 film is of high potential in waste plastic treatment application. The biological degradation of the remnant of the polystyrene composite film is being investigated.

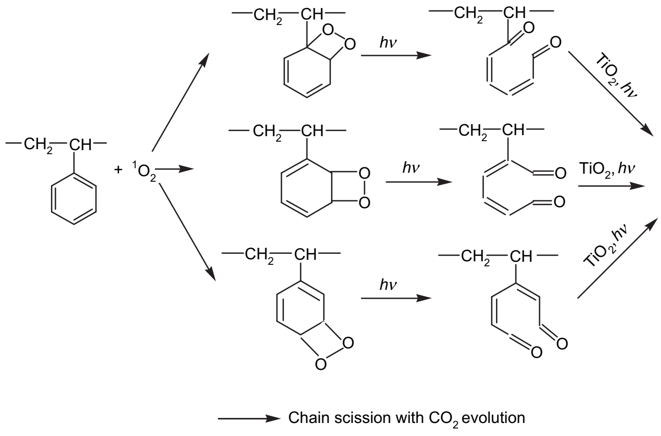


Fig. 10. Probable processes of the benzene ring cleavage.

5. Conclusions

The results in this study showed that the grafted-TiO_2 by polymer was well dispersed in the PS polymer matrix. In the presence of *g*-TiO_2 catalyst, the PS-*g*-TiO_2 composite film could undergo photocatalytic degradation efficiently under the UV-irradiation or the sunlight illumination, through its oxidative reaction with the active oxygen radicals. The weight loss reached 18.9% in 300 h sunlight exposure in air, while that of pure PS film was only 0.53%. The PS-*g*-TiO_2 composite is a hopeful new environment-friendly polymer material.

Acknowledgments

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