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Journal of Photochemistry and Photobiology A: Chemistry 143 (2001) 221–228

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Solid-phase photocatalytic degradation of PVC–TiO_2 polymer composites

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Received 19 April 2001; received in revised form 19 June 2001; accepted 20 June 2001

Abstract

The solid-phase photocatalytic degradation of poly(vinyl chloride) (PVC)–TiO_2 composite films was investigated under the ambient air in order to assess the feasibility of developing photodegradable polymers. The photodegradation of the composite films was compared with that of pure PVC films through performing weight loss monitoring, scanning electron microscopic (SEM) analysis, gel permeation chromatography (GPC), FT-IR and UV–VIS spectroscopy, and X-ray photoelectron spectroscopy (XPS). TiO_2-embedded PVC showed highly enhanced photodegradation. Irradiating the composite film for 300 h under air reduced its average molecular weight by two-thirds and weight by 27% while the irradiation under nitrogen atmosphere induced little degradation. The photocatalytic degradation of the composite film accompanied the increase in the FT-IR carbonyl peak intensity, the evolution of CO_2 and H_2O, and the *whitening* due to the visible light scattering from growing cavities. XPS analysis of the composite film showed that the surface concentration of oxygen increased while that of chlorine decreased with irradiation. The SEM images of the irradiated composite films showed the development of cavities around the imbedded TiO_2 particles and implied that active oxygen species which were photogenerated on TiO_2 surface desorb and diffuse across a few micrometers to react with the polymer matrix. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Titanium dioxide; PVC photodegradation; Solid-phase photocatalytic reaction; Polymer–TiO_2 composite

1. Introduction

Massive amount of poly(vinyl chloride) (PVC) is produced globally (23 million t per year) and consumed as various commodities [1]. Disposal of wasted PVC through incineration causes serious environmental problems due to the toxic by-product formation such as dioxins and corrosive acids [1–3]. The thermal treatment of PVC requires high temperature and cost while the PVC recycling has little economic benefits.

The PVC–TiO_2 composite represents a unique case of the photocatalytic degradation of solid wastes while most of photocatalytic remediation systems have dealt with aquatic or air pollutants [4–6]. The development of polymer products that degrade under ambient sunlight irradiation with little formation of toxic by-products could lead to an eco-friendly disposal of polymer wastes. Previous studies on the photocatalytic degradation of polymers mainly dealt with liquid-phase reactions. Hidaka et al. have studied the photocatalytic degradation of PVC particles [7] in aqueous TiO_2 suspensions or TiO_2-blended PVC films in water [8]. However, the photocatalytic degradation of the polymer composites needs to be further studied under the ambient air condition since the polymer wastes are usually exposed to the sunlight in the open air.

It is interesting to note that the solid-phase photocatalytic degradation of polymer–TiO_2 composites has been known and studied for quite a long time in relation to the *chalking* phenomenon in the pigmented paint/polymer systems [9]. Several studies on photodegradation of TiO_2-blended polymer in air such as polyethylene [10] and PVC [11,12] have been carried out. However, their main interests focused on inhibiting the photocatalytic activity of TiO_2 in relation to weathering of the polymer composites. The present study tried to take advantage of such effects on the contrary. Unlike their liquid- or gas-phase counterpart, the solid-phase photocatalytic reactions have been far less studied and little is known for their mechanistic pathways. It needs to be understood how they initiate and propagate within the solid matrix for the development of efficient photodegradable polymer composites.

In this study, PVC films embedded with TiO_2 particles (0–2 wt.%) were prepared and their photocatalytic degradation under the ambient air or nitrogen atmosphere was investigated. Mechanistic aspects of the solid-phase

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PII: S1010-6030(01)00499-3

photocatalytic reaction, photodegradation product formation, and their implication for developing photodegradable polymer composites were discussed.

2. Experimental

2.1. Materials

Powder of PVC [–$(CH_2CHCl)_n$–] was supplied by LG Chemical Co. The average molecular weight (M_w) was determined by gel permeation chromatography (GPC) to be around 200,000 with the polydispersity index (M_w/M_n) of 1.7. The PVC powder was free from additives such as plasticizers. The TiO_2 photocatalyst was Degussa P25, whose primary particles ranged in 20–40 nm diameter with mixed crystalline phases [13]. The transmission electron micrographs (TEM) of P25 showed that the primary particles were highly aggregated up to the size of 0.1–0.5 μm.

