

Photocatalyzed Degradation of Polymers in Aqueous Semiconductor Suspensions. 3. Photooxidation of a Solid Polymer: TiO₂-Blended Poly(vinyl chloride) Film

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The photooxidative degradation of a TiO₂-blended poly(vinyl chloride) (PVC) film and other PVC specimens was carried out under UV light and under solar exposure to test the feasibility that such polymeric materials can be mineralized. The effects of the degree of polymerization and the presence of a plasticizer (*o*-dioctyl phthalate; DOP) in the PVC on the photooxidation process were examined by scanning electron microscopy (SEM), by X-ray photoelectron spectroscopy (XPS), by gel permeation chromatography, and by gas chromatography for CO₂ evolution. The TiO₂-blended PVC thin film is more easily decomposed than PVC particles (or film) alone in a TiO₂ particulate dispersion. The collapse phenomena of polymeric films are closely dependent on the photodegradation rate of DOP in the PVC film. Ames mutagenic assays for the photodegraded solution in aqueous TiO₂/PVC dispersions showed a slight mutagenic activity in TA98 without S9 mix for products formed during the photodegradative oxidation.

Introduction

The evolution of strongly carcinogenic dioxins into the atmosphere from the incineration of such plastics as poly(vinyl chloride) (PVC), contained in most municipal refuse and dust particulates, is an environmental issue of major concern. Combustion of plastics with residence times greater than 2 s at temperatures above 800 °C in a large-scale industrial incinerator to dispose of large quantities of PVC materials produces hydrogen chloride gas (HCl) when the plastic is PVC; no dioxins are formed. However, when the combustion is carried out at temperatures (ca. 300 °C) that are typical of small municipal incinerators to dispose of domestic refuse, considerable quantities of dioxins are evolved into the atmosphere and/or contained in the fly ash. Air pollution and ground contamination in the vicinity of

such small municipal facilities have become a societal environmental issue necessitating resolution.

The photocatalytic method represents an attractive and efficient decomposition technique for PVC plastics by blending TiO₂ particles into the PVC solid polymer. Such TiO₂-blended PVC plastics should be degradable in open-air under solar exposure and moisture (or rain) after their domestic or industrial utilization for definite periods of time and where recycling may neither be available nor economically viable. Photocatalytic degradative methods for disposal of PVC plastics generate no dioxins, and the technique is a low-temperature process with evident economic advantages.

The solid/solid photoreaction of PVC pellets at illuminated TiO₂/water interfaces was the object of an earlier paper (1). Although few accounts of the photodegradation of water-soluble polymers, e.g., poly(vinyl alcohol) and poly(ethylene glycol) (2, 3), have appeared recently, the photodegradation of water-insoluble polymeric films or particulates in TiO₂ aqueous dispersions has received less attention (4, 5).

Herein, we report our recent work on the photooxidative degradation of TiO₂-blended poly(vinyl chloride) thin films by illumination of such blends in an aqueous environment by long wavelength UV radiation and by solar exposure to assess the feasibility of the heterogeneous photocatalytic technique in disposing of thin plastics and particulates. Results indicate that indeed polymeric materials can be photodegraded faster and to higher extents in the presence of some suitable photocatalyst (herein TiO₂) than alone. Indeed, one of the strategies in undertaking this study was to establish a learning curve for the potential manufacturing of new PVC polymers (and others) containing TiO₂ that are photodegradable in open humid (normal atmospheric humidity) spaces under solar exposure.

Experimental Section

Chemicals and Reagents. Solid particulates of poly(vinyl chloride) {PVC: $-(CH_2CHCl)_n-$ } were supplied either by Kishida Chemical Co. Ltd. or by Shinetsu Chemical Co. Ltd. The average size of the PVC particles from the Kishida Chemical Co. was ca. 100–200 μm, determined by scanning electron microscopy measurements; average molecular weight was ca. 81 550, determined by gel permeation chromatography. PVC samples from the Shinetsu Chemical Co. had molecular weights of 33 000, 65 000, 105 000, 151 000 and 239 000. The *o*-dioctyl phthalate {DOP: o -C₆H₄-[COOCH₂CH(CH₂CH₃)CH₂CH₂CH₂CH₃]₂} reagent used as a plasticizer additive was provided by Wako Pure Chemicals. The TiO₂ photocatalyst was Degussa P-25 (BET surface area, 53 m² g⁻¹; particle size, 20–30 nm by transmission electron microscopy; 83% anatase and 17% rutile determined by X-ray diffraction).

TiO₂-blended PVC thin films were prepared as follows. Five lots of 20 mg of PVC particles were each dissolved in 5 mL of tetrahydrofuran (THF) by sonication. The solution containing the 100 mg of PVC was further sonicated in a glass Petri dish (Ø = 66 mm) until it was fully transparent, after which 40 mg of TiO₂ was added in small quantities while continuing to sonicate. Note that the titania particles tended to float on top the solution. Subsequently, the THF was evaporated under ambient temperature and atmospheric pressure to produce the TiO₂-blended PVC thin film. It was washed several times with deionized water to remove the last traces of THF solvent. The thickness of the film was 210 μm; the surface area of the film was 136 cm², whereas the areal density of TiO₂ present in the blend was about 0.73 mg cm⁻². The nature of the TiO₂-blended PVC thin films was

