

Enhanced Photodegradation Efficiency of Polyethylene-TiO₂ Nanocomposite Film with Oxidized Polyethylene Wax

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ABSTRACT: A novel photodegradable polyethylene-oxidized polyethylene wax-TiO₂ (PE-OPW-TiO₂) nanocomposite film was prepared by embedding the organically modified TiO₂ nanoparticles into commercial PE in the presence of OPW. The photocatalytic degradation behavior under ultraviolet light or solar light was investigated by examining the weight loss of the composite films, UV-vis transmittance spectrum, scanning electron microscope (SEM), and gel permeation chromatogram (GPC). The results show that OPW, as a dispersant and a compatibiliser, markedly improves the dispersion and compatibility of TiO₂ nanoparticles in PE resins. The PE-OPW-TiO₂ com-

posite film demonstrates much higher photodegradation efficiency and much better mechanical property than either the PE-TiO₂ composite film or the pure PE film. The weight-average molecular weight (M_w) of the PE-OPW-TiO₂ composite film decreased 94.3% and the number-average molecular weight (M_n) decreased 84.5% after 38 days solar light irradiation. The photocatalytic degradation mechanism of the film is briefly discussed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 378–384, 2010

Key words: degradation; dispersions; photochemistry; polyethylene; composites

INTRODUCTION

Polyethylene (PE), the most popular polyolefin, is broadly used as the packaging material. Unfortunately, due to its insensibility to microbial decomposition, the huge amount of waste plastics gives rise to serious environmental concerns. A number of solutions have been proposed to reduce the plastic waste (such as reusing, recycling, and incineration), but each of them has its limitations and disadvantages.¹ Recently, photocatalytic method was suggested to resolve environmental problem of the non-degradable polymers. As an effective photocatalyst, TiO₂ nanoparticles are used by embedding them into the polymer matrix. The interaction between TiO₂ and UV radiation would generate free radicals, which might degrade polymers, such as polyvinyl chloride (PVC),^{2–4} polystyrene (PS),^{5–8} polyvinyl alcohol (PVA),⁹ and polyethylene (PE).^{10,11} It has been shown that the preliminary UV irradiation of TiO₂-polymeric composite material can “trigger off” its biodegradation.¹² This is due to the chain

scissions and the formation of functional groups in macromolecules during photo-oxidative degradation. Such degraded polymer, containing shorter chains and unsaturated hydroxyl and carbonyl groups, is easily consumed by microorganisms.¹³ The photocatalytic method thus becomes an attractive and efficient decomposition technique for plastic waste treatment.

In our previous work,¹¹ we have reported the solid phase photocatalytic degradation behavior of a LDPE-TiO₂ composite film. The film was prepared by a blowing machine with mixed TiO₂ nanoparticles and LDPE pellets. The LDPE-TiO₂ composite film could be photocatalytic degraded under UV light or solar light irradiation. However, the preparation of a uniform nanocomposite film is difficult between a nonpolar (polyolefin) and high polar materials (TiO₂ nanoparticles). The surface of the as-prepared LDPE-TiO₂ composite film is rough and has the obvious aggregation of TiO₂, whose size extends up to a few micrometers. The micrometer-sized agglomerates significantly reduce the photodegradation efficiency due to (a) decreasing the interfacial areas between polymer and the photocatalytic agent and (b) inducing rapid whitening.^{3,14} The photoinduced whitening quickly shortens the light penetration depth into the composite film, which hinders further photodegradation. If TiO₂ nanoparticles could be well dispersed in the polymer, the

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efficiency of photocatalytic degradation is expected to be improved to a great extent. In addition, the mechanical properties of composite film are also expected to be improved.

