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Solid-Phase Photocatalytic Degradation of Polystyrene with TiO_2/Fe(St)$_3$ as Catalyst

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ABSTRACT: A novel photodegradable TiO_2-Fe(St)$_3$-polystyrene (TiO_2-Fe(St)$_3$-PS) nanocomposite was prepared by embedding TiO_2 and Fe(St)$_3$ into the commercial polystyrene. Ferric stearate was added into polymer as cocatalyst in order to improve the dispersion in polystyrene and photocatalytic efficiency of TiO_2 nanoparticles. Solid-phase photocatalytic degradation of the TiO_2-Fe(St)$_3$-PS nanocomposite was carried out in an ambient air at room temperature under ultraviolet lamp. The properties of TiO_2-Fe(St)$_3$-PS composite film were compared with that of the pure PS film and the TiO_2-PS composite film, through weight loss monitoring, scanning electron microscope, gel permeation chromatogram, and FTIR spectroscopy. The photodegradation efficiency of TiO_2-Fe(St)$_3$-PS composite film was higher than that of the pure PS film and the TiO_2-PS composite film under the UV light irradiation. The average molecular weight (M_w) of TiO_2-Fe(St)$_3$-PS composite film decreased 63.08%, and the number of average molecular weight (M_n) decreased 79.49% after UV light irradiation for 480 h. Photo-oxidation leads to an increase in the low molecular weight fraction by chain scission, thereby facilitating biodegradation. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: TiO_2; ferric stearate; solid-phase photocatalytic degradation; polystyrene films

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INTRODUCTION

Polystyrene (PS), as a conventional plastic material, exhibits a good price/performance balance. A large quantity of PS and the expanded polystyrene (EPS) is used in food service and retail industry. Moreover, we usually use PS foam as wrapper to protect electronic instruments, household appliances, and other breakable goods from damage. However, the wasted PS plastics do not decompose in natural environment for a long time, which leads to the growing problems of environmental pollution. That people pay more and more attention to environmental pollution has promoted the development of degradable plastics.[1–4]

In recent years, photocatalytic degradation of plastics has been studied extensively.[5–8] TiO_2 has been generally regarded as the best photocatalyst, owing to its excellent characteristics such as inexpensiveness, good photostability, nontoxicity, and high activity.[9,10] Zhu and Coworkers[11] firstly used TiO_2 as photocatalyst to decompose PS in the form of solid-phase photocatalytic oxidation under ultraviolet (UV) light irradiation in air. The result displayed that the PS-TiO_2 composite sample was assuredly degraded to fragments with lower molecular weight. In the same way, PVC-TiO_2[12–14] and PE-TiO_2[15,16] composite sample had been investigated. All the results showed that the composite samples could be degraded under UV light or sunlight irradiation. However, owing to the strong polarity of TiO_2, it was difficult to disperse uniformly into the polymer matrix with lower polarity, which resulted in a decrease of solid phase photocatalytic degradation efficiency of the composite films. Choi and Coworkers[12]indicated that the uniform dispersion of nanosized TiO_2 particles in the polymer matrix needed to be achieved for commercial applications. Only 0.02 wt % TiO_2 in PVC would be enough to accomplish the photodegradation of the whole composite film if each 5 nm TiO_2 particle was in a well dispersed state. In order to achieve the well dispersion of nano TiO_2 particles in polymer matrix, many measures were carried out such as organic modification on the surface of TiO_2 particles by coupling reagent,[17–19] diblock copolymers,[20] surface-grafting polymer[21,22] or metal phthalocyanines and porphyrins,[23] etc. Transition metals carboxylates have been employed to initiate degradation in polymer films. The effect of the chain length of cobalt carboxylates, namely, laurate, palmitate, and