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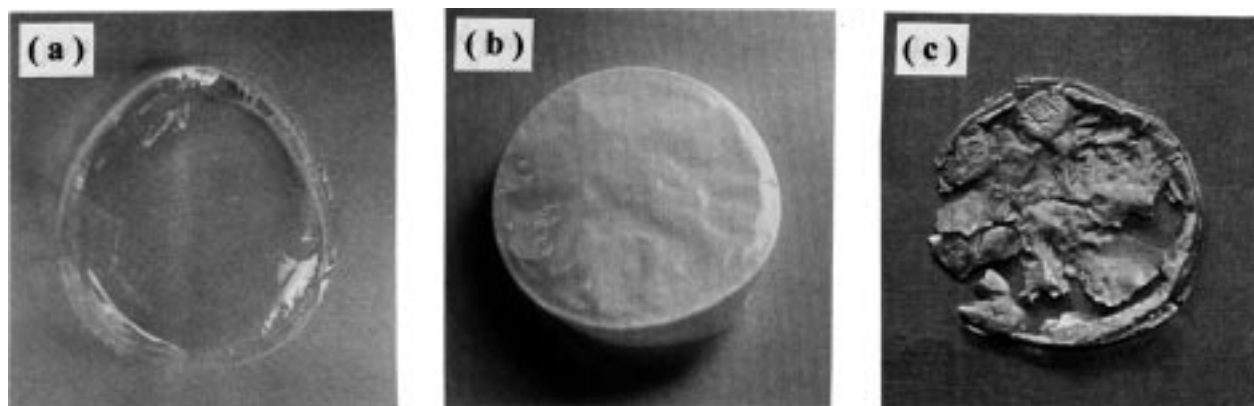


FIGURE 1. Normal photographs of a PVC thin transparent film (a) and of a TiO₂-blended PVC thin film before (b) and after (c) 20 days under artificial UV light exposure.

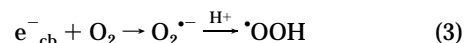
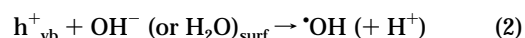
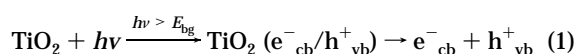
such that all the incident UV light irradiance, E_0 , was absorbed and scattered; i.e., $E_0 = E_{\text{abs}} + E_{\text{sc}}$, and none was transmitted through the film ($E_{\text{tr}} = 0$).

Photodegradation Procedures and Analytical Methods. The TiO₂-blended PVC thin film was placed in 100 mL of deionized water contained in a 200-mL Pyrex glass beaker. UV illumination was performed either with a 75-W mercury lamp or by solar exposure. Solar irradiation experiments were begun on August 24, 1995, on the Meisei University Campus (35°38'31.1" N, 139°24'46.4" E). The concentration of chloride ions was determined using a JASCO ion chromatograph and an I-524A column; the eluent solution consisted of 250 mL of phthalic acid (2.5 mM), 23 mL of tris(hydroxymethyl)aminomethane (3 mM), and 727 mL of water at pH 4. Scanning electron microscopic observations on specimens of TiO₂-blended PVC thin films were done on a Hitachi S-570 electron microscope; the PVC films were also examined by X-ray photoelectron spectral (XPS) measurements with a Shimadzu model ASIX 1000 spectrometer. The distribution of molecular weights in the PVC particles/TiO₂ dispersion system after appropriate irradiation periods was determined by gel permeation chromatography with an Asahipak GF-510 HQ column and a JASCO liquid chromatograph equipped with a refractive index detector; the eluent was tetrahydrofuran. The temporal evolution of carbon dioxide was monitored by gas chromatography with an Ookura Riken chromatograph (model 802; TCD detection) using a Porapak Q column; helium was the carrier gas.

Mutagenicity Assays. The bacterial strains used were *Salmonella typhimurium* TA98 and TA100. Mutagenicity tests were carried out according to the methods of Ames et al. (6) with a slightly modified procedure for the preincubation step (7). The S9-mix enzyme, which was composed of cofactor I and sterilized water (9 mL)/S9 (1 mL), was employed as a metabolic activation system. The S9 enzyme prepared from rat livers, which were pretreated with phenobarbital and 5,6-benzoflavone, was purchased from Kikkoman Co. (Chiba, Japan); the cofactor was purchased from Oriental Yeast Co., Ltd. (Tokyo, Japan). All chemicals were dissolved in dimethyl sulfoxide (DMSO). Each sample was tested after a 20-min preincubation period at four doses.

TiO₂ Photodegradation System. In the photodegradative process implicating TiO₂ particulates, absorption of light with energy greater than ~3.2 eV (wavelengths below ~387 nm) generates electron/hole pairs that upon separation yield conduction band electrons and valence band holes (eq 1). Migration of these carriers to the surface in competition with a variety of other decay channels leads to trapping of the holes by OH⁻ groups or by H₂O to produce [•]OH radicals (eq 2) and trapping of the electrons by Ti^{IV} and/or by the ubiquitous oxygen molecules at the particle surface to yield

the superoxide radical anion, O₂^{•-}, which on protonation forms the hydroperoxide radical [•]OOH (eq 3).



