

Different Photodegradation Processes of PVC with Different Average Degrees of Polymerization

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ABSTRACT: The influence of ultraviolet (UV)-irradiation on the photodegradation mechanism of different average degrees of polymerization (\overline{DP}) of poly(vinyl chloride) (PVC) with UV-irradiation time was investigated by viscosity-average molecular weight determination, UV-vis spectroscopy, Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), contact angle measurement, and scanning electron microscopy (SEM). PVC films with different \overline{DP} (800, 1000, 1300, 3000) were prepared by solution casting. It was carried out exposing specimens to a xenon-arc light source with a spectral irradiance of 0.68 W/(m² nm) at 63°C. It was found that the photodegradation mechanism of the lower \overline{DP} of PVC (\overline{DP} = 1000) was different from the higher \overline{DP} of PVC (\overline{DP} = 3000). This was because the lower \overline{DP} of PVC was a homopolymer, while the higher \overline{DP} of

PVC was often produced by copolymerizing with a certain quantity of crosslinking agent (e.g., DAP and DAM). UV-vis and FTIR spectroscopy studies provided some results concerning the structure of the irradiated PVC, and the carbonyl index and C—Cl index were induced to study the process of PVC photodegradation with different \overline{DP} . TGA showed that the degradation temperatures of different weight loss increased with the irradiation time. The surface morphology of the irradiated polymer films with different \overline{DP} was observed by contact angle measurement and SEM. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 528–540, 2008

Key words: poly(vinyl chloride); UV-irradiation; photodegradation; average degree of polymerization

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most important and widely used thermoplastics because of its valuable properties, such as low production cost, good processability, easy modification, and excellent chemical and fire resistance.^{1,2} Because of this excellent performance, PVC materials are often chosen for many outdoor applications, such as house siding panels, waste water tubes, and window profiles.^{3,4} However, the PVC resin itself does not weather well. The photodegradation problem is of great importance throughout PVC usage. It is generally known that the following factors induce photodegradation processes of PVC in the natural environment: sun rays, temperature, moisture, humidity, impurities of different kinds (including both inorganic and organic chemical compounds), as well as bacteria and molds.^{1,5,6} However, photodegradation is usually mainly initiated by solar UV-radiation, followed by air and pollutants, whereas water, organic solvents, temperature, and mechanical stresses enhance these processes.^{3,5} In spite of the large number of studies and publications of more than 30 years, the mechanism of the photodegradation of PVC is not fully understood; many differ-

ent results have been reported, as PVC photodegradation is a highly complicated process.^{1,3,6–11} The ideal PVC macromolecule contains only C—C, C—H, and C—Cl bonds. Therefore, it is not expected to absorb light of wavelength longer than 190–220 nm.⁵ The susceptibility of PVC substances to incident light of 300–400-nm wavelength, on the contrary, is well known.⁷ As commercially available PVC contains small amounts of different abnormal structures (defects), such as random unsaturation (allylic chlorine), chain end groups, and branch points (tertiary-bonded chloride atoms and oxidized structures).⁵ Many studies of PVC photodegradation are thus involved with the identification of some structural defects along the polymer chains that could initiate the process. Among these defects, unsaturated groups have been studied as possible initiation sites.⁷ It is widely recognized that PVC photodegradation is a very complex process due to the coexistence of two presumably sharply inter-related chain reactions: zip dehydrochlorination and oxidation.⁹ Zip dehydrochlorination leads to the formation of long, conjugated polyene sequence (—CH=CH—)_n in the polymer chains, which give the red-brown color of degraded.¹² Photoelimination creates Cl radicals that are able to initiate oxidation chains. HCl is able to catalyze the decomposition of hydroperoxide or peroxide, and polyenes play a photosensitizing or photostabilizing role, depending essentially on their length.^{9,10}

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The oxidative chain process leads to the formation of hydroperoxides, dialkyl peroxides, and carbonyl groups, together with crosslinking and chain scission reactions. It has been shown that if the HCl evolution is accelerated prior to oxygen, in contrast, the average length of the conjugated species and the extent of crosslinking are limited.^{5,7,10,12} Photoelimination reactions can be explained by UV-vis spectroscopy, as resulting polyene absorption of <600–700 nm wavelength and oxidation reactions are recognized by the growth of the infrared (IR) absorption bands for $>C=O$ at $\sim 1720\text{ cm}^{-1}$.^{3,4,8} Because of the slow diffusion of oxygen into PVC, oxidation substances develop only in the upper 50 μm of a plate, whereas polyenes are generated at $\leq 300\text{ }\mu\text{m}$.⁹

PVC ($\overline{DP} = 800, 1000, 1300$) that is generally prepared by suspension polymerization is a homopolymer. It contains only C–C, C–H, and C–Cl bonds and small amounts of different abnormal structures. However, PVC ($\overline{DP} = 3000$) with a very high average polymerization degree has often been produced by copolymerizing with a certain quantity of crosslinking agent. Regarding the production process of high average polymerization degree resin, using a crosslinking agent, many patents have been granted.¹³ The main crosslinking agents are diallyl esters, such as diallyl phthalate (DAP) and diallyl maleate (DAM).^{13–15} Crosslinking agents are listed in Figure 1.¹³ The amount of DAP or DAM is 0.1–0.5% based on vinyl chloride.^{14,15}

Generally, one allylic group of DAP copolymerizes with vinyl chloride at first, leading to the formation of a linear PVC primary chain with a pendant double bond (PDB). When PDB is reinitiated by a radical and is bonded with another macromolecule by chance, \overline{DP} may be increased as a result. The larger the macromolecule, the greater the number of DAP units and PDBs in a polymer chain.^{13,16} So PVC ($\overline{DP} = 3000$) contains carbonyl groups, double bonds, ether bonds, and so on, besides C–C, C–H, and C–Cl bonds.

The purpose of the present work is to investigate the photodegradation mechanism of PVC with the different average degrees of polymerization. For this purpose, thin PVC films ($\overline{DP} = 800, 1000, 1300, 3000$) were prepared by solution casting, carried out in an accelerated way by using an artificial source of UV-radiation for varying periods of time. Photodegradation of PVC films with different average degrees of polymerization was monitored by viscosity-average molecular weight determination, UV-vis spectrophotometry, and thermogravimetric analysis (FTIR and TGA). The changes in the surface morphology of the irradiated polymer films with different \overline{DP} were observed by contact angle measurement and scanning electron microscopy (SEM). Although the photodegradation of PVC has been studied intensively, there is a lack of information on the effect of the average

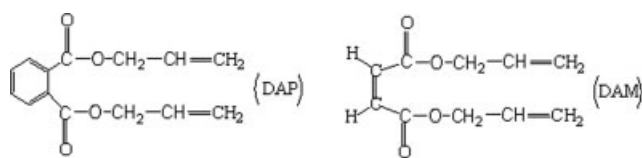


Figure 1 Structure of crosslinking agents.

degrees of polymerization. It is interesting to investigate whether the photodegradation mechanism of the higher \overline{DP} of PVC is different from the lower \overline{DP} of PVC.

EXPERIMENTAL

Materials

The powder of PVC (P800, the average degree of polymerization (\overline{DP}) = 800) was produced by Tianjin Dagu Chemical Industry Co (Tianjin, China). The powder of PVC (TK1000, $\overline{DP} = 1000$) was supplied by Shin-Etsu Chemical Co (Kashima, Japan). The powder of PVC (S1300, $\overline{DP} = 1300$) was produced by Shanghai Chlor-Alkali Chemical Co (Shanghai, China). The powder of PVC (P3000, $\overline{DP} = 3000$) was obtained by Zhenjiang Resin Factory (Zhenjiang, China). All PVC powders were commercial polymer, without any chemical or thermal treatments. Tetrahydrofuran (THF) (pure per analysis, Tianjin Kermel Chemical Reagent Development Center, China) was used as supplied. Cyclohexanone (pure per analysis and diiodomethane (pure per analysis) were supplied by Nanjing Zhongdong Chemical Glass Instrument Ltd China (Nanjing, China).