2.2. Preparation of PVC–TiO_2 composite films

PVC–TiO_2 composite films were cast as follows. The polymer stock solution was prepared by dissolving 50 g of PVC in 1 l of tetrahydrofuran (THF) under vigorous stirring for 24 h. In order to minimize the size of TiO_2 aggregates that were embedded in the PVC matrix, the smaller fraction of TiO_2 aggregate was separated by a centrifugal method. An aqueous suspension of 0.1 g TiO_2/l was sonicated for 30 min and centrifuged twice at 4000 rpm for 10 min. The resulting supernatant was collected and evaporated to dryness in a rotary evaporator (Büchi Rotavapor R-114) to get less-aggregated TiO_2 powder. In a typical preparation, 75 mg of the centrifuged TiO_2 powder was suspended in 100 ml of PVC stock solution to give 1.5 wt.% of TiO_2 content with respect to the total mass of PVC. An aliquot of 3 ml PVC–TiO_2 solution was spread on a slide glass (75 mm × 50 mm) and dried for 2 days. The thickness of the resulting PVC–TiO_2 composite film was measured to be 25–30 μm by a micrometer. The thickness estimated from the weight of the composite film and the PVC density agreed with the above values, which implied that the cast film had little porosity. The transmittance of the PVC–TiO_2 composite film was typically around 80% at $\lambda = 600$ nm.

2.3. Photolysis and characterization of the PVC–TiO_2 composite film

All the films were irradiated under a 200 W mercury lamp. In order to simulate solar light conditions, incident UV light onto samples passed through a Pyrex cover that cut-off the wavelength shorter than 300 nm. The distance between the sample and the lamp was 22 cm. The light flux onto the sample was measured to be 1.5 mW/cm^2 ($300\,\mathrm{nm} < \lambda < 400\,\mathrm{nm}$) using a powermeter (Newport 1815-C with a 818-UV silicon diode detector). The photolysis proceeded under ambient air in a lamp-housing box (35 cm × 30 cm × 35 cm) where the temperature during irradiation was maintained around 45°C. Each photolysis experiment used a triplicate set of samples. A typical size of the film sample was around 2.3 cm^2. In order to investigate the effect of oxygen the photolysis was also carried out under nitrogen atmosphere. The PVC sample was placed in a small cell with a glass window. The cell volume was filled with N_2 under continuous purging and sealed from the ambient air before starting UV irradiation.

Each sample was weighed before and after irradiation to monitor the weight loss as a result of photodegradation. A UV–VIS spectrophotometer (Shimadzu UV-2401) and a FT-IR spectrometer (Bomem MB104) monitored the spectral transmittance or absorbance of the composite and pure PVC films before and after irradiation. The irradiated sample surfaces were examined by X-ray photoelectron spectroscopy (XPS: Kratos XSAM 800pci). The surface morphological images of the composite film were taken by using a field emission scanning electron microscope (FE-SEM: JEOL JSM 6330F) with the pre-treatment of Pt deposition. A 0.5-L IR gas cell (Gemini) with a pathlength of 0.6 m was used to monitor the evolution of gaseous products from the degrading composite film. The average M_w of the PVC samples was determined by GPC (Polymer Lab, PL-GPC210) equipped with a PL mixed C (×2) column and a refractive index detector. Polystyrene standards were used for the M_w calibration. For GPC analysis, all the PVC samples were dissolved in THF, then filtered through a 0.2 μm PTFE syringe filter in order to remove TiO_2 particles.

3. Results and discussion

3.1. Light absorption and penetration in the PVC–TiO_2 composite film

The TiO_2 particle in the polymer matrix can absorb or scatter the incident light with extinguishing the transmitting light. The incident light intensity, I_i can be expressed as

$$I_i = I_t + I_a + I_s + I_r = I_t + I_\varepsilon + I_r \quad (1)$$

where I_t is the transmitted light, I_a the absorbed light by TiO_2, I_s the scattered light by TiO_2, I_r the reflected light from the film surface, and $I_\varepsilon = I_a + I_s$ is the extinguished light. Fig. 1a shows the apparent absorption spectra of the composite films with varying TiO_2 contents. The apparent absorbance (A_{app}) includes the components from the light absorption (I_a), scattering (I_s), and reflection (I_r). As the TiO_2 content increased, a band-gap transition of TiO_2 appeared in the absorption spectrum with increasing scattering background in the visible region.

Light penetration into the composite film is a function of the concentration, dispersity and size of TiO_2 particles in the

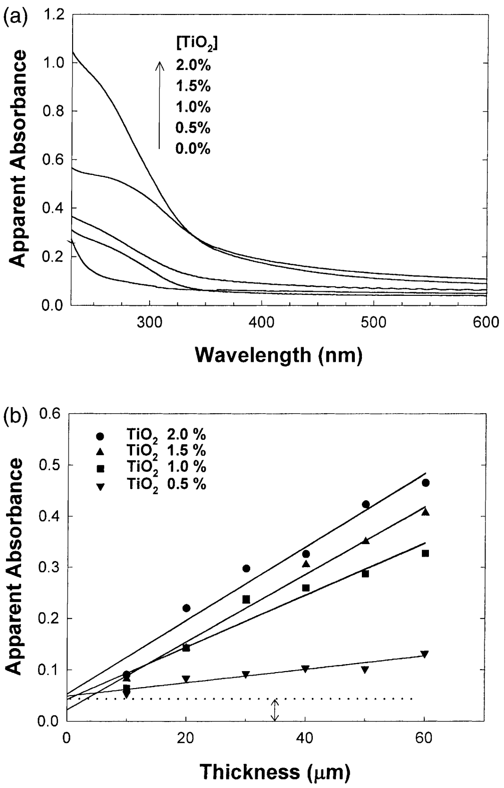

Fig. 1. (a) UV–VIS absorption spectra of the PVC–TiO_2 composite films with varying TiO_2 contents; (b) apparent absorbance (A_{app}) of the composite films at $\lambda = 350$ nm as a function of the film thickness.