Results and Discussion

The nature of the PVC film alone and of the TiO₂-blended PVC thin film is illustrated in Figure 1, panels a and b, respectively. The surface of each specimen was smooth to the touch, and only the PVC film was transparent. In the TiO₂-blended PVC films, the titania particles were embedded in the interior of the film network and also deposited on the film surface.

An advantage of the transparency of the PVC film and blending the TiO₂ photocatalyst is that UV light can reach and be absorbed to some extent by the encapsulated TiO₂ particles. Moreover, this blending should enhance the rate of photodegradation by TiO₂ because of the intimate contact between the photocatalyst surface and the PVC molecules. Figure 1c illustrates the fate of the TiO₂-blended PVC film after a 20-day UV exposure. Note the serious damage caused to the surface of the blended film following this exposure period. The surface of the naked PVC thin film exhibits a layered morphology as observed by SEM analysis of the cross-section of the film.

Figure 2 illustrates a series of scanning electron micrographs of TiO₂-blended PVC films before UV irradiation (panels a and b) and after a 20-day UV exposure period (panels c and d).

Figure 2a shows the nature of the back side of the TiO₂-blended PVC film (magnification: ×10000): a flat surface was very smooth to the touch. Figure 2b depicts the front side of the film at a magnification factor of 1000 prior to illumination; the front side was very uneven with TiO₂ particles. The content of TiO₂ on the front side was larger than that on the back side. The TiO₂-blended PVC film consisted of various layers to yield a cumulatively constituted thin-layer membrane. Figure 2c shows a slightly damaged surface morphology after the 20-day exposure period of the back side of the film, contrasting the observations in Figure 2d (both at 1000 magnification) that clearly reveal severe damage, e.g., note creation of holes in the film as a result of the photocatalyzed degradation process upon irradiating the film from the front side direction.

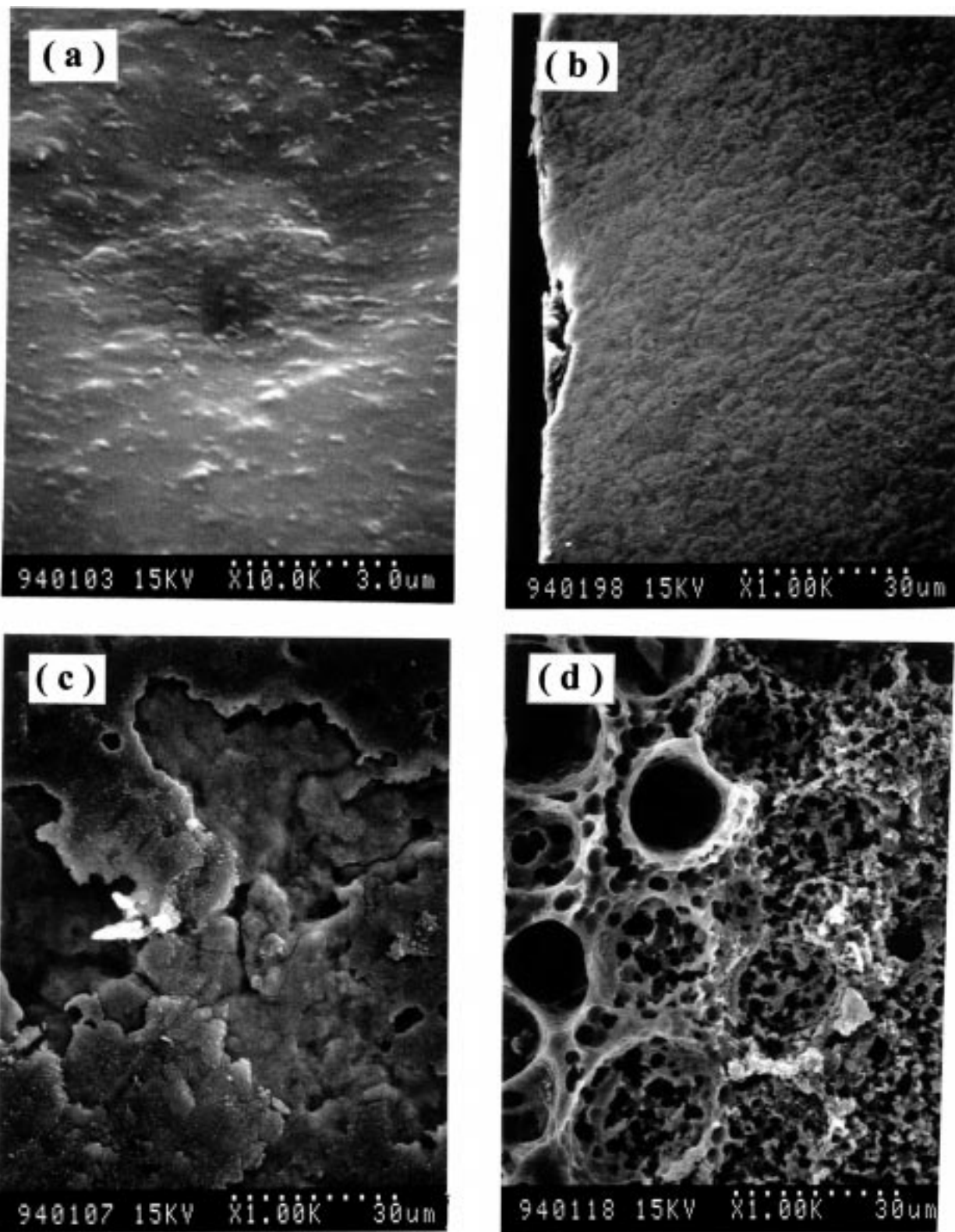


FIGURE 2. Scanning electron micrographs of the TiO_2 -blended PVC thin film: back-side view (a) and front-side view (b) of the film before illumination; (c) slightly damaged film surface from illuminating the back-side surface, and (d) considerably damaged film surface from illuminating the front side after a 20-day illumination period.