Film preparation

PVC films were prepared as follows. The best solvent for PVC is tetrahydrofuran (THF), but this solvent participates in degradation.^{11,17} The films were prepared by dissolving 1.42 g of PVC in 40 g of THF under vigorous stirring for 30 min. It was necessary to control the hygrometry and the rate of evaporation of solvent during casting to maintain good optical quality and very limited turbidity. The film transmission should be greater than 80% in the near-UV range. After 3 h, the solution was spread on a slide stainless steel model (250 \times 120 \times 0.5 mm) and air-dried for 16 h. After the solvent evaporation, the samples were dried in a vacuum at room temperature for 56 h. Finally, the samples were dried in a vacuum at 80°C for 6 h.^{12,18} The thickness of the resulting PVC film was measured to be $\sim 60\text{ }\mu\text{m}$.

Accelerated ultraviolet-weathering tests

Accelerated artificial UV-weathering tests were conducted in a Xenon Test Chamber (Q-SUN1000, Q-

Panel, Cleveland, OH) that reproduces the damage caused by sunlight. The samples were subject to continuous exposures according to the procedure outlined in China standard GB9344-88 using UV light exposure at 63°C (black-panel thermometers) with a xenon arc as the light source [spectral irradiance: 0.68 W/(m² nm)] at 340 nm. The accelerated weathering test was completed after 336 h (total time). The finely PVC films were placed on the plate in a chamber for uniform exposure of UV radiation.

UV-vis spectrophotometer

The absorption spectra of the PVC films were recorded at room temperature, using air as the reference before UV exposure and after regular periods of irradiation. The spectrum ranging within 200–600 nm was ascertained on a UV3101PC UV-vis spectrophotometer (Shimadzu, Japan).

Fourier transform infrared

FTIR spectra of unweathered and UV-irradiated samples were obtained on a NEXUS 670 FT-IR (Nicolet, Madison, WI) equipped with EZ OMNIC software at a resolution of 4 cm⁻¹ with a coaddition of 100 scans for each spectrum. The IR spectra were recorded in transmittance units within the 4000–400-cm⁻¹ range; 100 scans at 400–4000 cm⁻¹ were made for each spectrum to improve the signal-to-noise ratio. The intensity (or peak area, i.e., the integral intensity) of the carbonyl (1650–1850-cm⁻¹) bands was used to estimate photodegradation.^{19,20}

Contact angle measurement

Contact angles of two liquids (diiodomethane and deionized water) on PVC film before and after irradiation were measured at constant temperature (20°C), using a goniometer equipped with system of drop shape analysis (DSA100, Krüss, Hamburger, Germany). The liquid drop (1.5 µL) was placed onto the polymer surface by a microsyringe. The drop image was recorded by video camera and digitalized. The profile of single drop was numerically solved and fitted by mathematical functions. Each contact angle is the average of minimum five measurements, with a precision of 2°. The surface free energy (γ_s) and their dispersive (γ_s^d) and polar (γ_s^p) parts were calculated using the Owens–Wendt methods.²¹

Scanning electron microscopy

The surface morphological images of different PVC films before and after irradiation were taken by a SEM (JSM-5900, Japan Electron Optics Laboratory, Tokyo, Japan) with the pre-treatment of Au deposi-

tion applied to some of them. The accelerating voltage of SEM was 15 kV.

Thermogravimetric analysis

TGA was recorded using the NETZSCH thermal analysis (STC449C, Selb, Bavaria, Germany) system in the presence of nitrogen (30 mL/min) from room temperature to 500°C at a predetermined heating rate of 20°C/min. The thermogravimetric weight loss curve (TG, %) and the derivative curve of the weight loss (DTG, %min⁻¹) were recorded as a function of time and temperature.

Viscosity-average molecular weight determination

The viscosity-average molecular weights of irradiated PVC samples were determined by the intrinsic viscosity values and its relation to molecular weight via the Mark–Houwink equation as reported earlier.^{22–24}

The Mark–Houwink equation, relating the viscosity-average molecular weight, M_{η} , to the limiting viscosity number (intrinsic viscosity), $[\eta]$, was given for polymers by²⁵:

$$[\eta] = KM_{\eta}^{\alpha}$$

where K and α were constants specific to the solvent and temperature used in the measurements. In the present work, $K = 8.5 \times 10^{-3}$ ml/g, $\alpha = 0.85$.²⁶

A Ubbelohde viscometer ($\Phi = 0.5$ – 0.6 mm) was used for the relative viscosity of PVC in cyclohexanone soaked in a constant temperature bath at 25 ± 0.1 °C, with a stopwatch to measure the time needed for the solvent and polymer solution to flow through the capillary tube. The viscometer was cleaned between runs using the solvent. Solutions were prepared with five different relative concentrations: 1C, 6/7C, 6/8C, 6/9C, and 6/10C. Then the flow time of five different concentrations were measured. At least three readings were made at each of the five concentrations of each sample until variations in flow time were kept within 0.2 s. Relative viscosity, $\eta_{rel} = t/t_0$, where t and t_0 referring to the flow time of polymer solution and pure solvent respectively, were calculated and converted to inherent viscosity η_{inh} from the equation $\eta_{inh} = \ln \eta_{rel}/c$. From this the specific viscosity was calculated ($\eta_{sp} = \eta_{rel} - 1$) and converted to reduced viscosity $\eta_{red} (= \eta_{sp}/C)$. Inherent viscosity values (η_{inh}) and reduced viscosity values (η_{red}) were plotted against concentration to obtain intrinsic viscosity by extrapolation to zero concentration.^{27,28}

RESULTS AND DISCUSSION

Viscosity-average molecular weight analysis

The effects of UV-irradiation time and the average degree of polymerization on M_{η} of PVC are depicted

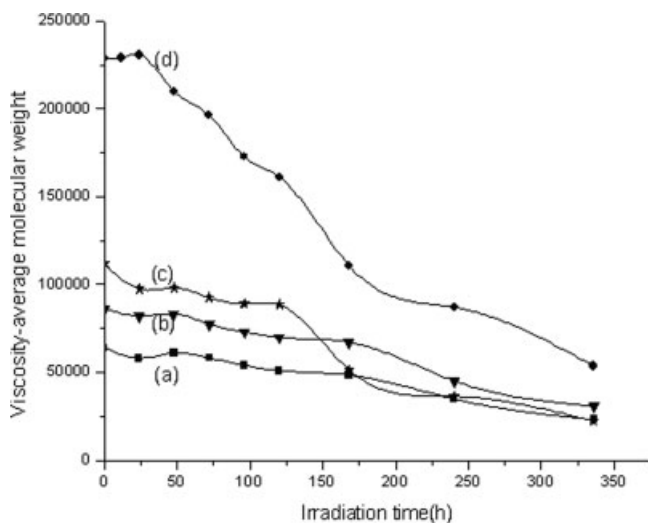


Figure 2 Changes of viscosity-average molecular weight of the different \overline{DP} of PVC with the UV-irradiation time from 0 h to 336 h: (a) $\overline{DP} = 800$; (b) $\overline{DP} = 1000$; (c) $\overline{DP} = 1300$; (d) $\overline{DP} = 3000$.

in Figure 2, which shows that M_n of four \overline{DP} kinds of PVC decrease as irradiation time increases, but the variation tendencies are different. For the lower \overline{DP} of PVC (800, 1000, and 1300), M_n decreases rapidly in all samples after 24-h irradiation, proof of chain scission¹; however, prolonging irradiation time to 48 h causes M_n to increase, confirmation that polymer undergoes competitive reactions: chain breaking and crosslinking.²⁹ There is a delicate balance between oxidation/chain scission/embrittlement and dehydrochlorination/polyene length distribution.⁸ The rapid increase of M_n was explained by macroradicals formed in primary reactions.¹ For the higher \overline{DP} of PVC (3000), M_n first increases after 12-h and 24-h irradiation, then decreases rapidly with increasing irradiation time. It is suggested that the higher \overline{DP} of PVC undergoes efficient photocrosslinking, especially at the beginning of UV-irradiation. The primary chains contain many DAP units, PDBs, and double bonds; with UV-irradiation, they have a higher probability of participating in chain crosslinking reaction. The molecular weight of the PVC primary chains that tended to crosslinking is much higher than that of the commercial vinyl chloride homopolymer.¹⁶ The rapid decrease of M_n in all samples after 120 h indicates that prolongation of irradiation leads to predominant degradation. It has been known that chain scissions result essentially from oxidation reactions, which are controlled by oxygen concentration.⁹ The chain scissions of PVC caused by irradiated make oxygen easily enter into polymer, which leads to the fast chain scission. The M_n loss rate was the highest for the PVC film ($\overline{DP} = 3000$); it decreased rapidly with irradiation and led to the total reduction of 30% in 120 h, while $\overline{DP} = 800, 1000, \text{ and } 1300$ showed only 20%, 19%, and

21% M_n loss, respectively, under identical experimental conditions. However, it is impossible to explain all changes in exposed samples because of the complexity of photochemical reactions occurring simultaneously. The gel substances appear in all \overline{DP} of PVC after 240 h of UV-irradiation. Therefore it is found that there are some differences between the lower \overline{DP} and the higher \overline{DP} of PVC in the UV-irradiation process. The $\overline{DP} = 1000$ and 3000 of PVC were chosen for the further study.