polymer matrix and the thickness of the film. Fig. 1b plots A_{app} of the composite film at $\lambda = 350$ nm as a function of the film thickness. The transmitting light intensity, I_t can be related to the thickness, d as follows:

$$I_t(\lambda) = [1 - R(\lambda)]I_i(\lambda)\,e^{-\varepsilon_\lambda d} \tag{2}$$

where R is a reflectance, and ε, an extinction coefficient of the composite film. From Eq. (2)

$$\begin{aligned} A_{app}(\lambda) &= -\frac{1}{2.3}\ln\left[\frac{I_t(\lambda)}{I_i(\lambda)}\right] \\ &= -\frac{1}{2.3}\ln[1 - R(\lambda)] + \frac{\varepsilon_\lambda d}{2.3} \end{aligned} \tag{3}$$

Therefore, a plot of A_{app} versus d gives a straight line with a slope of $\varepsilon_\lambda/2.3$ (Fig. 1b). The ε_{350} values obtained from the slope were 30, 117, 152 and 166 cm^{-1} for the PVC film loaded with 0.5, 1.0, 1.5, and 2.0 wt.% TiO_2, respectively. The reflectance, R can be obtained from the intercept that was indicated as a dotted line in Fig. 1b. The R values were estimated to be 0.09 ± 0.03 with little dependence on the TiO_2 content. The reciprocal of ε_λ corresponds to a light penetration depth, l.

$$l = \frac{1}{\varepsilon_\lambda} \tag{4}$$

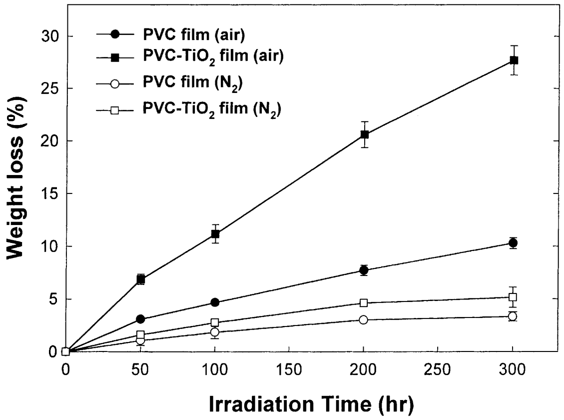

Fig. 2. Weight loss of the pure PVC or PVC–TiO_2 (1.5 wt.%) composite films during irradiation under air or nitrogen atmosphere.

At the TiO_2 concentration of 1.5 wt.% in PVC, $\varepsilon_{350} = 152\,cm^{-1}$ and $l_{350} = 66\,\mu m$, which is about twice as large as the film thickness (~30 μm). Therefore, the active UV light that can excite TiO_2 is able to penetrate through the whole composite film with 1.5 wt.% TiO_2.

3.2. Photocatalytic degradation of the composite PVC films

Fig. 2 displays the photoinduced weight loss of the polymer films under air or nitrogen atmosphere. The weight loss rates were much higher for the PVC–TiO_2 than the PVC film, and under air than nitrogen. The weight of the PVC–TiO_2 film steadily decreased with irradiation under air and led to the total 27% reduction in 300 h while the PVC film showed only 10% weight loss under the identical experimental condition. The presence of O_2 was essential for the efficient photolytic degradation of PVC. The photocatalytic degradation of the PVC matrix in the solid-phase seems to be initiated by active oxygen species (e.g. O_2^-, $HO_2^\bullet$, $HO^\bullet$) that are generated from O_2 reacting with conduction band (CB) electrons like many other liquid- or gas-phase photocatalytic reactions [4–6]. The fact that the weight loss of the PVC films under nitrogen did not proceed any further after 200 h irradiation implied that the trace oxygen that was dissolved or trapped in the film was depleted at this stage.