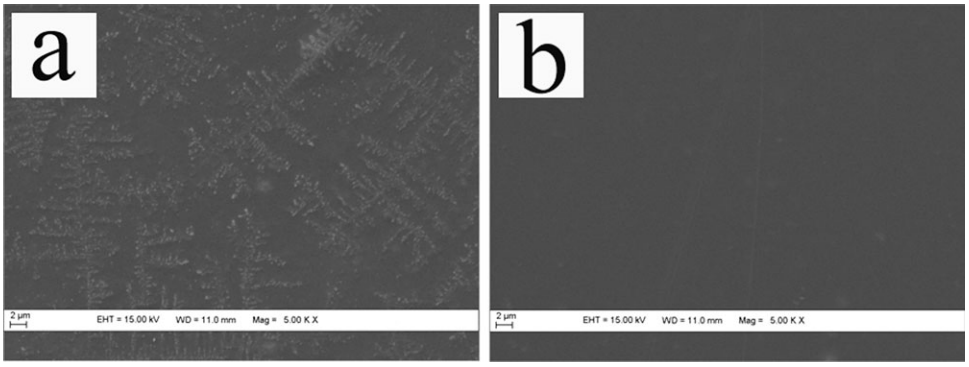

Figure 1. SEM images of the TiO_2-PS (a) and TiO_2-Fe(St)$_3$-PS (b) films.

stearate, on the photodegradation behavior of PE was reported by Roy et al.[24] The authors concluded that the effectiveness in promoting photodegradation was in the order: Stearate > palmitate > laurate. The role of these metals/metallic compounds on the photodegradation of polyethylene has been extensively studied by several authors.[25] The researcher indicated that iron stearate was the most effective in the early stage of photodegradation behavior of polyethylene (PE), when using various transition-metal like iron, cobalt or manganese stearates as prodegradants. In addition, three long alkyl chains (C_{18}) in ferric stearate are helpful for the dispersion of inorganic particles in the low polarity polymer. Therefore, ferric stearate was chosen as cocatalyst to promote the photodegradation of PS films.

In this work, a novel TiO_2-Fe(St)$_3$-PS composite film was synthesized using TiO_2 and Fe(St)$_3$ as composite photocatalyst. The surface morphology of the films was observed by scanning electron microscopy (SEM) to estimate the dispersion of composite photocatalyst in PS matrix. The photodegrading properties of the composite film were investigated in an ambient air at room temperature under ultraviolet irradiation.

EXPERIMENTAL

Materials

PS foam was from the package material of electronic instruments without further purification. The average molecular weight (M_w) of PS was measured by gel permeation chromatography (GPC). Its M_w was 2.6×10^5 g mol^{-1} and the polydispersity index (M_w/M_n) was 2.23. TiO_2 photocatalyst was Degussa P_{25} which was bought from Degussa with 70% in anatase phase and 30% in rutile, whose primary particle diameter was between 30 and 50 nm. Ferric stearate was synthesized by the reaction of ferric trichloride with sodium stearate according to the procedure reported in the literature.[26] KH550 silicone coupling agent was supplied by Shanghai Yaohua Chem.

Preparation and Characterization of TiO_2-PS and TiO_2-Fe(St)$_3$-PS Composite Films

The TiO_2-Fe(St)$_3$-PS composite films were prepared as follows: 3 g PS foam was dissolved in 30 mL tetrahydrofuran (THF) under vigorous stirring for 12 h to obtain the PS solution. At the same time, 0.003 g Fe(St)$_3$ and 0.027 g TiO_2 powder was uniformly dispersed into 5 mL THF which was mixed with KH550 silicone coupling agent (1 wt %) beforehand by ultrasonic vibration for 20 min. Then the suspension was added into the PS solution to get a mixture, the ratio of photocatalyst Fe(St)$_3$/TiO_2 to PS was 1.0 wt %. After keeping on stirring the mixture for another 12 h, the composite films were prepared by spreading the viscous solution onto the slick glass (10×10 cm^2) and dried in airproof system for 48 h at the room temperature. In order to compare the photocatalytic activity, the pure PS films and TiO_2-PS films were prepared in the similar process above as well. The surface morphologies of the composite samples were recorded by scanning electron microscope (SEM, EVO-LS15) to observe the dispersion of nanoparticles in the polymer.