UV-vis spectrophotometer

The photodehydrochlorination of PVC is monitored by UV-vis spectroscopy. During exposure to UV, samples undergo yellowing, and the broad absorption band in the UV and visible region is observed. The difference described in the previous section is confirmed by UV-vis spectrophotometer. The larger changes in the electronic spectra during UV-irradiation are found for the lower \overline{DP} of PVC [Fig. 3(a)]. Only negligible changes appear in the higher \overline{DP} of PVC [Fig. 3(b)]. The increased absorbance in the UV-vis range for samples containing PVC can be explained by the formation of conjugated double bonds (band corresponding to the $\pi \rightarrow \pi^*$ transition) in this polymer resulting from its photodehydrochlorination. This is a zip reaction, which develops progressively along the polymer chain.¹⁹ The absorption peaks of the conjugated double bonds, i.e., $(\text{CH}=\text{CH})_n$, at 315, 328, 368, 394, and 421 nm (the respective wave lengths of absorbance maxima) are attributed to the n values of 4, 5, 7, 8, and 9.^{1,19,30,31} Thus, shifting the absorbance to longer wavelengths (i.e., the bathochromic effect) is evidence that longer polyenes were formed in our samples. Absorption in the short wavelength UV region ($\lambda \leq 300$ nm) is caused mainly by isolated double bonds, dienes ($n = 2$) and trienes ($n = 3$).^{19,32} Moreover, other chromophores, such as carbonyl groups and carbonyl groups coupled with unsaturated bonds, absorb in this region. The overlapping bands make the interpretation of the results difficult.¹⁹

For the purpose of comparing samples of different \overline{DP} , the relative changes of absorbance at selected wavelengths, were plotted, i.e., at 421 nm (corresponding to nine conjugated double bonds)^{1,19,31} and at 300 nm (corresponding to shorter polyenes and to partly overlapping absorption of carbonyl groups),² as a function of exposure time. Two sets of kinetic curves can be seen in the both plots (Figs. 4, 5): curves attributed to higher changes in PVC films ($\overline{DP} = 1000$) and curves showing much lower changes in PVC films ($\overline{DP} = 3000$). It is clearly seen that the photodehydrochlorination occurs in the lower \overline{DP} of PVC films, while it nearly does not occur in the higher \overline{DP} of PVC films. However, from the changes of the vis-

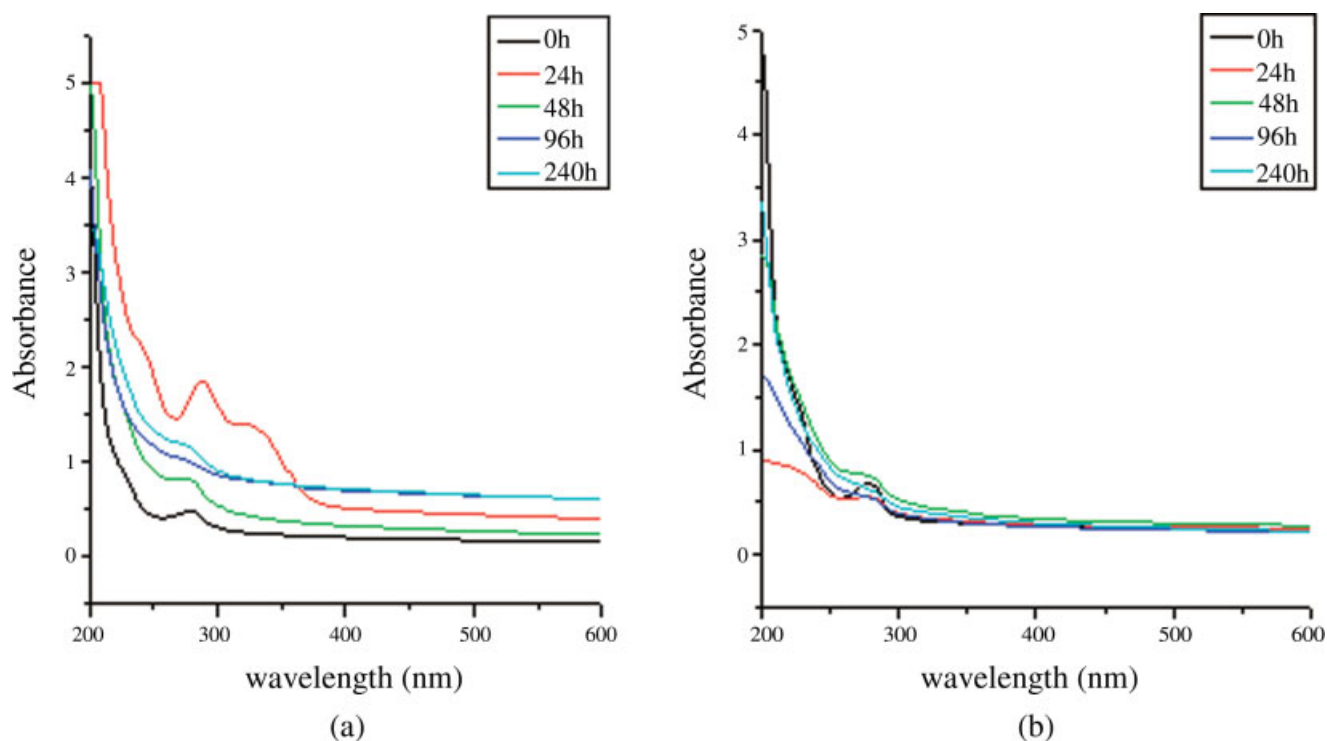


Figure 3 Absorption spectra of PVC (a) $\overline{DP} = 1000$, (b) $\overline{DP} = 3000$ after 0–336 h of UV-irradiation. The numbers above the curves indicate the irradiation time (h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

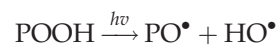
cosity-average molecular weight with irradiation time, both undergo photodegradation. This suggests that there are different mechanisms of photodegradation between the lower and higher \overline{DP} of PVC. The photodegradation reaction of PVC ($\overline{DP} = 3000$) is primarily crosslinking and chain breaking because of copolymerizing with DAP or DAM, which contain carbonyl groups, double bonds, ether bonds, and so on. The photodegradation reaction of PVC ($\overline{DP} = 1000$) mainly is dehydrochlorination and then chain breaking.