For this end, the oxidized polyethylene wax (OPW) was introduced as a dispersant and compatibilizer for the LDPE-TiO₂ nanocomposite. OPW consists of a mixture of solid hydrocarbons that are oxidized in the molten state with air. The oxidation process adds acid, ester, alcohol, and carbonyl groups to the wax chains.¹⁵ Previous investigations were carried out using it as a modifier in plastic property.^{16,17} Luyt and Malunka¹⁸ reported that the addition of wax may improve the mechanical property of the polymer matrix. Generally, the wax is strongly miscible with LDPE and has a plasticizing effect on polyolefin.¹⁵ As the oxygen-containing groups of wax may interact strongly with the organic modifier in surface of TiO₂ nanoparticles, it is possible that the presence of OPW will improve the interaction between LDPE and organically modified TiO₂ nanoparticles. Moreover, OPW is expected to facilitate biodegradation because of the presence of oxidized elements in its chemical structure. Rosa et al.¹⁹ reported that OPW reduced the phase separation between the polymers and slightly increased the rate of biodegradation of polyhydroxybutyrate/LDPE (PHB/LDPE) blends. To our best knowledge, there has been no any report on the influence of OPW in photocatalytic degradation polymer field.

In this work, a novel photodegradable PE-OPW-TiO₂ nanocomposite film was prepared by embedding the organically modified TiO₂ nanoparticles into commercial PE in the presence of OPW. Its photocatalytic degradation under ultraviolet light or solar light in the ambient air was investigated by examining the weight loss of the composite films, UV-vis transmittance spectrum, scanning electron microscope (SEM), and gel permeation chromatogram (GPC). The purpose of the research was to investigate whether OPW could improve the dispersion of TiO₂ nanoparticles in polymer and enhance the photodegradation efficiency of PE-OPW-TiO₂ composite film and the mechanical property of it in comparison with the PE-TiO₂ film. The experimental results are positive.

EXPERIMENTAL

Materials

Commercial low-density polyethylene (LDPE) pellets were supplied by Sinopec Shanghai Petrochemical Company. The silicane coupling agent dimethylcyclotrisiloxane (DMC) was supplied by Chem. & New Mat. Company, Wuhan University. TiO₂ nanoparticles used in this work are Degussa P25, 70% in

anatase phase and 30% in rutile, whose primary particle diameter is in a range of 30–50 nm. TiO₂ was modified by DMC to improve the compatibility with polymer.²⁰ OPW and LDPE superfines were purchased in Nanjing Experimental Micropowder Factory.

Master batch preparation

Master batch of LDPE/TiO₂/OPW was prepared with a high-temperature melt-blending method. First, LDPE superfine, organically modified TiO₂ nanoparticle and OPW superfine were completely blended in a high-speed stirrer with the weight ratio of 3 : 1 : 1. The weight percent (wt %) of OPW in the master batch was kept the same as TiO₂. Then the mixture powders were melted at high temperature and granulated with the aid of a single screw extruder (SJ, Zhang Jia Gang Plastics Machinery Company, China).

Film preparation

PE-OPW-TiO₂ composite films were prepared via blow-formation method at a single-screw blow-forming system (Laiwu Plastics Machinery Company, China). As-prepared LDPE/TiO₂/OPW master batch was mixed with polyethylene pellets in selected ratio. The final content of both TiO₂ and OPW in different LDPE-OPW-TiO₂ composite films was controlled at 1, 2, and 3 wt %, respectively. The thickness of the film was measured to be 20–30 μm by a thickness gage. PE-TiO₂ (TiO₂: 1 wt %) composite film without OPW was prepared according to the method described in Ref. 11. The surface morphologies of the composite samples were studied using a Zeiss EVO LS-15 SEM.

Mechanical tests

The elongation at break of the films were performed at room temperature using a universal testing machine (CMT6503, Shenzhen SANS Test Machine Company, Shenzhen, China) according to ISO 527-2, 1993 (E) at a cross-head speed of 10 mm min⁻¹. The sample dimensions were 80 mm gage length, 10 mm gage width, and around 25 μm thickness, with 50 mm distance between two clamps. Five specimens in each sample were tested to establish testing reproducibility. The average value was presented for each sample.

Photocatalytic degradation and characterization of the composite films

The photocatalytic degradation experiment was carried out under UV or solar light irradiation in ambient air. The typical size of all samples was 5 cm ×

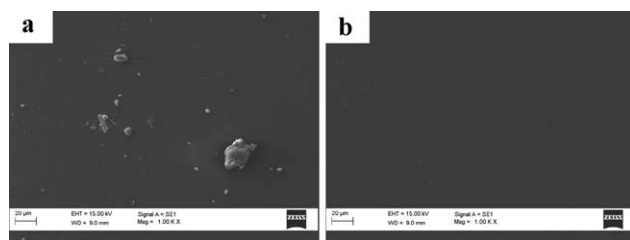


Figure 1 The SEM images of the PE-TiO₂ (a) and PE-OPW-TiO₂ (b) films.