The Photocatalytic Degradation of the Composite Films

The pure PS film, TiO_2-PS and TiO_2-Fe(St)$_3$-PS composite films were irradiated under 30 W ultraviolet lamp (Jiangsu Juguang) in the air. The surface area of the films was 12.25 cm^{-2} (3.5×3.5 cm^2). The distance between the samples and the lamp was 8 cm. The degradation extent of the films was estimated directly by their weight loss. The spectrum character of these films before and after irradiation was measured with a Nicolet 6700 FTIR spectrophotometer using the film directly without KBr pellets. The surface morphologies of all these samples before and after irradiation were observed with a EVO-LS15 SEM employing an operating voltage of 15 kV. The average molecular weights of the films before and after the irradiation were measured by GPC (PL-GPC50 Polymer Laboratories, UK). For GPC analysis, all the PS samples were dissolved in THF, and then filtered through a 0.2 μm polytetrafluoroethylene (PTFE) syringe filter in order to remove TiO_2 particles.

RESULTS AND DISCUSSION

The Dispersion of TiO_2 Nanoparticles in PS

SEM was used to estimate the dispersion of TiO_2 nanoparticles in PS matrix. Figure 1 shows the SEM images of the composite films. It can be seen that TiO_2 without adding Fe(St)$_3$ conglomerated seriously, in other words, the untreated TiO_2 had the poor dispersion in the PS polymer [Figure 1(a)]. However, mixing of a small quantity of Fe(St)$_3$ and TiO_2 can greatly improved its dispersion in the PS. The surface of the TiO_2-Fe(St)$_3$-PS composite film was comparatively smooth, with few aggregation. These morphology of the composite films indicated that adding a small amount of Fe(St)$_3$ can extraordinarily

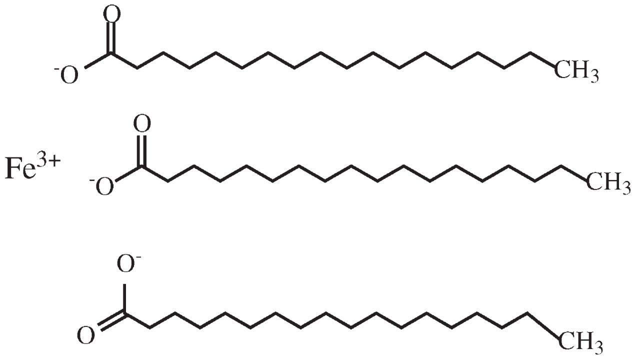

Figure 2. Molecular structure of ferric stearate.

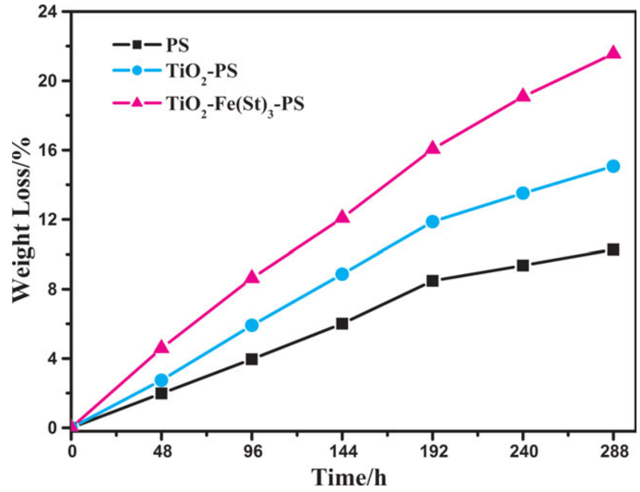

Figure 3. Weight loss of three kinds of films under UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

improve the dispersion of TiO_2 in the PS polymer, which was attribute to the molecular structure of $Fe(St)_3$ (Figure 2). Three long alkyl chains (C_{18}) in ferric stearate served as a bridge between inorganic TiO_2 particles and low polarity PS.