FTIR spectroscopy

FTIR spectroscopy was used as a complementary technique to monitor functional groups and quantify the surface chemical changes after UV exposures. The FTIR spectra of different average degrees of polymerization of unirradiated and UV-irradiated PVC samples are illustrated in Figures 6 and 7. The main spectral changes are seen within the $1650\text{--}1850\text{-cm}^{-1}$ frequency range. It can be noted that some oxygenated substances that contaminate commercial PVC resins, are detected in the spectra of unirradiated PVC [Figs. 6(a) and 7(a)].²⁰

However, exposure to UV-irradiation significantly increases the intensity of absorption bands in the region of $1850\text{--}1650\text{ cm}^{-1}$. Two new absorption bands appeared in the IR spectra ~ 1722 and 1772 cm^{-1} , as

PVC was photooxidized [Figs. 6(b),(c) and 7(b),(c)]. This can be attributed to carbonyl (C=O) groups. The absorption band at 1722 cm^{-1} was the carbonyl group between two methylene groups ($-\text{CH}_2\text{COCH}_2-$).³³ While the process is also associated with the formation of oxidative substances, such as α - and β -chloro-carboxylic acids (1716 cm^{-1}) and α - and β -chloro-ketones ($1730\text{--}1770\text{ cm}^{-1}$),³⁴ some investigators have observed the predominance of a peak located at $1715\text{--}1720\text{ cm}^{-1}$ attributed to α -methylene ketone or carboxylic acid, which probably results from band overlapping of the two species and the acid resulting from ketone photooxidation.^{33,35} These bands between 1650 cm^{-1} and 1850 cm^{-1} are complex because many different substances are formed in UV-irradiated PVC in the presence of air, for example, ketones, aldehydes, esters, carboxylic acids, alcohols, peroxides, and hydroperoxides,⁵ and some of them are relatively stable. However, numerous photolysis form during the process of degradation, giving new radicals initiating further decomposition of macromolecules:



What is more, the carbonyl groups are photosensitive and undergo Norrish type I and type II reactions.⁵ The carbonyl bands become broader with increasing exposure time. As photooxidation is initiated by the abstraction of labile atoms by the radical impurities

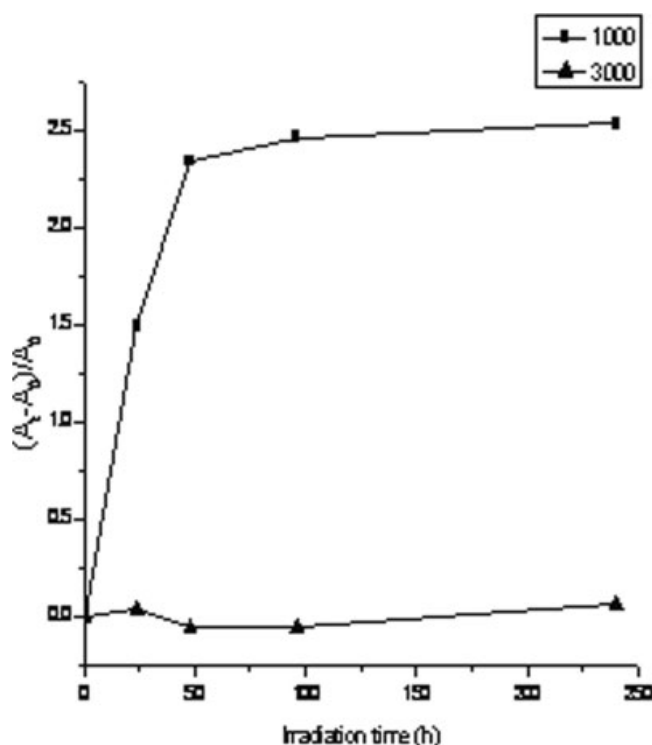
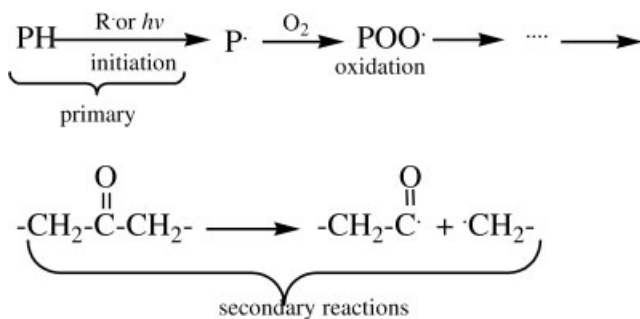


Figure 4 Changes of the absorbance at 421 nm for PVC: (a) $\overline{DP} = 1000$, (b) $\overline{DP} = 3000$ after 0–336 h of UV-irradiation. A_0 , the absorbance of the unirradiated sample; A_t , the absorbance after time t irradiation.

formed in primary processes, especially hydrogen and chlorine atoms neighboring unsaturated bonds or carbonyl groups are susceptible to break off, which are presented in the nondegradation process of PVC. For example, the C–Cl bond energy in saturated organic compounds is ~ 330 kJ/mol, but C–Cl vicinal to C=C (allylic chlorines) is lower (230–310 kJ/mol).¹⁹ The next step (propagation) is the fast reaction of macroradicals (P^\cdot) with atmospheric oxygen, which leads to carbonyl group formation and finally to chain breaking with a reduction in the polymer molecular weight:



where PH is the polymer molecule.^{5,19} The appearance of the oxidative substances on the surface of weathered samples was an indication of oxidative photodegradation; it provided supporting evidence of chemi-

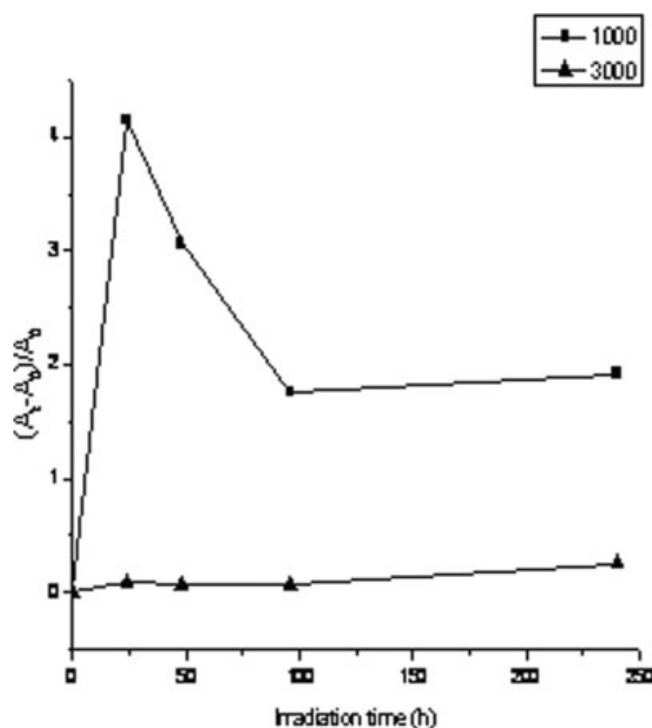


Figure 5 Changes of the absorbance at 300 nm for PVC: (a) $\overline{DP} = 1000$, (b) $\overline{DP} = 3000$ after 0–336 h of UV-irradiation. A_0 , the absorbance of the unirradiated sample; A_t , the absorbance after time t irradiation.

cal composition changes on the surface of weathered samples. This photooxidation degradation was also reflected in the formation of exposed sample, to a certain extent, by the FTIR spectra. Simultaneously, the intensities of C–Cl bands at $600\text{--}700$ cm^{-1} gradually decreased, which is additional evidence of the elimination of HCl from PVC under UV-irradiation.^{20,36}

An attempt was made to correlate the carbonyl absorption at ~ 1730 cm^{-1} and C–Cl absorption at ~ 692 cm^{-1} in order to understand the effect of the time of UV-irradiation on photodegradation of PVC. This was achieved by comparing the evolution of the

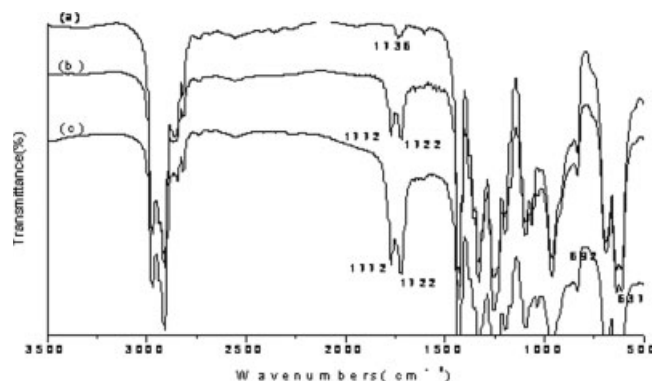


Figure 6 Infrared spectra of PVC films ($\overline{DP} = 1000$) cast from THF with increasing time of exposure to UV-irradiation: (a) unirradiated PVC film; (b) PVC film irradiated for 96 h; (c) PVC film irradiated for 240 h.