5 cm. The samples were placed in a lamp-housing box (100 cm × 40 cm × 40 cm) and irradiated under a 30 W ultraviolet lamp (ZSZ-D, Changsha Guangming Company). The light intensity was controlled by adjusting the distance between the lamp and the samples. In our experiment, it was 1.0 mW cm⁻² at primary wavelength of 254 nm measured using a UV intensity meter (UV-I, Beijing Shida Company). The degradation extent of the film was evaluated by the weight loss. Each sample was weighed every 14 h during 120 h of irradiation. Three sets of experiments were tested to establish testing reproducibility.

When investigating the photocatalytic degradation of these films under solar light illumination, the samples were placed in the quartz vessel on a terrace in sunshine condition in July in Wuhan, China. Average irradiation time was 6–8 h in 1 day. The light intensity was measured everyday at 10 : 00, 13 : 00, and 16 : 00 using a UV intensity meter (UV-II, Beijing Shida Company). The average of all values was ~ 2.8 mW cm⁻² at a primary wavelength of 420 nm. The weight loss was measured every 2 days.

UV–vis spectrophotometer (Hitachi UV-3400) was used to investigate the spectral transmittance of the sample before and after the irradiation. The scanning electron microscope (SEM, Hitachi X-650) was used to observe the surface morphologies of the sample. The average molecular weights of the films before and after the irradiation were measured by gel permeation chromatogram (GPC, Waters 2690D Separation Module, Waters 2410 Refractive Index Detector). For GPC analysis, samples were dissolved in 1,2,4-trichlorobenzene and then they were filtered through a 0.2 μm PTFE syringe filter to remove TiO₂ particles. The temperature was 423 K for the injector, column, and detector, and the temperature was 323 K for the pump, with 1,2,4-trichlorobenzene as the solvent and an elution speed of 1 mL min⁻¹.

RESULTS AND DISCUSSION

The dispersion of TiO₂ nanoparticles in composite films

The dispersion of TiO₂ nanoparticles plays an important role in photodegradation efficiency and in

the mechanical properties of PE-TiO₂ composite film. Poor dispersion due to agglomeration of TiO₂ nanoparticles has been known to be one of the main causes to deteriorate the photocatalytic degradation efficiency. The dispersion of TiO₂ in PE-TiO₂ and PE-OPW-TiO₂ films is observed by SEM micrograph. The TiO₂ nanoparticles agglomerate severely in PE-TiO₂ composite film, and some macroscopic agglomerations are observed [Fig. 1(a)]. Even there are macroscopic particles observed by unaided eye in the surface of PE-TiO₂ composite film. However, the SEM image of PE-OPW-TiO₂ [Fig. 1(b)] shows a very different morphology, indicating an excellent dispersion of TiO₂ nanoparticles was obtained. The oxidized polyethylene wax, as a dispersant and compatibilizer, indeed greatly improved the dispersion property of the TiO₂ nanoparticles in PE resins.

Mechanical properties of the composite films

The influence of OPW and TiO₂ nanoparticles on the mechanical properties of PE film was investigated by the elongation at break (ϵ_b) of the film, which was a key factor for PE film application. It is generally known that the addition of nanosized materials into the polymer modifies the mechanical properties of the polymer. A good dispersion of nanoparticles increases ϵ_b of the composite film.²¹ The values of ϵ_b of the films investigated in this work are listed in Table I. The ϵ_b of the composite films containing TiO₂ alone is lower than that of the pure PE film. The agglomeration of TiO₂ nanoparticles in PE polymer matrix (refer to the SEM image in Fig. 1), could be responsible for the mechanical property loss, as the agglomerations induced large amounts of defects in the polymer matrix. The PE-OPW-TiO₂ film possesses much higher ϵ_b value than both the pure PE film and PE-TiO₂ film, which is attributed to the excellent dispersion of TiO₂ nanoparticles in the polymer matrix.