The X-ray photoelectron spectral (XPS) analyses for the elements of carbon, oxygen, titanium, and chlorine at the surface and in the interior of the TiO_2 -blended PVC film before (a) and after UV exposure for 20 days (b) were performed using the Ar-ion laser etching technique. The results are summarized in Figure 3 as a function of etching time for a TiO_2 /PVC blended film containing no DOP plasticizer. [Note:

The 20-min etching time represents an etching depth of 100 \AA at a rate of 5 \AA min^{-1} .] The inset of Figure 3a exhibits the initial XPS pattern of the TiO_2 -blended PVC film before illumination.

Initially, the quantity of each element at the surface (i.e., at zero etching time) followed the order $C_{(1s)} > O_{(1s)} > Ti_{(2p)} > Cl_{(2p)}$. The component ratio of every element present in

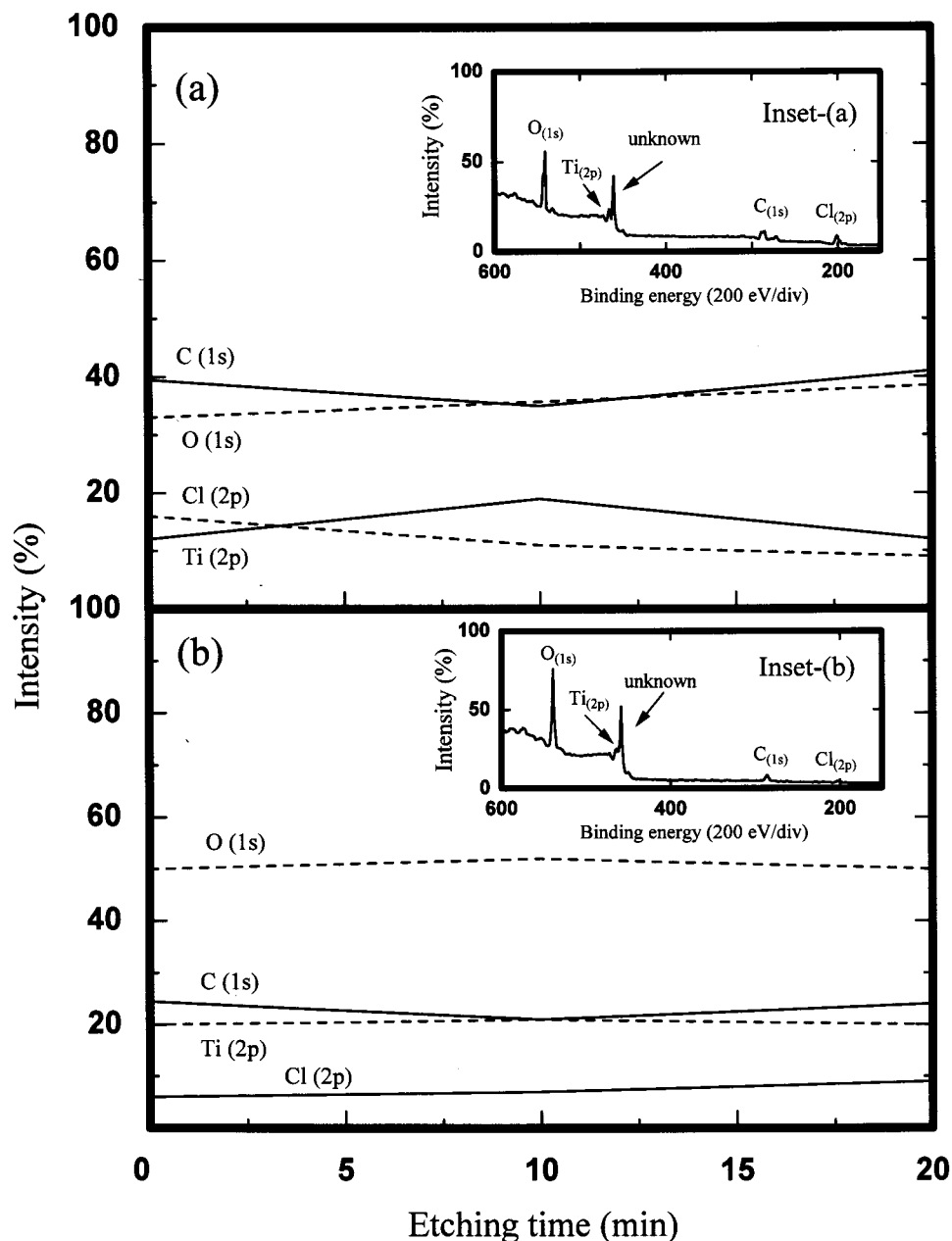


FIGURE 3. X-ray photoelectron spectral analysis of the elemental atoms on the film surface and in the interior of the TiO_2 -blended PVC film: (a) nonirradiated film without the *o*-dioctyl phthalate (DOP) plasticizer and (b) after a 20-day UV exposure period. Inset in panel a shows the XPS pattern of the film surface; inset in panel b shows the XPS pattern of the film surface after the 20-day exposure period. The rate of etching was 5 \AA min^{-1} . In both panels a and b, solid curves refer to the $\text{C}_{(1s)}$ and $\text{Cl}_{(2p)}$ XPS signals, whereas the dashed lines denote the signals for $\text{O}_{(1s)}$ and $\text{Ti}_{(2p)}$.