Weight Loss Analysis of the Films After Irradiation

Figure 3 shows the photoinduced weight loss curves of the polymer films under UV irradiation in the air. Obviously, the weight loss rate of the TiO_2-$Fe(St)_3$-PS film was the highest in the three kinds of films. The weight loss of TiO_2-$Fe(St)_3$-PS film steadily increased with the irradiation time and reached 22 % after irradiating for 288 h. While in the same experimental condition, the weight loss of pure PS film was only 10% and the TiO_2-PS film reduction was 15%. The results indicated that adding small quantity of $Fe(St)_3$ can enhance the photocatalytic degradation efficiency of composite film owing to uniformly dispersion of organic particles in polymer, which agreed well with SEM observations.

The Surface Morphology of the Films After Photodegradation

SEM was carried out to observe the surface morphology of the films after UV irradiation for 480 h, as shown in Figure 4. The surface of the PS, TiO_2-PS and TiO_2-$Fe(St)_3$-PS films were all smooth before irradiation (Figure 1). It was obviously observed the decomposed state of the composite films after irradiation. For TiO_2-$Fe(St)_3$-PS composite film, there were numerous big cavities forming not only on the surface but also inside the film [Figure 4(c)]. The structure of the film was destroyed and there was a large amount of area chalking in surface of film. The surface morphology of TiO_2-PS film [Figure 4(b)] had the similar condition to the TiO_2-$Fe(St)_3$-PS film, but the degradation content was evidently not as good as the TiO_2-$Fe(St)_3$-PS film. On the other hand, only small cavities and cracks were observed on the surface of the pure PS film [Figure 4(a)]. These indicated that PS polymer could be degraded with TiO_2 photocatalyst and adding a small amount $Fe(St)_3$ could reinforce the photocatalytic degradation of PS films.

Variation of Molecular Weight of Films

The change of the molecular weight is the most important factor to estimate the degradation of the polymer. The photocatalytic degradation of the PS films was accompanied by the reduction of their molecular weight, which was measured by GPC. Table I displayed the variation of weight average molecular weight (M_w) and number average molecular weight (M_n) of the pure PS sample, TiO_2-PS composite sample and TiO_2-$Fe(St)_3$-PS composite sample before and after irradiation. As was seen from Table I, the M_w and M_n for the three samples were almost the same before irradiation, in other words, the molecular weight of the polymer film was almost unchanged by embedding TiO_2 or TiO_2/$Fe(St)_3$ inorganic particles. However, after irradiating for 480 h, the M_w and M_n of the three samples all decreased. The results may imply that there are bond scissions in the polymer whatever the pure PS film or the TiO_2-PS and TiO_2-$Fe(St)_3$-PS composite films. With the initial photocatalytic

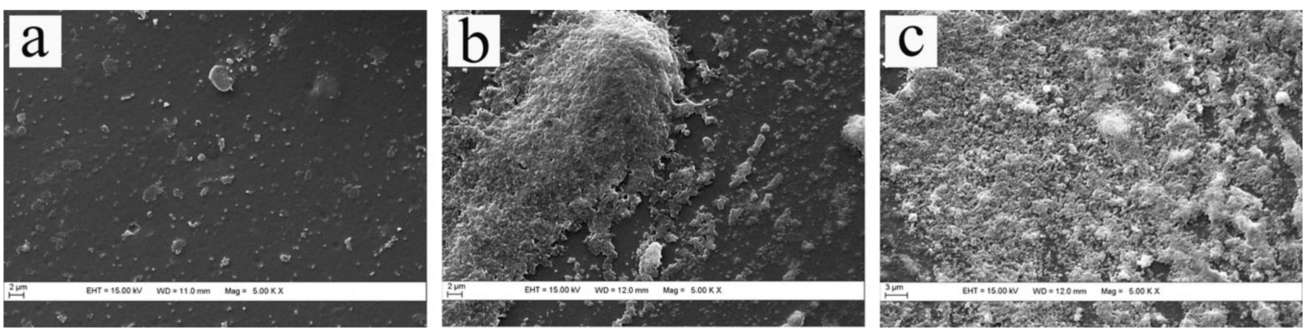

Figure 4. SEM images of the polymer films after irradiation for 480 h. (a) The pure PS film, (b) TiO_2-PS film, and (c) TiO_2-$Fe(St)_3$-PS film.

