

Polypropylene Plasticization and Photodegradation with a TiO₂/Poly(ethylene oxide)/Methyl Linoleate Paint Photocatalyst System

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ABSTRACT: The photodegradation of polypropylene (PP) film was performed by a TiO₂/polyethylene oxide (PEO)/plant oil paint photocatalyst system. The photodegradation underwent two stages of development as follows: Initially PP reacted with linoleic acid radical originated from the photoreaction of plant oil component. Second, the linoleic acid graft-polymer was decomposed, and then PP chain scission was caused. The process was studied using methyl linoleate (ML) in detail. The melting point of the 24 h-photodegraded PP slightly decreased, and those of the 48 h- and 96 h-ones drastically did as compared with the pristine PP. The crystallinity (χ_c) decreased at the 48 h photodegradation time and drastically increased at the 96 h one. The 24 h-photodegraded PP showed the 77% Young's modulus, 88% tensile strength, and 103% strain at break values to those of the pristine PP. The ML graft-polymerization and decomposition brought about the PP plasticizing and chemi-crystallization, causing the PP degradation. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39909.

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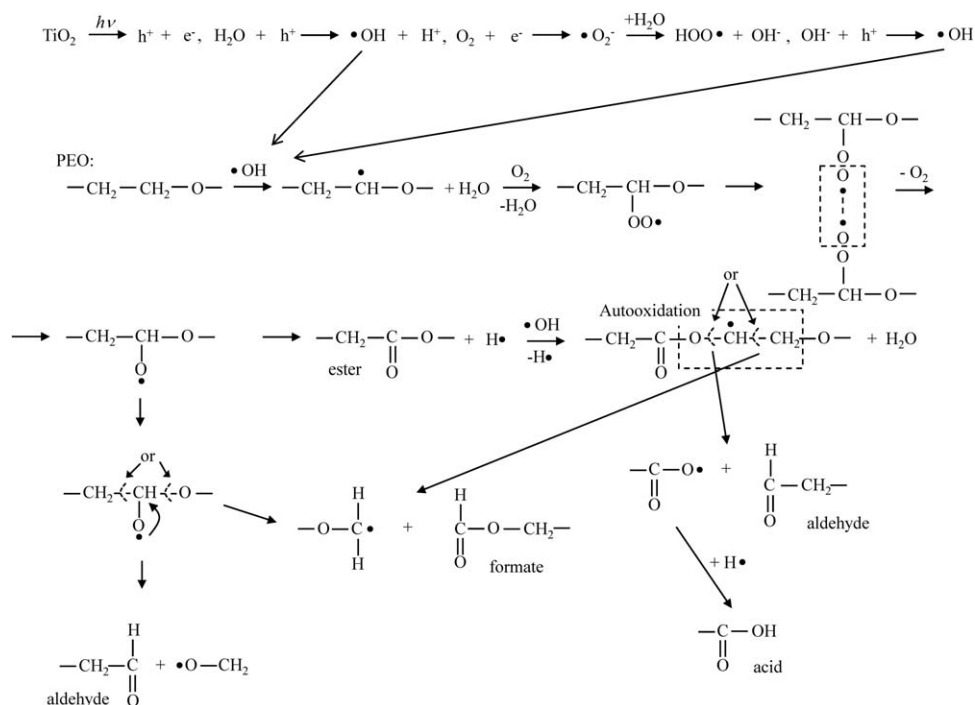
INTRODUCTION

Synthetic polymeric materials have been widely used because of low density, good processability and low cost etc. The commercial market has been developed for a long time, and intensive efforts have been expended on the stabilization of the materials by scientists and engineers. As a result, polymeric materials are given an enormous stability. The biodegradability is considerably less, and the materials easily accumulate in environment. Therefore, the intense use has given rise to an intensive interest in new polymer systems such as photo- and/or bio-degradable materials.^{1–11} Novel degradation method has attracted much attention from the viewpoint of environmental compatibility.

PP is one of common polymeric materials and is widely used as industrial ones. Although PP has many attractive properties, the waste one does not decompose in landfills and is not good for the environment. It is a nonbiodegradable polymer. Generally large molecule such as PP cannot easily enter into cells of microorganisms. Therefore, PP is hard to be metabolized in microorganisms. If it is spontaneously degraded to low molecular weight products, the biodegradability certainly appears. In fact, we reported that PP showed biodegradability by a novel pro-oxidant.^{10,11} The mechanism of the PP biodegradation involves two stages which are abiotic oxidation and microbial oxidation, and its rate strongly depends on the abiotic oxidation

stage initiated by pro-oxidant. Therefore, the pro-oxidant development is most important for preparation of such biodegradable PP.