the TiO_2 /PVC blended film was also examined at a depth between 0 and 100 \AA . The carbon content, $\text{C}_{(1s)}$, decreased slightly to 50 \AA depth and then increased to 100 \AA , whereas the $\text{Cl}_{(2p)}$ increased at first and then decreased for the same etching depth. Oxygen content increased in the film interior, at least to 100 \AA , whereas the $\text{Ti}_{(2p)}$ content decreased on moving into the film's interior, indicating a lesser concentration of TiO_2 particulates inside the film. After argon etching to 100 \AA , the amount of these elements in the interior of the blended film varied as $\text{C}_{(1s)} \approx \text{O}_{(1s)} \gg \text{Cl}_{(2p)} > \text{Ti}_{(2p)}$.

Following the 20-day UV exposure period, XPS analyses of the TiO_2 -blended PVC film showed different quantitative features of the elements both at the surface (zero etching time) and in the interior (20-min etching time; depth of 100 \AA) of the TiO_2 -blended PVC film. At the film surface the quantities of each element analyzed followed the order: $\text{O}_{(1s)} \gg \text{C}_{(1s)} > \text{Ti}_{(2p)} > \text{Cl}_{(2p)}$ (Figure 3b). Etching to a depth of 100

\AA gave similar results. A comparison of the quantity of the elements for the photodegraded film with that of the initially nonilluminated film shows that the oxygen content increased somewhat with increase in UV exposure time; that is, the component ratio of $\text{O}_{(1s)}$ to $\text{Ti}_{(2p)}$, initially about 2:1 at the surface, increased to about 2.5:1 for the 20-day illuminated film. A principal cause for this increase in $\text{O}_{(1s)}$ is the presence of such oxygenated species as $\cdot\text{OH}$, $\cdot\text{OOH}$, and $>\text{C}=\text{O}$ groups at the surface and in the interior. Overall, the XPS signal intensity of elements in the interior of the UV-illuminated TiO_2 -blended PVC film showed little variations with argon etching to a depth of 100 \AA . It is noteworthy that for the nonilluminated blended film, the $\text{O}_{(1s)}/\text{Ti}_{(2p)}$ ratio increased from ca. 2:1 (consistent with the ratio of $\sim 2:1$ in TiO_2) to about 4:1 at 100 \AA below the film's surface that is likely due to additional occluded oxygen during the preparation. As well, the $\text{O}_{(1s)}$ to $\text{C}_{(1s)}$ ratio, which ranges from about 0.8 (at

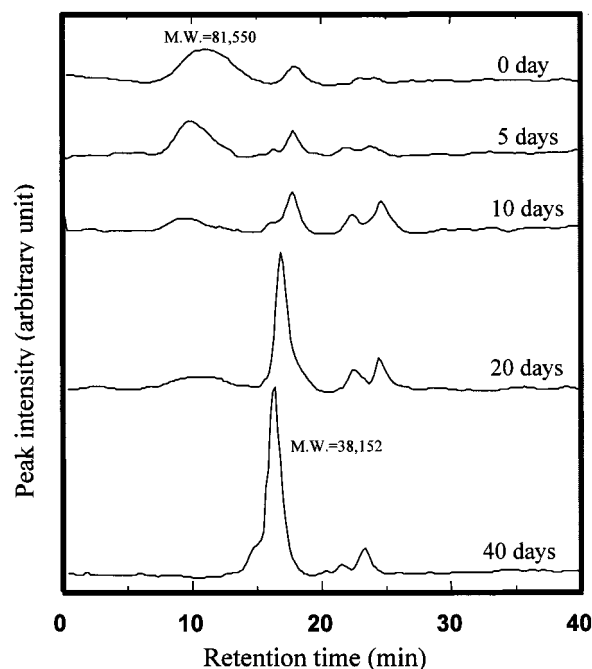


FIGURE 4. Temporal gel permeation chromatographic profiles in the photodegradation of PVC particulates (mol wt = 81 550) containing the DOP plasticizer in an aqueous TiO_2 dispersion under UV illumination with a Hg lamp.

0 Å) to 1.1 at 100 Å (Figure 3a), increased to about 2.1–2.5 for the UV-illuminated TiO_2/PVC film (Figure 3b). Most instructive, however, is the comparison between the XPS signals for $\text{Cl}_{(2p)}$ for the nonilluminated and UV-irradiated film. The $\text{Cl}_{(2p)}$ signal dropped from ~16% to ~6%, respectively, at the film surface on illumination, whereas at 100 Å in the interior of the film the XPS signal intensity for $\text{Cl}_{(2p)}$ is ca. 9%, identical to the nonilluminated film. This and the small rise in $\text{Cl}_{(2p)}$ in Figure 3b confirms the notion that photodegradation takes place predominantly at the surface and gradually in the film's interior, reflecting the degree to which light penetrates in the film. No quantitative elemental analysis was carried out on this TiO_2/PVC -blended film.