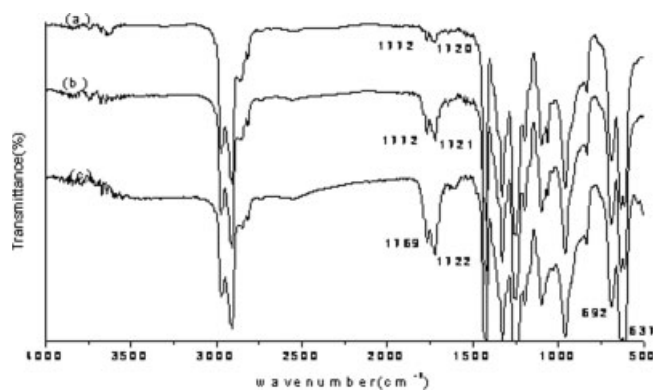


Figure 7 Infrared spectra of PVC films ($\overline{DP} = 3000$) cast from THF with increasing time of exposure to UV-irradiation: (a) unirradiated PVC film; (b) PVC film irradiated for 96 h; (c) PVC film irradiated for 240 h.

normalized absorption band at $\sim 1730 \text{ cm}^{-1}$ (carbonyl groups) and 692 cm^{-1} (C—Cl) for both unweathered and weathered samples. The band at $\sim 1426 \text{ cm}^{-1}$ of C—H groups in the neat PVC was used as an internal reference to normalize the results.^{25,31,36,37} The carbonyl index or normalized carbonyl absorption $\sim 1730 \text{ cm}^{-1}$ was calculated using the following equation:

$$\text{Carbonyl index} = \left(\frac{A_{1730}}{A_{1426}} \right),$$

where A_{1730} is the integrated surface areas of the absorption bands at $\sim 1730 \text{ cm}^{-1}$, and A_{1426} is the integrated surface areas of the absorption bands at $\sim 1427 \text{ cm}^{-1}$.

Moreover, the C—Cl index or normalized absorption bands $\sim 692 \text{ cm}^{-1}$ was calculated using the following equation:

$$\text{C—Cl index} = \left(\frac{A_{692}}{A_{1426}} \right),$$

where A_{692} is the integrated surface areas of the absorption bands at $\sim 692 \text{ cm}^{-1}$.

Table I shows the normalized carbonyl absorption at 1730 cm^{-1} (carbonyl index) with the different average degrees of polymerization. The concentrations of oxidative substances (carbonyl index) were found to increase quickly with UV-irradiation time. The carbonyl index of PVC ($\overline{DP} = 1000$) changes from 7.8 to 62.0 and 164.0, when the UV-irradiation time changes from 0 h to 96 h and 240 h. The change in the carbonyl index was an indication of oxidative photodegradation.²⁰ However, the carbonyl index of PVC ($\overline{DP} = 3000$) changes from 14.0 to 53.8 and 112.0, when the UV-irradiation time changes from 0 h to 96 h and 240 h. The greater increase in the carbonyl index in PVC ($\overline{DP} = 1000$) compared with PVC ($\overline{DP} = 3000$) suggests that the PVC ($\overline{DP} = 1000$) is more subject to photooxidation. It should be mentioned that it is not

TABLE I
Changes of Normalized Carbonyl Absorption at 1730 cm^{-1} (Carbonyl Index) with the Different Average Degrees of Polymerization and UV-Irradiation Time

PVC sample, \overline{DP}	UV-irradiation time (h)	Carbonyl index, $\frac{A_{1730}}{A_{1426}} \times 100$
1000	0	7.8
	96	62.0
	240	164.0
3000	0	14.0
	96	53.8
	240	112.0

inconsistent with the results of the changes of M_n . The reasons are as following: The PVC ($\overline{DP} = 3000$) is produced by copolymerizing with a certain quantity of crosslinking agent that contains carbonyl groups, double bonds, ether bonds, and so on, so chain scission reactions occur more easily, leading to the more rapid reduction of M_n . The main photodegradation reactions for PVC ($\overline{DP} = 1000$) are dehydrochlorination, and then photooxidation, so the carbonyl index increases more quickly, whereas the M_n decreases more slowly. In addition, for unirradiated PVC, the carbonyl index of PVC ($\overline{DP} = 3000$) is much higher than that of PVC ($\overline{DP} = 1000$). It is because that the PVC ($\overline{DP} = 1000$) is homopolymer, whereas the PVC ($\overline{DP} = 3000$) is a copolymer that contains carbonyl groups, double bonds, ether bonds, and so on. The results of analysis for C—Cl index are shown in Table II for the different average degrees of polymerization PVC with the different UV-irradiation time. The C—Cl index of PVC ($\overline{DP} = 1000$) changes from 53.6 to 40.8, when the UV-irradiation time changes from 0 h to 240 h. However, the change of PVC ($\overline{DP} = 3000$) in which the dehydrochlorination does not occur is very little. As the decrease of C—Cl index, PVC ($\overline{DP} = 1000$) is more subject to dehydrochlorination as dehydrochlorination accelerates photooxidation. Therefore, it is suggested that the mechanism of photodegradation of the higher \overline{DP} of PVC ($\overline{DP} = 3000$) is different from the lower \overline{DP} of PVC ($\overline{DP} = 1000$). The reaction of photodegradation of the higher \overline{DP} of PVC

TABLE II
Changes of Normalized C—Cl Absorption at 692 cm^{-1} with the Different Average Degrees of Polymerization and UV-Irradiation Time

PVC sample, \overline{DP}	UV-irradiation time (h)	C—Cl index, $\frac{A_{692}}{A_{1426}} \times 100$
1000	0	53.6
	96	52.9
	240	40.8
3000	0	52.8
	96	54.5
	240	53.5

TABLE III
TG Results for PVC Decomposition with Different
Irradiation Time ($\overline{DP} = 1000$)^{*}

Temp (°C)	Irradiation time (h)		
	0	96	240
T ₁₀	206	292	273
T ₂₀	295	306	297
T ₃₀	303	317	309
T ₄₀	310	328	321
T ₅₀	321	340	333
T ₆₀	335	358	351
T ₇₀	352	433	444
T ₈₀	433	475	481
T _{p1}	301	312	323
T _{p2}	304	470	466

* T_{10,20,30,40,50,60,70,80}, temperature corresponding to 10,20,30,40,50,60,70,80 wt % of weight loss, respectively; T_p, peak temperature corresponding to a maximum weight loss rate.

($\overline{DP} = 3000$) is chain breaking. What is more, the carbonyl groups are photosensitive and undergo Norrish type I and type II reactions.⁵ The main photodegradation reaction for the lower \overline{DP} of PVC is dehydrochlorination in the initial stage of UV-irradiation, and then the crosslinking and chain scission reactions occurred after long irradiation.