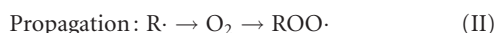
In order to acquire biodegradability, the PP degradation must be able to promptly occur under a mild condition. It seems that the photodegradation is desirable for the abiotic oxidation stage. PP photodegradation using TiO₂ photocatalysis has been studied.^{12–15} As shown in Scheme 1, TiO₂ is photoexcited and produces an electron and positive hole. The electron and positive hole react with H₂O and O₂, and then form OH•.^{16,17} OH• has a high reactive ability and initiates the PP degradation.^{13,16} The degradation rate is, however, considerably slow because of non-existence of H₂O in PP matrix. The loading effect of TiO₂ on PP degradation is not so noticeable. In order to improve the degradation rate, we added PEO to the TiO₂ photocatalyst.^{7,8} PEO is hydrophilic and can adsorb moisture in the atmosphere. The TiO₂ can react with an adsorbed H₂O in the PEO phase, resulting that the OH• produces. Moreover, as shown in Scheme 1, the reaction of the PEO and OH• produces acid and aldehyde compounds, which bring about the facilitation of the PP degradation.^{18,19} In addition, H₂O is reproduced, and then these reactions are repeated until the PEO component is completely consumed. The higher PP photodegradation rate is due to the coexistence of TiO₂ and PEO components.^{7,8} The loading



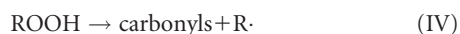
Scheme 1. Degradation mechanism for PEO/TiO₂ under light irradiation.

method has, however, been confined to melt mixing with PP material. The melt mixing method has been required due to poor diffusion of the photodegradation initiator, and the usage of the mixing-type catalyst has limited application. Development of the paint-type photocatalyst has been required for commonly-used PP product.

In our previous work,²⁰ we succeeded in photodegradation of a polystyrene (PS) film with a TiO₂/PEO/ML paint photocatalyst system. The additional ML component certainly blocked a PS crosslinking reaction and accelerated the photodegradation rate. PP degradation mechanism is called as “autooxidation”^{21–25} and is similar to that of PS. There is much literature on mechanisms of autooxidation.^{21–25} Many researchers agree fundamentally with the following mechanistic scheme:



Chain branching (including chain scission):



These are a kind of cycle reaction. Oxidative degradation advances with this autooxidation. Among these reaction steps, the hydroperoxide decomposition (IV) is the rate-determining step. A facilitation of the hydroperoxide decomposition leads to a facilitation of degradation. However, PP is semi-crystalline unlike amorphous PS. Degradation advance of crystalline polymer is generally slower than that of amorphous one. In addition,

PP crystalline part was frequently increased during photodegradation.^{26–31} The behavior is due to crystal growth using the PP segments released by the chain scission and has been called as chemi-crystallization. PP degradation process is more complicated than that of PS one.

In this study, photodegradation of PP film was performed by painting of novel photocatalyst systems based on TiO₂/PEO. Instead of costly ML, a commercial plant oil containing a ML substitute (linoleic acid) was used as the component of the photocatalyst system, and the additive effect was studied in the photodegradation activity. An effect of the TiO₂ size on the activity was studied as well. The detailed degradation process was confirmed with the TiO₂/PEO/ML photocatalyst paint to simplify the system. These studies were performed with a Fourier transform infrared (FTIR), scanning electron microscope (SEM), differential scanning calorimetry (DSC), tensile testing, and nuclear magnetic resonance (NMR) spectroscopy.

METHODS

Materials

PP (meso pentad fraction=98%) was supplied by Japan Polypropylene Co. The number-average molecular weight (M_n) and the polydispersity (M_w/M_n) were 4.6×10^4 and 5.7, respectively. The PP was used without stabilizers. PEO was purchased from Wako Pure Chemical Industries, Ltd. The average molecular weight was 5.0×10^5 . Normal size TiO₂ (normal-TiO₂: anatase-type, diameter = ca. 5 μm) and nano size TiO₂ (nano-TiO₂: anatase-type, particle size < 25 nm) were purchased from Wako Pure Chemical Industries, and Sigma-Aldrich, respectively. Plant oil (canola oil: RIKEN Nosan-Kako) was commercially obtained.

ML was purchased from Wako Pure Chemical Industries. These were used without further purification.

Preparation of PP film

The PP pellets were molded into the film ($50 \times 50 \times 0.05 \text{ mm}^3$) by compression molding at 190°C under 5 MPa for 5 min.