The temporal course of the decomposition of PVC particles (MW = 81 550; DOP present) in irradiated TiO_2 suspensions was also monitored by gel permeation chromatography at various time intervals up to 40 days illumination; this is illustrated in Figure 4 depicting the temporal dependence of the molecular weight distributions in this PVC specimen.

After 1 h of UV illumination, the PVC chain was cleaved as attested to by the decrease in molecular weight distribution to 38 152, representing about 53% decomposition of the PVC polymer.

The effects of the degree of polymerization and the presence of the *o*-dioctyl phthalate plasticizer on the photooxidative decomposition process were examined for PVC particles having molecular weights of 81 550 (with DOP), 33 000, 65 000, 105 000, 151 000, and 239 000 in an aqueous TiO_2 (100 mg) dispersion. The temporal evolution of chloride ions is depicted in Figure 5, and the first-order kinetic data are summarized in Table 1. Overall, the concentration of chloride ions released after a 20-day UV exposure decreased with an increase in the degree of polymerization in the order 33 000 > 65 000 ~ 105 000 > 151 000 > (81 550) > 239 000. Dechlorination of the PVC sample with molecular weight of 81 550 that contained the DOP plasticizer was slow initially (also note the ca. 4-day induction period) as compared to the 239 000 PVC sample, which showed the fastest evolution of chloride under UV exposure.

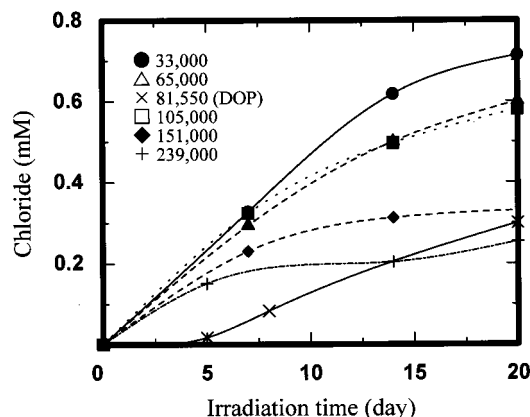


FIGURE 5. Graph illustrating the effects of the degree of polymerization (mol wt of 81 550 contains the DOP plasticizer, 33 000, 65 000, 105 000, 151 000, and 239 000) and the presence of the DOP plasticizer on the evolution of chloride ions from illuminated TiO_2 (100 mg) dispersions. Curves refer to first-order growth kinetics fit to the experimental data.

TABLE 1. Kinetics of Chloride Ion Evolution and Yield of Chloride on UV Exposure of TiO_2 -Blended PVC Thin Films Using PVC of Different Molecular Weights

mol wt of PVC material	k (10^{-2} day^{-1})	$t_{1/2}$ (days)	$[\text{Cl}^-]^a$ (mM)
33 000	5.6 ± 1.8	12	0.73
65 000	6.2 ± 0.5	11	0.60
81 550 ^b	1.5 ± 0.6	47	0.30
105 000	8.93 ± 0.02	7.8	0.58
151 000	14.7 ± 0.5	4.7	0.36
239 000	17 ± 15	~4	0.25

^a After 20 days of UV exposure; obtained from the first-order kinetic fits. ^b Contains the DOP plasticizer; induction period about 4 days.

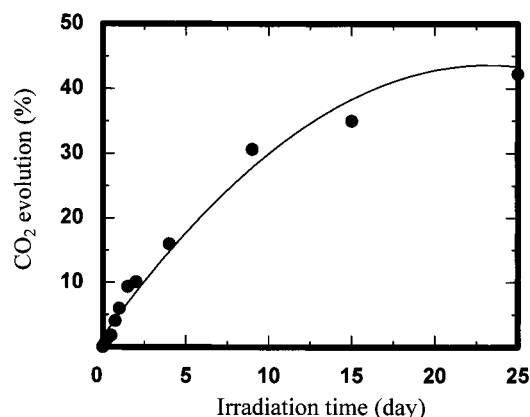


FIGURE 6. Evolution of carbon dioxide from the TiO_2 -photocatalyzed mineralization of the DOP plasticizer alone under illumination with a mercury lamp. The solid curve reflects the first-order growth kinetics fit to the experimental data points.

DOP is a plasticizer having relatively large frontier electron densities on the carbonyl group and on the ring's π bond. It was expected, therefore, that DOP might be the more likely target for the $\cdot\text{OH}$ radicals (eq 2) in the photooxidation of TiO_2 -blended PVC films. We therefore examined the photooxidative mineralization of this plasticizer in aqueous TiO_2 dispersions; the temporal evolution of carbon dioxide is illustrated in Figure 6, which shows that nearly 42% of carbon dioxide evolved after 25 days of UV irradiation with $k_{\text{CO}_2} = (13.0 \pm 1.0) \times 10^{-2} \text{ day}^{-1}$ and $t_{1/2} = 5.3$ day. The mineralization yield was smaller than expected; the process occurring via various intermediates.