Thermogravimetric analysis

From TG (thermogravimetric) and DTG (derivative thermogravimetric) curves recorded in nitrogen flow (Fig. 8), it is observed that all the samples decompose at the temperature from 50°C to 500°C. A two-stage weight loss is observed. The TG curves of all PVC films show that the first stage, located between 50°C and 380°C, represents >70 wt% weight loss. The second stage, ranging from 380°C to 500°C, represents ~25 wt% weight loss with ~5.0 wt% for the weight of the final solid residue. Corresponding to the two-stage weight loss on the TG curves, two peaks are observed on the DTG curves. For example, on the DTG curve of unirradiated PVC where the stages are more clearly visible, the first peak at 304°C, and the second peak at 473°C. Similar to the unirradiated PVC, two stages of weight loss can be observed on the TG curves of PVC, which are irradiated for 96 h and 240 h. Correspondingly, two peaks can be observed on the DTG curves. More detailed results are presented in Table III. Many studies have shown that the thermal degradation of PVC proceeds in two distinct stages of weight loss: a stage within the temperature range of 50–360°C and another stage occurring within the range of 360–500°C.^{38–41}

PVC thermal decomposition with different irradiation time is shown in Figure 8 and Table III. UV-irradiation time appears to have an obviously significant

influence on the two peaks during PVC thermal decomposition. In the first stage, the DTG peak temperature of maximum weight loss rate (T_{p1}) with 240 h irradiating reached at a higher temperature, T_{p1} = 323°C as with respect to T_{p1} = 304°C before irradiating and T_{p1} = 312°C with 96 h irradiating. It is suggested that the first stage corresponding to dehydrochlorination with subsequent formation of conjugated double bonds,^{40–42} accompanied by the formation of small amounts of hydrocarbons, mainly aromatics, such as benzene, toluene, naphthalene, indene, anthracene, and *o*-xylene.^{38,39,41} This difference may be explained by some unstable structures, such as unsaturated double bond, branched chain eliminated, and so on, during long irradiation, which retard dehydrochlorination, as well as by the formation of small amounts of hydrocarbons. At the same time, it is indicated that UV-irradiation causes the PVC degradation, which is in agreement with the results obtained by means of the viscosity-average molecular weight analysis and FTIR. In the second stage, however, there are no significant differences in the decomposition of various PVC with different irradiation time. Because in this stage it was reported to correspond to a set of oxidative reactions occurs on dehydrochlorinated polymer chains⁴⁰ and the scission of polyene sequences formed during the second stage,³⁸ which was characteristic for each sample.⁴⁰ In the end, a black carbonaceous residue is obtained.

Figure 9 shows the results of TG/DTG of the PVC sample irradiated 240 h with $\overline{DP} = 1000$ and 3000 measured during heating from 50–500°C at the rate 20°C·min⁻¹ in nitrogen. From DTG results presented in Figure 8, it is found that no substantial differences were observed by thermal analysis in the thermal behaviors of the sample with different average degrees of polymerization. Therefore, the degradation substances of both samples are probably similar.

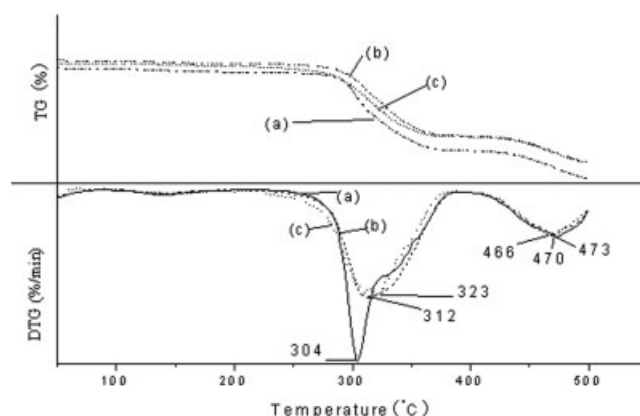


Figure 8 TG and DTG curves of PVC thermal decomposition in nitrogen for different irradiation time: (a) = 0 h, (b) = 96 h, (c) = 240 h.

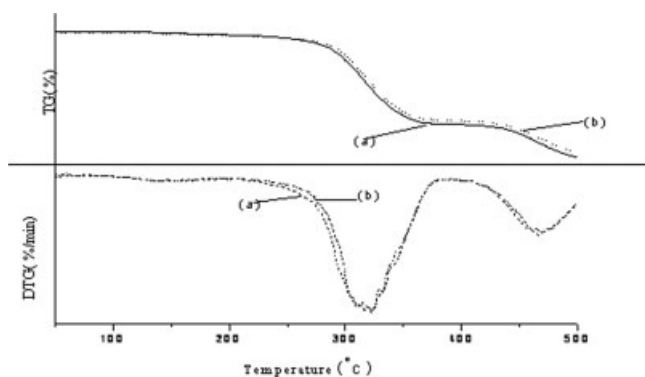


Figure 9 TG and DTG curves of PVC (irradiated 240 h) thermal decomposition in nitrogen for the different average degrees of polymerization: (a) $\overline{DP} = 1000$, (b) $\overline{DP} = 3000$.

Contact angle analysis

Although viscosity-average molecular weight measurements, UV-vis, and FTIR spectroscopy provided evidence of photodegradation, these methods have a main drawback, i.e., they do not indicate the surface conditions, such as the functional groups on the surface. The method of static contact angle (θ) measurement was used to calculate the polymer surface free energy. The changes in the contact angle and surface free energy in UV-irradiated PVC are presented in Tables IV and V. Contact angle is a measure of non-covalent forces between liquid and the first monolayer of material. Thus, in the case of strong interactions between phases, the liquid drop spreads on the solid and wets it. The quality of the surface, its roughness, and porosity strongly influences the contact angle values.²¹ The wettability of diiodomethane on PVC is much higher (small θ values) than water (higher θ values), because the molecules of a highly polar liquid are less attracted by PVC macromolecules, which have relatively low polarity. It can be seen that the surface free energy (γ_s) and polar component of surface free energy (γ_s^p) strongly increase, but the dispersive component (γ_s^d) decreases a little after UV-irradiation (Table V). γ_s^p is the polar component of surface energy γ_s ; it is attributed to the formation of polar groups and enrichment of surface in functional groups.³¹ This high increase of PVC polarity indicates that an efficient oxidation on polymer

surface occurs. The polymer surface is activated by UV-irradiation, which explains such efficient oxidation leading to the formation of different types of carbonyl, hydroxyl, and hydroperoxide groups that strongly influence $\gamma_s^{p21,31}$. γ_s^d is the dispersive component of surface energy, and the density of polymer surface has great influence on γ_s^{d31} . For the PVC ($\overline{DP} = 3000$), γ_s^d increases with the increase of irradiation time, because the main photodegradation reactions are crosslinking and chain scission reactions, leading to the density of polymer surface and γ_s^d both increase with irradiation time. However, for the PVC ($\overline{DP} = 1000$), γ_s^d decreases with the increase of irradiation time, because the main photodegradation reactions are dehydrochlorination and chain scission reactions, leading to the decrease of the density of the polymer surface and of γ_s^d .

It should be mentioned that the γ_s^p for unirradiated PVC are somewhat varied with the different \overline{DP} . The γ_s^p of PVC ($\overline{DP} = 1000$) is 2.88 mN/m, while the γ_s^p of PVC ($\overline{DP} = 3000$) is 8.52 mN/m. The reason is that the PVC ($\overline{DP} = 3000$) which is produced by copolymerizing with some DAP or DAM itself contains some functional groups, such as carbonyl. So there are some differences between the different \overline{DP} of PVC during the process of photodegradation. It is well known that during the photodegradation of PVC a lot of low-molecular products are formed.⁵ Some are volatile, but others, which are accumulated in the outer layer, can be soluble in liquids used for θ measurements. Another reason is the possibility of formation of small invisible defects in the sample. Surface deformation, including the creation of small cracks, crazes, and voids, reflects the contact angle measurements. SEM was used to detect the surface morphology of the irradiated PVC films.

SEM analysis

To examine the surface morphology of the irradiated polymer films, SEM analysis was performed. SEM confirms the viscosity-average molecular weight measurement, UV-vis spectroscopy, FTIR, TGA, contact angle measurement results, showing that the surface morphology in PVC is dependent on the \overline{DP} , as well as the time of UV-irradiation. Figures 10(a)–(c) and

TABLE IV
Contact Angles ($^\circ$) of Different Liquids on the Different Average Degrees of Polymerization of PVC after UV-Irradiation during 0–336 h

Liquid used	Contact angle of liquid on PVC film after UV-irradiation					
	$\overline{DP} = 1000$			$\overline{DP} = 3000$		
	0 h	96 h	240 h	0 h	96 h	240 h
Water	83.9	74.7	66.0	71.8	69.1	64.3
Diiodomethane	36.7	30.4	28.7	36.8	35.6	30.6

TABLE V
Surface Free Energy (γ_s) and Its Dispersive (γ_s^d) and Polar (γ_s^p) Components in UV-Irradiated PVC Films with Different Average Degrees of Polymerization