The above weight loss data imply that some degradation products volatilized into the air. The volatile products that evolved from the degrading PVC film during UV irradiation were monitored by using a FT-IR gas cell. Fig. 3 shows that the main gaseous products were CO_2 and H_2O. The rate of CO_2 evolution, which was displayed in the inset, was faster in the early stage and gradually decelerated, which was successfully described by a first-order kinetics (solid-line fit). The apparent first-order kinetics of CO_2 evolution implies that the polymer chains in direct contact with the TiO_2 surface were depleted with irradiation. The fast

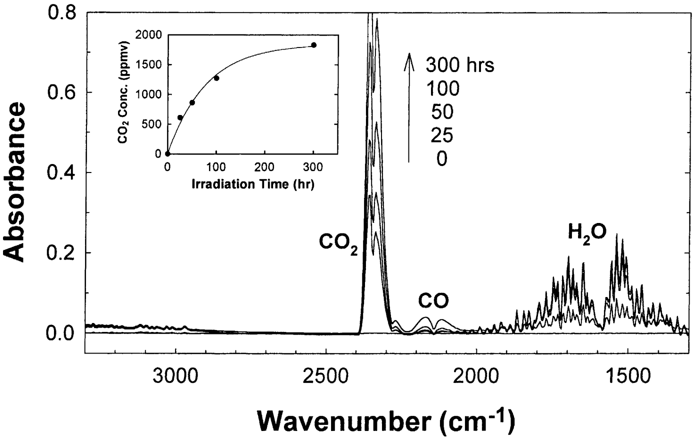

Fig. 3. FT-IR spectra of volatile products evolved from the irradiated PVC–TiO_2 (1.5 wt.%) film under air. The inset shows the evolved CO_2 concentration as a function of the irradiation time.

CO_2 evolution at the initial stage is ascribed to the reaction of photooxidants generated on TiO_2 surface with adjacent polymer chains. As the polymer matrix surrounding TiO_2 particles is etched away, further oxidation should depend on the slow desorption process of photooxidants with showing a decelerated CO_2 evolution rate. The evidence for the desorbing photogenerated oxidants is shown in Fig. 5 and discussed in the later section. The fitted first-order constant of $0.0127\,h^{-1}$ implies that most of polymer chains surrounding TiO_2 particles were depleted within 80 h in this case. A small amount of CO and trace hydrocarbons that were evidenced by the C–H stretching peaks around $3000\,cm^{-1}$ were also observed. No sign of HCl production could be seen while it is a well-known main product of thermal and direct photolytic degradation of PVC [1,14].

The photocatalytic degradation of the PVC films was also followed by GPC. Fig. 4 shows that M_w of the composite film steadily decreased with irradiation time. Most of the higher M_w fraction that eluted in 13–15 min disappeared as a result of the photodegradation and the average M_w reduced to a third after 300 h irradiation. A similar analysis for the irradiated pure PVC films (data not shown) showed that M_w reduced by half in 300 h. This indicates that the bond scission in the backbone of the polymer is ascribed to both the direct photolytic and the photocatalytic reaction.

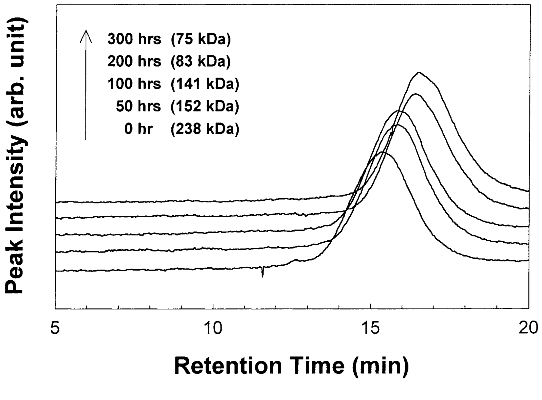

Fig. 4. Gel permeation chromatograms of the PVC–TiO_2 (1.5 wt.%) film that were photodegraded under air. Numbers in parentheses are the average M_w of the PVC samples. The chromatograms are sequentially shifted upward for clarity.

In order to examine the surface morphology of the irradiated polymer films, scanning electron microscopic (SEM) analysis was carried out. Fig. 5a and d show the surface images of the PVC–TiO_2 composite films that were irradiated for 0, 25, 50 and 100 h under air, respectively. The SEM images reveal that the degradation of the PVC matrix started from the PVC–TiO_2 interface and led to the formation of cavities around TiO_2 particle aggregates. The individual cavity got highly inter-connected with irradiation and coalesced to a size of $\sim 10\,\mu m$. This is similar to the previous observation [8], which reported the formation of holes in an illuminated TiO_2-blended PVC film in water. On the other hand, only 10–20 nm sized holes formed on the irradiated surface of the pure PVC films (Fig. 5h). While the number of the holes increased with irradiation time (the hole number density: 29, 46, and $71\,\mu m^{-2}$ for 25, 50, and 100 h irradiated samples, respectively), the hole diameter remained constant. In accordance with the weight loss data shown in Fig. 2, the surface of the PVC–TiO_2 film that was irradiated under nitrogen atmosphere showed little sign of degradation (Fig. 5g), which confirmed the necessity of oxygen for the solid-phase photocatalytic reaction. Since the oxygen concentration in the PVC matrix is highly limited except for the presence of micro-air bubbles or absorbed oxygen in the film, the photocatalytic degradation of PVC seems to initiate in the oxygen-rich surface region and erode into the bulk. The backside of the irradiated composite film (Fig. 5f) showed much less degradation. Although the penetrating light intensity into the bottom of the composite film ($30\,\mu m$ thickness) decreased by only $\sim 40\%$ (Eq. (2)) at the initial stage, the growing cavities scattered out more incident light