Table I. The Variation of Molecular Weight of Polymer Films with Irradiation Time Increasing

Sample	Irradiation time (h)	M_w ($\times 10^5$ g/mol)	M_n ($\times 10^5$ g/mol)	Polydispersity (M_w/M_n)
Pure PS	0	2.60	1.17	2.23
TiO_2-PS	0	2.60	1.12	2.31
TiO_2-Fe(St)$_3$-PS	0	2.60	1.16	2.24
Pure PS	480	2.44	0.86	2.84
TiO_2-PS	480	1.67	0.41	4.07
TiO_2-Fe(St)$_3$-PS	480	0.96	0.24	3.94

degradation, the biological degradation was possible to occur for the remnant.[27–29] The M_w of the TiO_2-Fe(St)$_3$-PS film decreased 63.08%, which is only 35.78 and 6.15% for TiO_2-PS film and pure PS film, respectively. The M_n of the TiO_2-Fe(St)$_3$-PS film decreased 79.49% which was the highest in three kinds of films. The results demonstrate clearly the degradation efficiency of TiO_2-Fe(St)$_3$-PS film is much higher than both TiO_2-PS film and pure PE film.

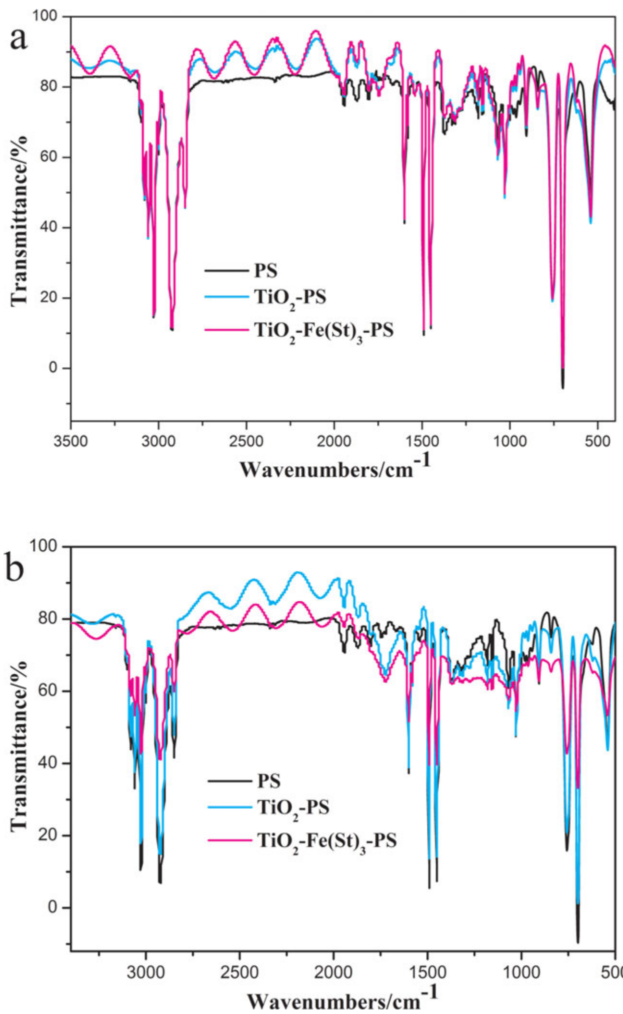

Figure 5. FTIR spectra of the polymer films before and after irradiation. (a) The different films before irradiation and (b) the different films after irradiation for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Spectroscopic Characterization