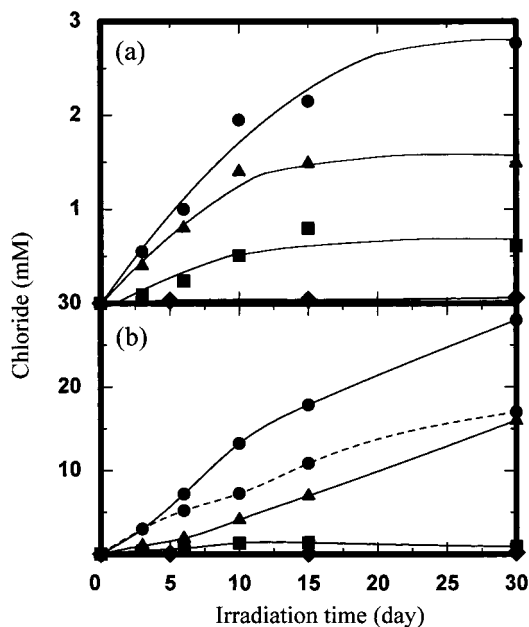


FIGURE 7. Temporal evolution of chloride ions under artificial UV irradiation (Hg lamp) for PVCs containing DOP (a) and with no DOP (b). Solid circles, TiO_2 -blended PVC film; solid triangles, PVC film plus TiO_2 suspension; solid squares, PVC particles plus TiO_2 suspension; solid diamond, PVC film without TiO_2 . Dotted solid circles in panel b refer to a TiO_2 -blended PVC film under solar UV exposure. Curves denote the first-order growth kinetics to the data points.

Evidently, the hydrophobicity of the dioctyl residues in the DOP plasticizer when incorporated in the TiO_2 /PVC-blended film must contribute significantly to the slow degradation of the film. Note that this slow degradation cannot be attributed to DOP acting as an inner filter, preventing the TiO_2 photocatalyst from being light activated since DOP does not absorb in the UVA/UVB region; its absorption spectrum in ethanolic media shows bands only at 275 and 241 nm.

Formation of chloride ions from the degradation of the TiO_2 -blended PVC films, PVC thin films on TiO_2 particles, and PVC particles in TiO_2 dispersions under illumination by a Hg lamp are illustrated in Figure 7, panels a and b. The PVC material used in Figure 7a was supplied by Kishida Chem. Co. Ltd. and contained the DOP plasticizer, whereas the PVC sample of Figure 7b was supplied by Shinetsu Chem. Co. Ltd. but contained no DOP. First-order kinetics for the evolution of Cl^- ions and the yield of chloride after a 30-day UV exposure are collected in Table 2. The TiO_2 -blended PVC film, PVC film/ TiO_2 dispersion, and PVC particles/ TiO_2 dispersion are compared to ascertain what accelerating effect the contact distance of PVC to TiO_2 has on the dechlorination process: TiO_2 -blended PVC film (2.8 mM Cl^-) > PVC film with TiO_2 dispersion (1.6 mM) > PVC particles and TiO_2 particles (0.61 mM) > PVC film alone (~0.06 mM). Figure 7b exhibits a similar trend also for a 30-day illumination period: TiO_2 -blended PVC film (29 mM) > PVC film with TiO_2 dispersion (16 mM) > PVC/ TiO_2 particles (1.9 mM) > PVC film alone (0.19 mM).

The photodegradation of the TiO_2 -blended PVC film that contained no DOP was faster than for the PVC film alone; degradation of the PVC film in TiO_2 dispersion, however, was faster for the system containing the DOP plasticizer (see Table 2). In all cases, the extent of photodegradation of the various systems noted in Table 2, as evidenced by the concentration of chloride ions formed, was greater by nearly a factor of 10 when no DOP plasticizer was contained in the PVC samples (known as "hard PVC"). The photodegradation of a PVC film with and without the DOP plasticizer and in

TABLE 2. Kinetics of Chloride Ion Evolution and Yield of Chloride Ion on UV Exposure of Different Samples

sample	k (10^{-2} day^{-1})	$t_{1/2}$ (days)	$[\text{Cl}^-]^a$ (mM)
With DOP Plasticizer			
TiO_2 /PVC-blended film	8.1 ± 1.5	8.5	2.8
PVC film + TiO_2 suspension	14 ± 3	5	1.6
PVC particles + TiO_2 suspension	~10	~7	0.61
PVC film alone	~11	~6	0.06
Without DOP Plasticizer			
TiO_2 /PVC-blended film	3.2 ± 0.6	~22	29
TiO_2 /PVC-blended film ^b	3.6 ± 0.4	19	17
PVC film + TiO_2 suspension	~0.5	(140)	16
PVC + TiO_2 suspension	~8	~9	1.9
PVC film	~2	~34	0.19

^a After 30 days of UV exposure; obtained from the first-order kinetic fits. ^b After 30 days of solar exposure (see text for conditions).

the absence of TiO_2 is illustrated in Figure 7, panels a and b (data points described by solid diamonds); the quantity of Cl^- ions formed was 0.06 and 0.19 mM, respectively, representing about 4% and 0.6% of the quantity of chloride from the dechlorination of TiO_2 -blended PVC films under the conditions used. Note also that although the rate of dechlorination of PVC films (with or without DOP) alone is similar to the rate of dechlorination of these films in the presence of TiO_2 particulates, the extent of dechlorination is 25 times and 84 times smaller, respectively, when no TiO_2 is present. The total mineralization yield of PVC and the stoichiometric yield of chloride and CO_2 were not determined in this study as the focus was to demonstrate feasibility of the photocatalytic method to degrade polymeric materials in a heterogeneous solid matrix.