Effects of TiO₂ content on the ϵ_b of PE-OPW-TiO₂ films are shown in Figure 2. The PE-OPW-TiO₂ composite films exhibit much higher ϵ_b than pure PE film. The ϵ_b value reaches the maximum when the content of TiO₂ near 1%. It decreases a little with the increase of content after 1%. The diminishing tendency in ϵ_b value was considered from following two points: (1) the possible agglomeration of

TABLE I
The Elongation at Break (ϵ_b) of the Films

Sample	PE film	PE-TiO ₂ (1 wt %) film	PE-OPW-TiO ₂ (1 wt %) film
The elongation at break (%)	94.57 ± 17	59.16 ± 13	156.24 ± 16

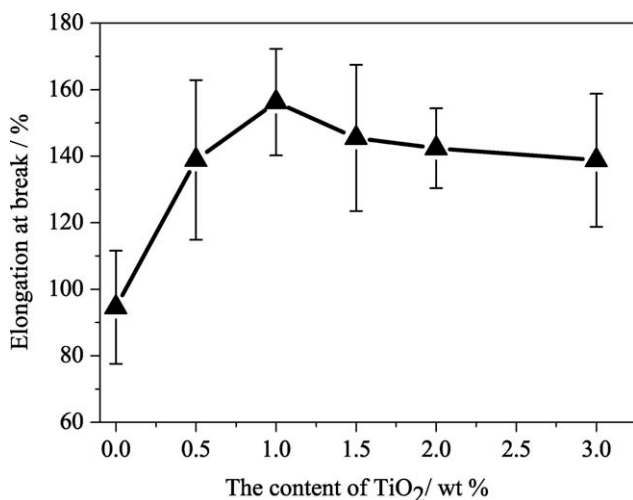


Figure 2 Effects of TiO₂ content on the elongation at break of the film.

nanoparticles with the increase of the TiO₂^{21,22} and (2) the co-crystallization of the OPW with LDPE.¹⁸

Spectral analysis of samples

The UV-vis transmittance spectra of the pure PE and composite films are shown in Figure 3. The

transparency of PE-OPW-TiO₂ composite film is close to that of the pure PE in long wavelength range [Fig. 3(a)]. It descends under the range of 400 nm compared with the pure film, which is owing to the absorption UV radiation of TiO₂ nanoparticles. However, the films exhibit the different changes in transmittance after UV irradiation. The transparency of pure PE film had few changes [Fig. 3(b)] and that of PE-TiO₂ composite film slowly decreased with irradiation time [Fig. 3(c)]. That of PE-OPW-TiO₂ composite film had rapidly decreased [Fig. 3(d)]. The PE-OPW-TiO₂ film became white and had a low light transparency after UV irradiation for 20 h. These phenomena proved that the structure of composite film had been destroyed and the film had already begun to degrade.

Weight loss analysis of the films under the different irradiation

Figure 4 displays the photoinduced weight loss curves of the polymer films during UV irradiation in the ambient air. The weight loss rate of PE-OPW-TiO₂ composite film steadily increased with irradiation time in the ambient air. The weight loss rate of PE-OPW-TiO₂ film also increased with the