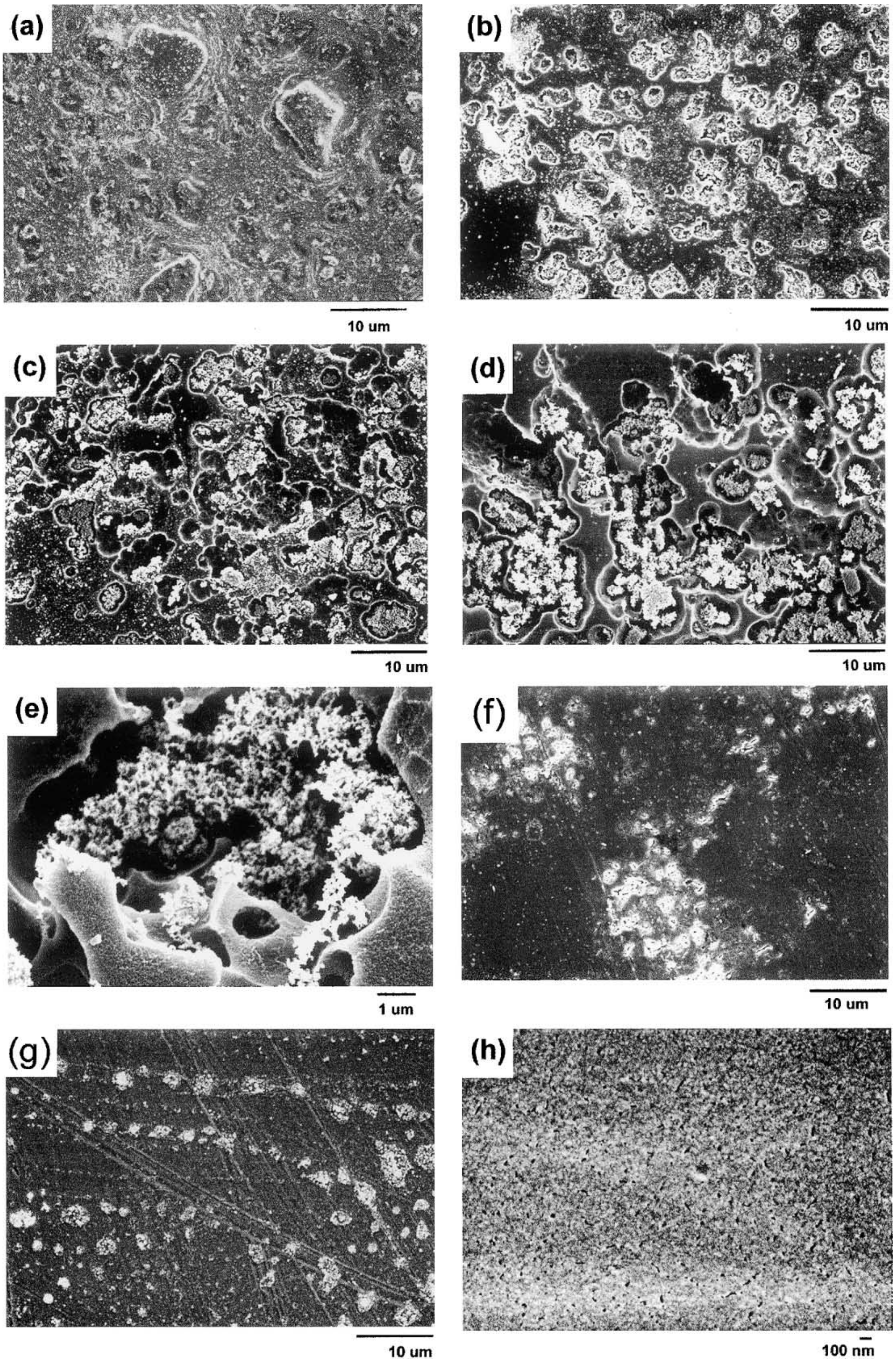

Fig. 5. SEM images of the pure PVC or PVC–TiO_2 (1.5 wt.%) composite films. (a) PVC–TiO_2 film before irradiation; (b) PVC–TiO_2 film, 25 h irradiated; (c) PVC–TiO_2 film, 50 h irradiated; (d) PVC–TiO_2 film, 100 h irradiated; (e) PVC–TiO_2 film, 100 h irradiated (enlarged view); (f) backside view of the PVC–TiO_2 film, 100 h irradiated; (g) PVC–TiO_2 film, 100 h irradiated under N_2; (h) pure PVC film, 100 h irradiated.

as the degradation proceeded (vide infra). Therefore, the backside of the film was protected from the irradiation with showing less degree of degradation.