Experiments carried out to assess the decomposition of TiO_2 -blended PVC film under solar exposure also reveal dechlorination of the specimens as illustrated by formation of chloride ions (Figure 7b; dotted solid circles). The average daylight was about 11.5 h per day, and the maximum solar light irradiance on any particular day between August 24 and September 22, 1995, in the UVA/UVB region of 290–400 nm ranged from 0 to 4.05 mW cm^{-2} . On a cloudy day, the irradiance decreased as low as ca. 0.018 mW cm^{-2} . The data reported in Table 2 demonstrate that it is also possible to photooxidize the TiO_2 -blended PVC film (no DOP) with solar UV light exposure; however, the quantity of chloride ions evolved for this blended film was about 1.7 times less than for the film exposed to artificial UV light, even though the rates of dechlorination are identical within experimental error (Table 2).

The thermal decomposition of PVC plastics is known to generate mutagenic polycyclic aromatic hydrocarbons, e.g., phenanthrene, pyrene, benzo[a]pyrene, and benzo[e]pyrene. It was therefore important to determine whether the photodegradation products might also be mutagenic. Figure 8 shows the mutagenic activity of products from the pyrolysis at 800 °C of the products obtained after a 7-day UV illumination period (gray-shaded histograms) relative to pyrolysis products from PVC specimens that had not been illuminated previously (black-colored histograms).

There was little evidence of mutagenic activity from the thermal decomposition (in an electric furnace) of organic volatile/condensable products obtained from the photodecomposition of the PVC film in the system that contained TA98 strain without the S9 mix, i.e., the TA98(–) system. The revertants for the TA98(+), TA100(–), and TA100(+) strains showed no variations as to whether the PVC film had been illuminated previously. No mutagenic activity was detected by the Ames method for the products emanating from

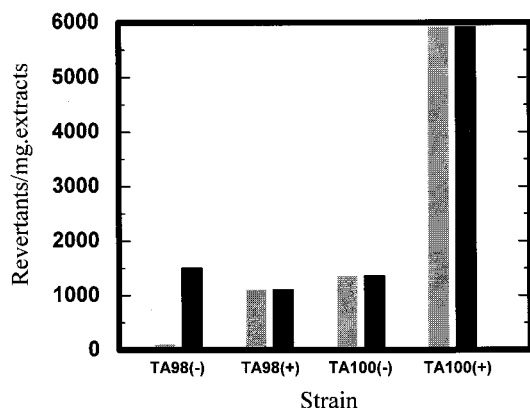


FIGURE 8. Mutagenic activity of organic volatile/condensable products during the pyrolysis (at 800 °C) of poly(vinyl chloride) and under UV exposure for 7 days. TA98(–) refers to the system without the S9 mix, TA98(+) refers to a system containing the S9 mix, TA100(–) denotes a system without S9 mix, and TA100(+) denotes a system with the S9 mix. The gray bars are a measure of the thermal decomposition treatment after UV illumination, whereas the black bars refer to the thermal decomposition process without any prior illumination.

UV illumination of PVC in heterogeneous aqueous TiO₂ dispersions.

Consequently, the TiO₂-blended PVC film system photodegraded more rapidly than the PVC particle/TiO₂ dispersion systems as evidenced by the extent of dechlorination. The blend of TiO₂ in the polymer matrix enhanced remarkably the decomposition rate. The presence of DOP as a plasticizer (soft PVC) caused a slow of the dechlorination rate of PVC. Under solar UV exposure, the PVC in the TiO₂-blended film could also be decomposed because of the close contact of the TiO₂ photocatalyst with the PVC matrix. The results

reported herein open the way to manufacture modified PVC plastics (and others) containing such additives as TiO₂ that might accelerate decomposition of plastics under solar light exposure if and when disposed in the environment. Clearly, characteristics of such modified plastics shall also need examination.

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Literature Cited

- (1) Hidaka, H.; Suzuki, Y.; Nohara, K.; Horikoshi, S.; Hisamatsu, Y.; Pelizzetti, E.; Serpone, N. *J. Polym. Sci. Part A Polym. Chem.* **1996**, *34*, 1311.
- (2) Horikoshi, S.; Ohta, M.; Hidaka, H.; Zhao, J.; Serpone, N. *Recent Res. Dev. Polym. Sci.* **1997**, *1*, 149.
- (3) Horikoshi, S.; Hidaka, H. *J. Jpn. Soc. Colour Mater. (SHIKIZAI)* **1998**, *71*, 176.
- (4) Ohtani, B.; Adzuma, S.; Nishimoto, S.; Kagiya, T. *Polym. Degrad. Stab.* **1992**, *35*, 53.
- (5) Allen, N. S.; Bullen, D. J.; McKellar, J. F. *J. Mater. Sci.* **1977**, *12*, 1320.
- (6) Ames, B. N.; McCannand, J.; Yamasaki, E. *Mutat. Res.* **1975**, *31*, 347.
- (7) Yahagi, T.; Nagao, M.; Seion, Y.; Matsushima, T. *Mutat. Res.* **1977**, *48*, 121.

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