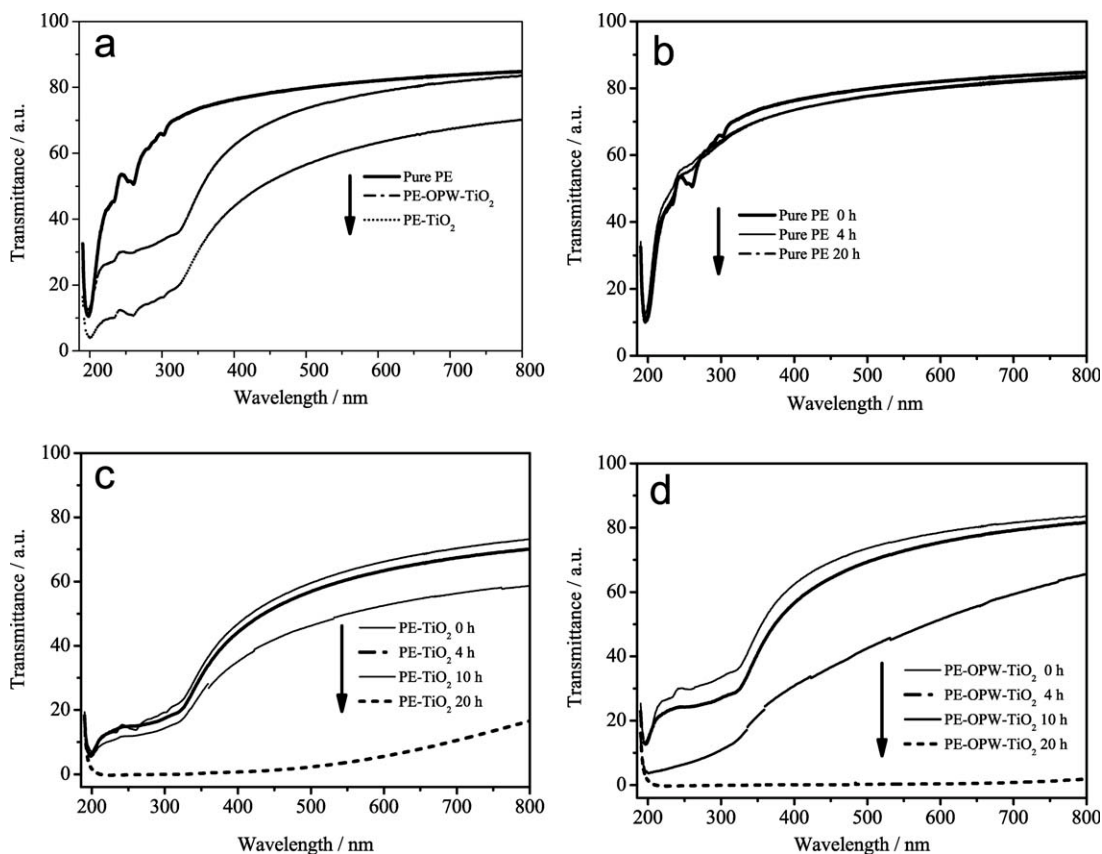


Figure 3 The UV-vis transmittance spectra of the pure PE and composite films. (a) The comparison of three kinds of films before irradiation, (b) PE film before and after irradiation, (c) PE-TiO₂ (1 wt %) film before and after irradiation, and (d) PE-OPW-TiO₂ (1 wt %) film before and after irradiation.

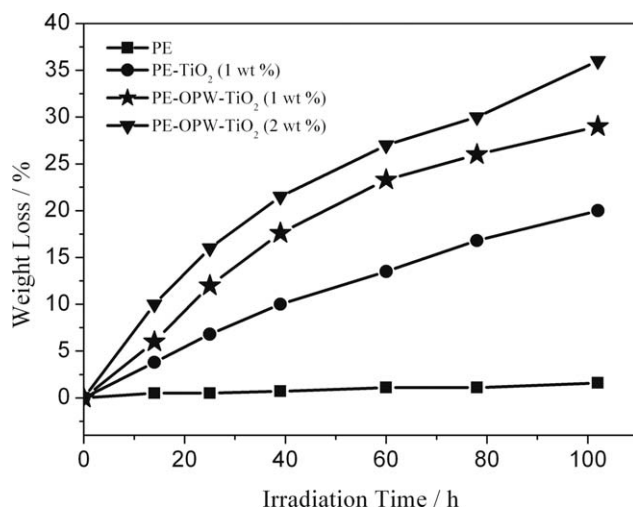


Figure 4 Weight loss curves of the polymer films during UV irradiation in the air (light intensity: 1 mW cm^{-2}).