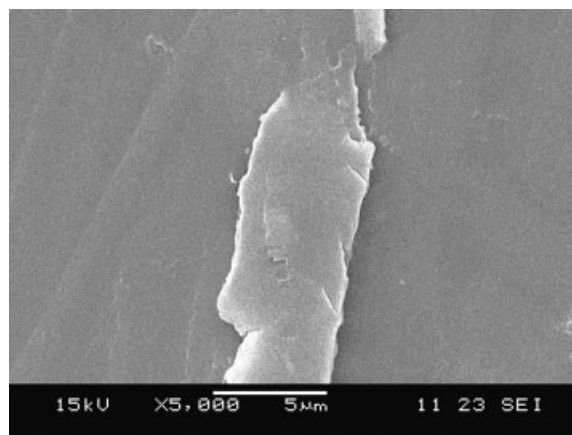
Surface free energy (mN/m)	$\overline{DP} = 1000$			$\overline{DP} = 3000$		
	0 h	96 h	240 h	0 h	96 h	240 h
γ_s	43.50	46.21	51.06	44.86	46.27	49.78
γ_s^d	40.62	39.91	38.57	36.34	36.46	37.94
γ_s^p	2.88	6.30	12.49	8.52	9.81	11.84

11(a)–(c) show the top surface which was irradiated directly by xenon arc and bottom surface which was unirradiated directly images of the PVC ($\overline{DP} = 1000$) that were irradiated for 0 h, 96 h, and 240 h under air, respectively. Before irradiation [Fig. 10(a)], the surface of PVC film is essentially smooth and neat on the sub-micron scale. For PVC film irradiated for 96 h [Fig. 10(b)], cracks apparently develop on the surface. When irradiated to 240 h [Fig. 10(c)], it can be seen obviously that cracks have increased in both length and depth. Meanwhile, the rest of the surface roughens dramatically. Surface roughening does not proceed simply by an erosive process that shifts the geometric borderline of the microscopic surface; rather, it is processed by a gradual disintegration of the compact material directly via the formation of cracks. These may arise from the formation of HCl during the elimination reactions or other volatile degradation substances.^{3,43} The bottom surface of the irradiated PVC films [Figs. 11(a)–(c) and 13(a)–(c)] shows much less degradation, because the penetrating light intensity into the bottom of the composite films decreased quickly at the initial stage and the growing cracks scattered out more incident light as the degradation process. Therefore, the bottom surface of the film was protected from the irradiation, showing less degradation.³²

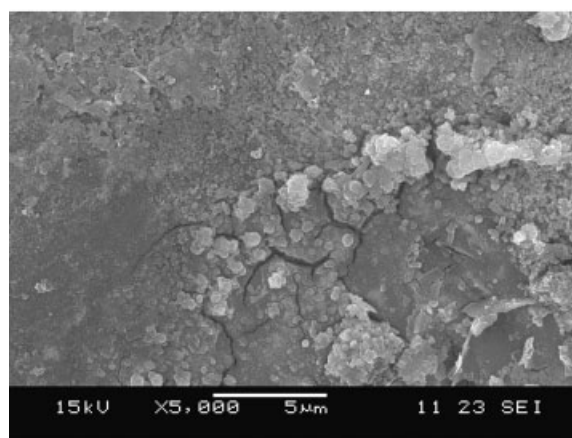
Figures 12(a)–(c) and 13(a)–(c) show the top and bottom surface images of the PVC ($\overline{DP} = 3000$) that were irradiated for 0 h, 96 h, and 240 h under air, respectively. The phenomenon is similar with the above, but there are some differences. When irradiated to 96 h [Fig. 12(b)], there are no evident cracks. Until irradiation for 240 h [Fig. 12(c)], some cracks appear. However, cracks are obviously less than the PVC films ($\overline{DP} = 1000$) irradiated for 240 h. It is suggested that in the initial stage of UV-irradiation there is not much HCl evolution. From these facts, it is reasonable to deduce that the main photodegradation reaction for the lower \overline{DP} of PVC is dehydrochlorination in the initial stage of UV-irradiation, while the main reaction for the higher \overline{DP} of PVC is the cross-linking and chain scission not dehydrochlorination in the initial stage of UV-irradiation, as indicated by the results of FTIR, UV-vis spectroscopy, and contact angle measurement.

CONCLUSIONS

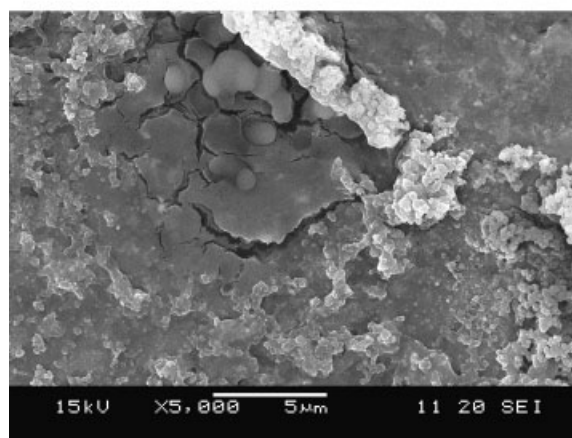
From the results of viscosity-average molecular weight determination, UV-vis spectroscopy, FTIR, TGA, contact



(a)

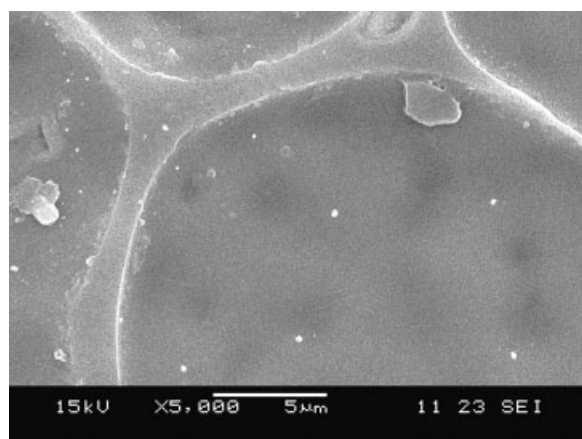


(b)

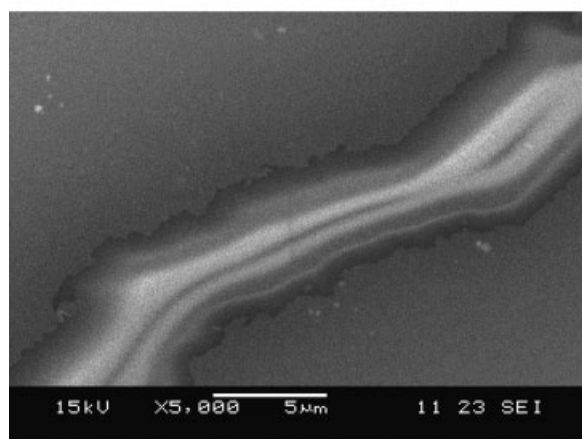


(c)

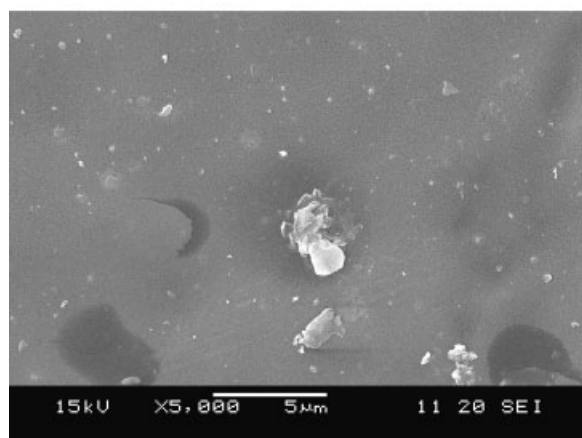
Figure 10 SEMs of the top surface of the PVC films with the direct irradiation ($\overline{DP} = 1000$) with different irradiation time: (a) before irradiation; (b) irradiated 96 h; (c) irradiated 240 h.