It is also noteworthy that the SEM images imply that the active oxygen species generated on TiO_2 surface desorb and diffuse through a finite distance to etch out the polymer matrix. Otherwise, the photocatalytic degradation would have stopped at an earlier stage (e.g. Fig. 5b) where the crevice developed between the TiO_2 surface and the polymer matrix inhibited the oxidizing species from directly contacting the polymer. As for PVC whose glass transition temperature (81°C) is well above room temperature [15], the mobility of the polymer chains is restricted. The enlarged view (Fig. 5e) of a cavity around TiO_2 particles clearly shows that the cavity boundary is well separated by 1–2 μm from the particle boundary. While it is often disputed whether the surface-generated reactive oxygen radicals such as $^{\bullet}OH$ strictly remain on the surface or diffuse from the surface [16], the above images support that the oxidizing radicals desorb from the TiO_2 surface in the present system. This argument is also consistent with a recent report [17], which observed that the active oxygen species generated on illuminated TiO_2 diffused away from the surface into the gas-phase.

3.3. Spectroscopic characterizations of the irradiated PVC

Since the cavities formed as a result of the photocatalytic degradation scattered visible light, *whitening* of the irradiated composite film was observed. The transmittance of the composite film gradually decreased with irradiation time as shown in Fig. 6a. However, the transmittance of the pure PVC film (Fig. 6b) was less affected by UV irradiation. The little change in the visible region reflects that the holes formed in the irradiated PVC film (see Fig. 5h) are too small to scatter out the visible light. The transmittance reduction in 200–300 nm region implies that some UV-absorbing chromophores such as oxygen-containing functionalities and double bonds were introduced as a result of photoreactions.

The functional groups in PVC were monitored by an IR spectroscopic method. Fig. 7 shows the change in FT-IR spectra of the (a) PVC–TiO_2 and (b) PVC films with irradiation time. There are three main peak regions in their FT-IR spectra: 3400–3300, 3000–2900, and 1770–1720 cm^{-1} centered peaks for the surface hydroxyl (>OH) groups on TiO_2, C–H bonds in PVC, and the carbonyl groups (>C=O), respectively. Both the composite and pure PVC film contained the *impurity* carbonyl moieties even before irradiation [1]. The carbonyl peak intensity grew with irradiation for both cases. Under nitrogen atmosphere, the carbonyl peak increased for the first 5 h irradiation probably due to the presence of trace oxygen trapped in the film and showed little change for further irradiation (data not shown). The appearance of the carbonyl groups in the photooxidized PVC has been well documented [1,9,18,19].

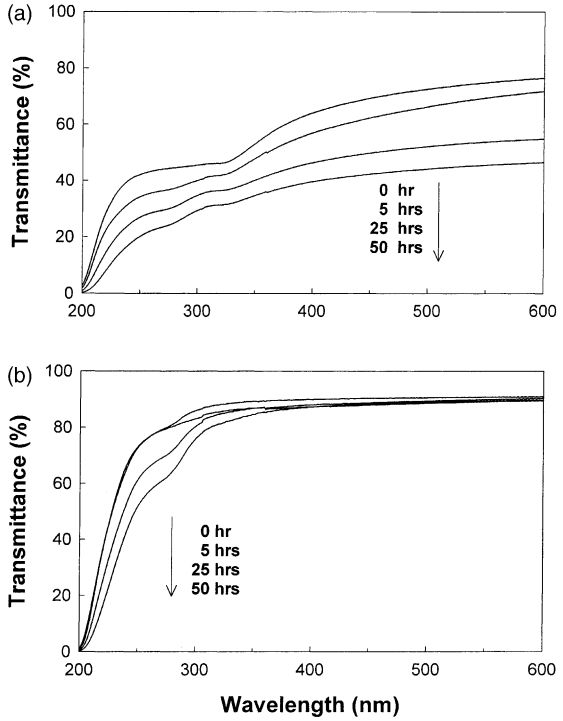

Fig. 6. UV–VIS transmittance spectra of (a) the irradiated PVC–TiO_2 (1.5 wt.%) film and (b) the irradiated pure PVC film.

The surface hydroxyl groups on TiO_2 react with valence band (VB) holes to generate hydroxyl radicals, which are responsible for most of the oxidizing power of TiO_2 photocatalysts. In aqueous suspensions or in contact with water vapors in the gas-phase, the surface OH group density remains unchanged during irradiation since the depleting OH groups are continuously replenished. On the other hand, in the present case where TiO_2 particles were buried in the polymer matrix, the surface OH groups were gradually depleted with irradiation as shown in Fig. 7a. Although the surface OH groups were almost completely depleted after 50 h irradiation, the photocatalytic degradation of PVC matrix steadily continued up to 300 h as shown in Figs. 2–5. Other sources of reactive oxygen radicals than the surface hydroxyl groups seem to take part in the photocatalytic degradation mechanism. The O_2 molecule reacting with CB electrons to generate reactive oxygen species is the most probable candidate. The C–H peak intensity in the PVC–TiO_2 film showed a slight decrease with irradiation while that in the PVC film little changed. This indicated that the C–H bonds cleaved in the PVC–TiO_2 film but remained intact in the PVC film under irradiation.