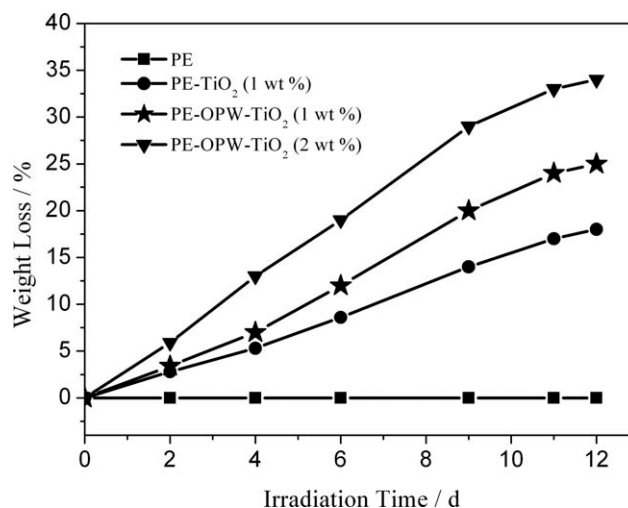


Figure 5 Weight loss curves of different films under the sunlight exposure.

increasing of the TiO_2 content in the film. It led to 29% (TiO_2 : 1 wt %) and 36% (TiO_2 : 2 wt %) reduction, respectively, after 102 h irradiation with the UV light intensity of 1 mW cm^{-2} . The PE- TiO_2 film showed 20% weight loss (TiO_2 : 1 wt %) and the pure PE film showed negligible weight losses under the identical experimental conditions. The weight loss rate of PE-OPW- TiO_2 composite film was much higher than that of PE- TiO_2 film and the pure film, which demonstrated that OPW remarkably enhanced the photocatalytic activity of TiO_2 nanoparticles in PE.

Figure 5 exhibits the weight loss curves of different films under the solar light exposure. The weight loss rate of PE-OPW- TiO_2 composite film is also much higher than that of PE- TiO_2 film and the pure film. The weight of pure PE film had almost no change under solar exposure. This result agrees with the fact that the pure PE is nondegradable in natural environment. As the weight loss of the PE-OPW- TiO_2 composite film achieved the total 25% (TiO_2 : 1 wt %) and 34% (TiO_2 : 2 wt %) after 12 days irradiation. It is worth mentioning here, the solar irradiation

experiment is carried out in a quartz vessel, which is isolated from the water and rain, fog and dew, etc., natural occurrences. It is widely accepted that water vapor presence improves the photodegradation efficiency of the nanocomposite film.^{23,24} Thus, it may be safe to appreciate that the PE-OPW- TiO_2 composite film could decompose more rapidly when it is exposed in the natural environment.

The surface morphology of the films after photodegradation

SEM analyses were carried out to examine the surface morphology of the irradiated films. Figure 6(a–c) shows the surface images of the pure PE, PE- TiO_2 (1 wt %), PE-OPW- TiO_2 (1 wt %) film after UV irradiation for 200 h. The surface of the pure film presents only a few cracks and the PE- TiO_2 film displays some cavities from the degradation. In contrast, the surface of the PE-OPW- TiO_2 film has been severely destroyed. A large amount of holes get interconnected and the whole film is chalking. The results demonstrate clearly the degradation efficiency of PE-OPW-

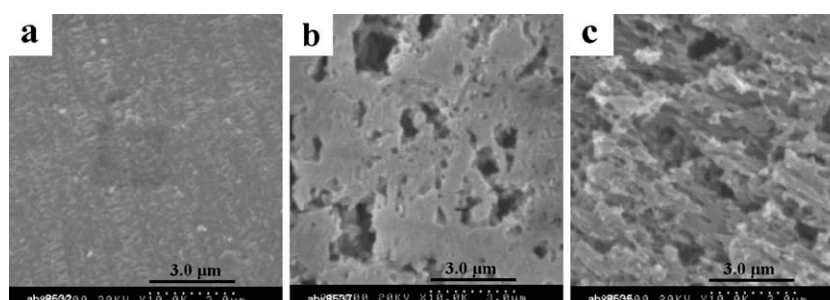


Figure 6 The SEM images of the polymer films after irradiation for 200 h with 1 mW cm^{-2} UV light intensity. (a) The pure PE film, (b) the PE- TiO_2 film, and (c) the PE-OPW- TiO_2 film.

biological degradation is possible to occur to further decompose the remnant of the plastic film. The PE-OPW-TiO₂ composite film is considered a hopeful new environment-friendly polymer material. The degradation method investigated in this work is a solid support for the application of this kind of polymer materials.

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