The photocatalytic degradation of the PS films was also examined by FTIR spectroscopy. Figure 5(a) shows the FTIR spectra of the pure PS film, TiO_2-PS composite film and TiO_2-Fe(St)$_3$-PS composite film before irradiation. The spectrum of the original TiO_2-PS and TiO_2-Fe(St)$_3$-PS composite films show the same characteristic absorption peaks as the pure PS film. The peaks in the region of 1490, 1448, 758, and 701 cm^{-1} were the characteristic peaks of phenyl ring. It showed that embedding TiO_2 or TiO_2/Fe(St)$_3$ particles did not affect the IR spectra character of the polymeric matrix. This also indicated that interaction between PS and TiO_2 or TiO_2/Fe(St)$_3$ was physical, not chemical. As is seen from Figure 5(b), there was a new absorption peak for the three kinds of films in the region of 1720 cm^{-1} after irradiation for 24 h, which was the characteristic absorption of carbonyl (C=O) group, in all of which, the intensity of carbonyl (C=O) group in the TiO_2-Fe(St)$_3$-PS composite film was the strongest, while that in the pure PS film was the weakest. After irradiation, the intensity of the characteristic absorption peaks of the phenyl ring in the three films all decreased, and the intensity in the TiO_2-Fe(St)$_3$-PS composite film was much weaker than in the pure PS film and TiO_2-PS composite film. Both the formation of the carbonyl groups and the decrease of intensity of phenyl ring suggested that the photo-oxidized reaction had taken place in the composite film.[30] In addition, the formation of carbonyl groups on the surface increases its hydrophilicity, which enhances the possibility of further degradation towards mineralization.[31]

Photocatalytic Degradation Mechanism Discussion

The photodegradation of PS under ultraviolet irradiation occurs via direct absorption of photons by PS macromolecule to generate excited states, then arises chain scission, branching crosslinking, and a series of oxidation reactions.[32] From all the results above, we have known that the composite samples showed higher photodegradation efficiency than the pure PS sample. The initiation in the photocatalytic degradation of TiO_2-PS and TiO_2-Fe(St)$_3$-PS composite samples are quite different from that of the pure PS sample. For the composite samples, there is not only the photolytic reaction of PS but also the photocatalytic reaction of PS on the surface of TiO_2. The photodegradation mechanism of TiO_2-PS has been researched in some former works,[11] which can be summarized as follows. TiO_2 is stimulated by absorbing UV light whose energy is higher than 3.2 eV, to generate electron/hole pairs in the conduction band (CB) and valence band (VB), respectively. The electrons can be captured by O_2 that adsorbs on the surface of TiO_2 to form O_2^-. At the same time, photogenerated holes are trapped by H_2O adsorbing on the surface of TiO_2 to create HO. Both the O_2^- and HO are two very important active oxygen species, which can attack the polymer chains, leading to the irregular bond scission and forming carbon-centered radicals such as –($CH_2{}^{\cdot}CPh$)— and —($^{\cdot}CHCHPh$)—; these radicals continue to occur a series of successive reactions to produce hydroxyl derivatives and carbonyl intermediates, such as ethene, formaldehyde, and acetaldehyde, and ethanol. These intermediates can be further oxidized, finally forming CO_2 and H_2O.

As illustrated above, TiO_2-Fe(St)$_3$-PS showed higher photocatalytic degradation efficiency than TiO_2-PS. The more reactive oxygen species generate, the faster plastic photodegradation goes on. In the absence of the electron and hole scavengers, most of the electron and hole recombine with each other within a few nanoseconds. If the scavengers or the surface defects are present to trap the electron or hole, electron-hole recombination can be prevented and the subsequent reactions caused by the electrons and holes may be dramatically enhanced. Since the higher electron-hole separation efficiency of TiO_2/Fe(St)$_3$ results in the more reactive oxygen species generation both on the surface and inside the film, PS presents a faster and more complete chalking over TiO_2/Fe(St)$_3$ than over TiO_2 photocatalyst. In addition, the well dispersion of nano-TiO_2 in polymer matrix is also helpful for increasing the photodegradation efficiency.

CONCLUSION

Adding Fe(St)$_3$ can greatly improve the dispersion of TiO_2 in PS polymer and promote the photocatalytic degradation efficiency of PS. The average molecular weight (M_w) of TiO_2-Fe(St)$_3$-PS composite film decreased 63.08%, and the number of average molecular weight (M_n) decreased 79.49% after UV light irradiation for 480 h. From the FTIR spectra, there are new absorption peaks of the carbonyl groups, which suggested that the photo-oxidized reaction had taken place in the composite film. Photo-oxidation leads to an increase in the low molecular weight fraction by chain scission, thereby facilitating biodegradation. The TiO_2-Fe(St)$_3$-PS composite is a hopeful new environment-friendly polymer material.

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