The XPS analysis of the irradiated film surface also confirmed that oxygen species were incorporated with irradiation. Table 1 summarizes the relative surface atomic concentrations of C, O, Cl, and Ti elements on the irradiated PVC–TiO_2 film surfaces. The initial surface showed the presence of *impurity* oxygen at the binding energy of 532 eV, which is assigned to typical oxygen functional groups such

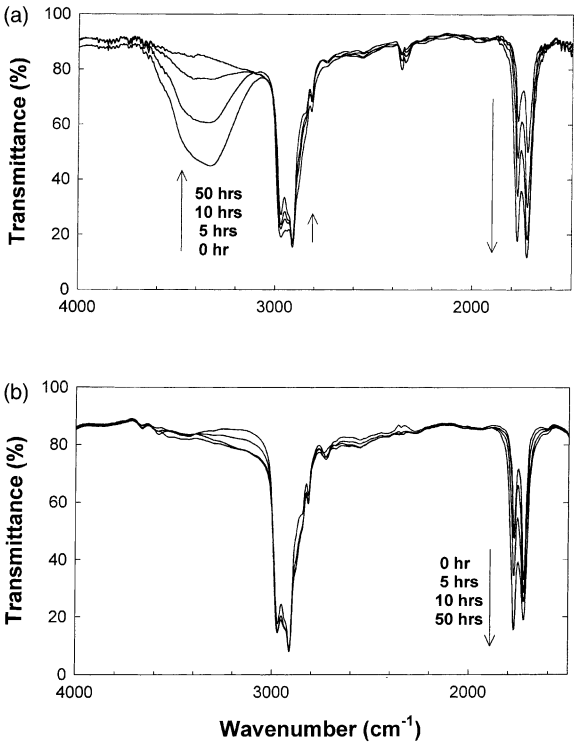

Fig. 7. FT-IR spectra of (a) the irradiated PVC–TiO_2 (1.5 wt.%) film and (b) the irradiated pure PVC film.

Table 1
XPS analysis on the relative surface atomic concentration (%) in the irradiated PVC–TiO_2 films

	Irradiated			
	0 h	50 h	100 h	300 h
C (1s)	70.1	55.7	53.2	50.9
O (1s)	4.1	23.1	25.6	29.0
Cl (2p)	25.7	17.1	15.9	14.4
Ti (2p)	0.1	4.1	5.3	5.8
C/Cl	2.73	3.26	3.35	3.53
(O–2Ti)/C	0.056	0.27	0.28	0.34

as carbonyl and alcohols [20]. The oxygen to carbon ratio in PVC (O–2Ti)/C, steadily increased with irradiation although most of oxygen was incorporated in the initial stage. The C/Cl ratio also increased with irradiation, which implied that the surface chlorine was preferentially removed than the carbon. The initial C/Cl ratio (2.73), which was higher than the stoichiometric ratio of 2.0, was ascribed to the surface impurity carbon since the present XPS analysis did not perform the pre-treatment of sputter cleaning.

3.4. Solid-phase photocatalytic degradation mechanism in PVC–TiO_2 composite films

The photolytic degradation of PVC has been extensively studied [1,9,19]. Although PVC contains only C–H, C–C, and C–Cl bonds which do not absorb light with $\lambda > 220$ nm, its photolytic degradation under longer wavelength radiation has been well known. This study also confirmed the photolytic degradation of PVC under Pyrex-filtered ($\lambda > 300$ nm) irradiation. Despite the mechanistic complexities involved in the photoinitiation step, it is generally accepted that the photolysis of PVC is initiated by chromophoric impurities such as carbonyl and hydroperoxide groups, unsaturated double bonds, and solvent residues [1]. The presence of oxygen functionalities in the pure PVC film was confirmed from the above FT-IR and XPS analysis. Therefore, the direct photolysis of PVC starts from the cleavage of C–Cl bond that is adjacent to the impurity chromophoric group and strongly depends on its impurity characteristics. Detailed mechanistic discussion on the direct photolysis of PVC is referred to other literatures [1,9,19].