(a)



(b)

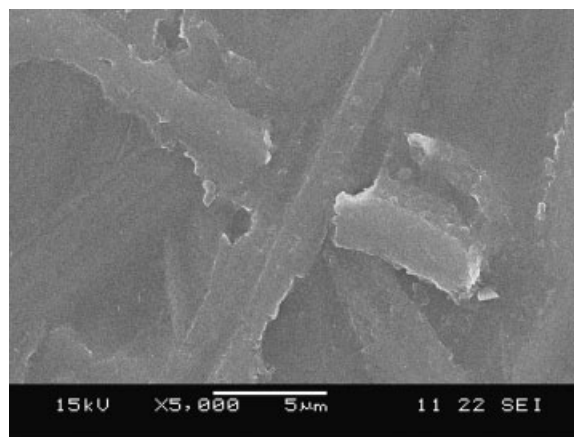


(c)

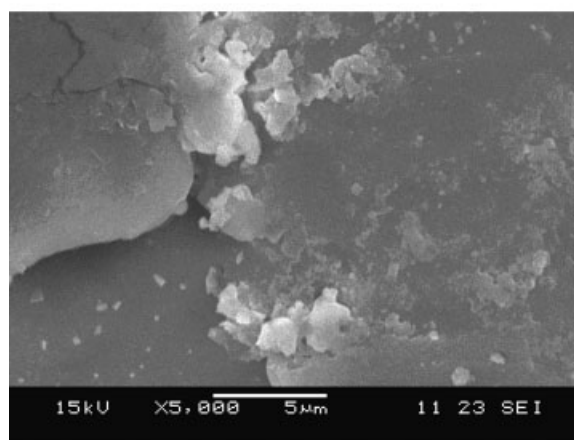
Figure 11 SEMs of the bottom surface of the PVC films ($\overline{DP} = 1000$) with different irradiation time: (a) before irradiation; (b) irradiated 96 h; (c) irradiated 240 h.

angle measurement, and SEM, it is found that the photodegradation mechanism of the lower \overline{DP} of PVC ($\overline{DP} = 1000$) is different from the higher \overline{DP} of PVC ($\overline{DP} = 3000$). It is because that the lower \overline{DP} of PVC is homopolymer, while the higher \overline{DP} of PVC often is

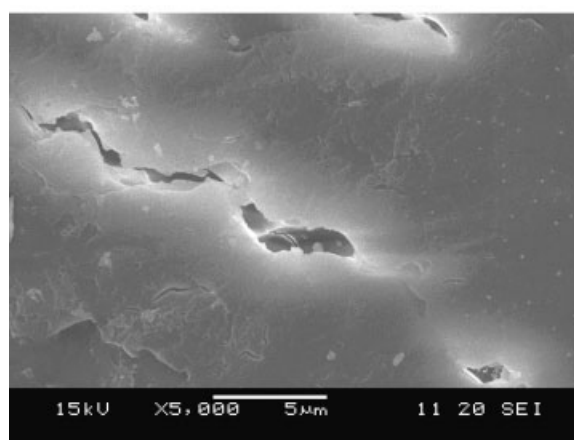
produced by copolymerizing with a certain quantity of crosslinking agent (e.g., DAP and DAM). The main photodegradation reaction for the lower \overline{DP} of PVC is dehydrochlorination in the initial stage of UV-irradiation.



(a)

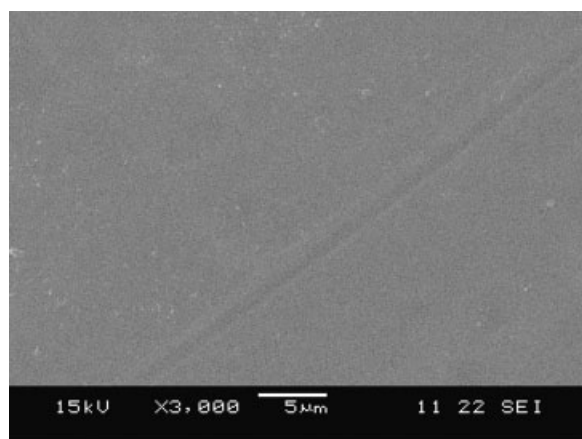


(b)

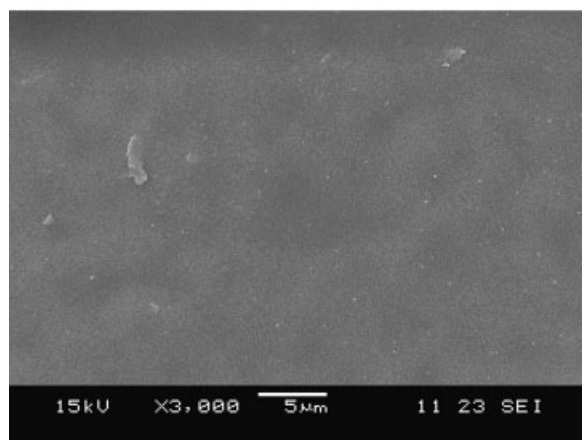


(c)

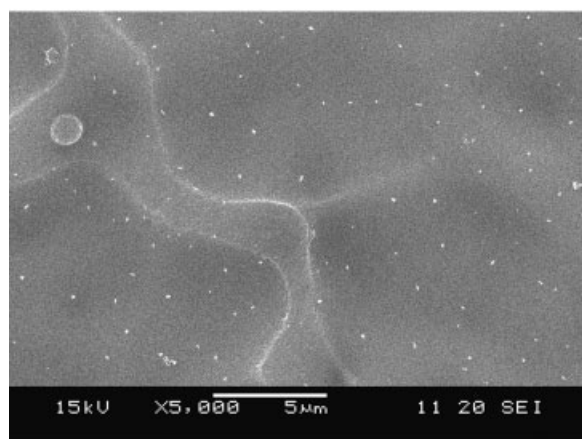
Figure 12 SEMs of the top surface of the PVC films ($\overline{DP} = 3000$) with the direct irradiation with different irradiation time: (a) before irradiation; (b) irradiated 96 h; (c) irradiated 240 h.



(a)



(b)



(c)

Figure 13 SEMs of the bottom surface of the PVC films ($\overline{DP} = 3000$) with different irradiation time: (a) before irradiation; (b) irradiated 96 h; (c) irradiated 240 h.

tion, then the crosslinking and chain scission reactions occurred after long irradiation. For the higher \overline{DP} of PVC, the main reaction is the crosslinking and chain scission, rather than dehydrochlorination in the initial stage of UV-irradiation. At the same time, the

photostabilization of PVC ($\overline{DP} = 3000$) is better than the PVC ($\overline{DP} = 800, 1000, \text{ and } 1300$).

The viscosity-average molecular weights of the four kinds of PVC decreased rapidly with the UV-irradiation time increasing. However, there were some different variation tendencies between the lower \overline{DP} and the higher \overline{DP} of PVC in the UV-irradiation process. UV-vis analysis shows that the double bonds of the lower \overline{DP} of PVC increase rapidly with the irradiation time and the higher \overline{DP} of PVC changes very little with the same condition. According to FTIR analysis, the carbonyl index increases quickly with the irradiation time. For the PVC ($\overline{DP} = 1000$), the C—Cl index decreases quickly but the C—Cl index changes a little for the PVC ($\overline{DP} = 3000$). The TGA observations confirm the thermal degradation of PVC process, but irradiated PVC shows greater heat stability. The increase in the polar component γ_s^p of PVC is attributed to the formation of carbonyl and hydroxyl groups in the photodegraded PVC with increased irradiation time. The density of the polymer surface has a great influence on the dispersive component γ_s^d . The γ_s^p of PVC ($\overline{DP} = 1000$) is higher than that of PVC ($\overline{DP} = 3000$). The reason is that the PVC ($\overline{DP} = 3000$) which is produced by copolymerizing with some DAP or DAM itself contains some functional groups such as carbonyl γ_s^d of PVC ($\overline{DP} = 3000$) increases with the increase of irradiation time, while γ_s^d of PVC ($\overline{DP} = 1000$) decreases. It suggests that the photodegradation varying with different \overline{DP} of PVC is different. The experimental findings and SEM analyses indicated that the bottom surface of the irradiated PVC films showed much less degradation compared with the top surface with the direct irradiation, as the penetrating light intensity into the bottom of the composite films decreased quickly at the initial stage and the growing cracks scattered out more incident light as the degradation proceeded.

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