However, the initiation in the photocatalytic degradation of PVC is quite different. Since the degradation initiates indirectly through oxidative radicals generated on TiO_2, the presence of chromophoric impurities is not necessary. The O_2 molecules seem to play a central role in both initiating and propagating the photocatalytic degradation reactions in PVC. The possible photoinduced reaction steps in the PVC–TiO_2 film are listed in Table 2. TiO_2 particles that absorb light with energy higher than 3.2 eV generate electron/hole pairs in the CB and VB, respectively (T1). Subsequent reactions with O_2 lead to the formation of several active oxygen species such as the superoxide anion (T2), singlet oxygen (T3), hydroperoxyl radical (T4), and hydroxyl radical (T6, T7). Although we do not know what the main oxidizing species in this solid-phase system is, it is the active oxygen species that initiate the degradation

Table 2
Photoinduced reaction steps in the PVC–TiO_2 film

T1	$TiO_2 + h\nu \rightarrow TiO_2^* (e_{cb}^- + h_{vb}^+)$
T2	$e_{cb}^- + O_2 \rightarrow O_2^{-}$
T3	$TiO_2^* + O_2 \rightarrow {}^1O_2$
T4	$O_2^{-} + H_2O\,(g) \rightarrow {}^{\bullet}O_2H + OH^-$
T5	$2{}^{\bullet}O_2H \rightarrow H_2O_2 + O_2$
T6	$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH$
T7	$h_{vb}^+ + H_2O\,(ad) \rightarrow {}^{\bullet}OH$
T8	${}^{\bullet}OH\,(ad) \rightarrow {}^{\bullet}OH\,(g)$
T9	$–(CH_2CHCl)– + {}^{\bullet}OH\,(g) \rightarrow –({}^{\bullet}CHCHCl)– + H_2O$
T10	$–(CH_2CHCl)– + {}^{\bullet}O_2H\,(g) \rightarrow –({}^{\bullet}CHCHCl)– + H_2O_2$
T11	$–CH{=}CH–CH_2CHCl– + {}^1O_2 \rightarrow –(HOO)CH–CH{=}CHCHCl–$
T12	$–({}^{\bullet}CHCHCl)– + O_2 \rightarrow –(CH(OO^{\bullet})CHCl)–$
T13	$–(CH(OO^{\bullet})CHCl)– + –(CH_2CHCl)– \rightarrow –(CH(OOH)CHCl)– + –({}^{\bullet}CHCHCl)–$
T14	$–(CH(OOH)CHCl)– + h\nu \rightarrow –(CH(O^{\bullet})CHCl)– + {}^{\bullet}OH$
T15	$–(CH(O^{\bullet})CHCl)– \rightarrow –(CH_2CHCl)CHO + {}^{\bullet}CHCl(CH_2CHCl)–$
T16	${}^{\bullet}CHCl(CH_2CHCl)– + O_2 \rightarrow\rightarrow$ successive cleavage with CO_2 evolution

reactions by attacking neighboring polymer chains (T9–T11). The degradation process spatially extends into the polymer matrix through the diffusion of the active oxygen species (e.g. T8). Once the carbon-centered radicals are introduced in the polymer chain, their successive reactions lead to the chain cleavage with the oxygen incorporation and CO_2 evolution (T12–T16).

4. Conclusions

This study reveals that the photocatalytic degradation is distinguished from the direct photolytic degradation of PVC in several aspects. Firstly, the photocatalytic degradation localized on the TiO_2–PVC interface and grew cavities around particles while the direct photolytic centers were uniformly distributed in the PVC matrix. As a result, the PVC–TiO_2 film quickly whitened with visible light scattering. Secondly, although both the photocatalytic and photolytic degradation induced the chain cleavage (i.e. M_w reduction) and the oxygen functionality incorporation, the photocatalytic degradation was much faster in the weight loss rate. Lastly, the degradation products seem to be different since the main direct photolytic product, HCl did not form from the photodegrading PVC–TiO_2 film. According to the XPS analysis that showed the surface chlorine content gradually decreased with irradiation, there must be other chlorine-containing volatile products. Since this study is by no means complete in the product analysis, further study should deal with the identification and quantification of the PVC decomposition products.

The present study demonstrates that the polymer–TiO_2 composite has a potential viability to be used as a photodegradable product. The photocatalytic degradation in the solid polymer matrix proceeded much faster than the direct photolytic degradation under air. In general, the photocatalytic degradation of PVC–TiO_2 in air showed the similar behavior to that in water [8]. On the other hand, the uniform dispersion of nano-sized TiO_2 particles in the polymer matrix needs to be achieved for commercial applications. This study is not successful in this respect: the TiO_2 particles ($d \sim 30$ nm) were incorporated into the polymer matrix in huge agglomerates whose size extended up to a few micrometers. The micrometer-sized agglomerates reduce the photodegradation efficiency significantly in two ways: decreasing the PVC–TiO_2 interface area and inducing a rapid *whitening*. The photoinduced *whitening* quickly shortens the light penetration depth into the composite film, which hinders further photodegradation. Nano-particles generate nano-cavities which scatter out little incoming light. If each 5 nm TiO_2 particle in a well dispersed state could etch out a 50 nm radius cavity around it, only 0.02 wt.% TiO_2 in PVC would be enough to accomplish the photodegradation of the whole composite film. Further studies are called for to resolve this issue.

Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-99–042-E00109).

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