Paint of Photocatalyst System on PP Film

The paint conditions on the PP film are as follows: (i) 50 ml ethanol solution containing 5 mg normal- TiO_2 and 500 mg PEO was prepared (normal- TiO_2/PEO), (ii) 25 ml ethanol + 25 ml plant oil or ML solution containing 5 mg normal- TiO_2 and 500 mg PEO was prepared (normal- $\text{TiO}_2/\text{PEO}/\text{plant oil}$ or ML), (iii) 25 ml ethanol + 25 ml plant oil or ML solution containing 0.2 or 0.05 mg nano- TiO_2 and 500 mg PEO was prepared (nano- $\text{TiO}_2/\text{PEO}/\text{plant oil}$ or ML). The solution was heated up to 50°C to be completely dissolved and then was painted on the film surface. The paint amounts were 0.1 g-photocatalyst system/g-film for 0.05 mm thickness film with the same surface ($50 \times 50 \text{ mm}$).

Photodegradation Condition

The $50 \times 50 \text{ mm}^2$ films were put into a vial (Pyrex reactor). The UV treatment was performed with a Riko rotary photochemical reactor (RH400-10W, Riko-Kagaku Sangyo) equipped with a high-pressure mercury vapor lamp of 400 W (UVL-400HA ultrahigh-pressure mercury lamp with an intensity of $5 \text{ mW}/\text{cm}^2$; Riko-Kagaku Sangyo). The treatment was performed at 30°C in air.

Fourier Transform Infrared (FTIR) Analysis

All film samples were washed with methanol solvent and dried before the FTIR measurement. The IR spectra of 16 scans were measured with an FTIR spectrometer (Perkin-Elmer Spectrum One) at a resolution of 2 cm^{-1} over the full mid-IR range ($400\text{--}4000 \text{ cm}^{-1}$).

Scanning Electron Microscope (SEM) Observation

SEM observation was carried out with a JEOL JSM-5800 at 20 kV. The film surface was sputter-coated with gold.

Differential Scanning Calorimetry (DSC) Measurement

All film samples were washed with methanol solvent and dried before the DSC measurement. The DSC measurements were made with a Shimadzu DSC-60. The film samples of about 2 mg weight were sealed in aluminum pans. The measurements of the samples were carried out at heating and cooling rates of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere, respectively. From the thermogram, melting temperature (T_m) and fusion enthalpy (ΔH) were determined. The crystallinity (χ_c) of the PP part in the composite was obtained by using the relationship:

$$\chi_c = (\Delta H / \Delta H^\circ) \times 100 \quad (1)$$

where $\Delta H^\circ = 209 \text{ J/g}$ for 100% crystalline PP was taken.³²

Tensile Testing

All film samples were washed with methanol solvent and dried before the tensile testing. Stress-strain behavior was

observed using a SHIMADZU EZ-S at a cross-head speed of 3 mm/min. The sample specimens were cut with dimensions $30 \times 5 \times 0.05 \text{ mm}^3$ shape in which the gauge length was 10 mm. We chose the specialized specimen (like ISO reed-shape) to adapt to the size of our tensile testing machine. All of tensile testing were performed at 23°C . The values of Young's modulus were obtained from the slope of the stress-strain curve (until about 1% of the strain value). All results obtained were the average values of five measurements.

Nuclear Magnetic Resonance (NMR) Spectroscopy Measurement

NMR spectrum was measured using a JEOL EX-400 spectrometer at 20°C in chloroform-*d*. Tetramethylsilane was added and used as an internal chemical shift reference.

RESULTS AND DISCUSSION

The FTIR spectrum of the 24 h-irradiated PP sample with the normal- TiO_2/PEO paint did not show a peak assigned to carbonyl group (around 1713 cm^{-1}). The result indicates that the photocatalyst paint has no ability to initiate the PP degradation. In our previous work,⁷ melt mixing of PP, TiO_2 , and PEO was performed, and the PP/ TiO_2/PEO composite was obtained. When the photodegradation of the composite was performed, the PEO component was photo-catalytically degraded by the TiO_2 , and then H_2O , $\text{OH}\cdot$ species (initiator), acid and aldehyde (accelerator) compounds were produced. Since these products had an ability to facilitate PP photodegradation,^{18,19} the combination of TiO_2 and PEO caused the PP photodegradation rate to increase dramatically.⁷ The $\text{OH}\cdot$ has high molecular mobility due to its small molecular structure and is hydrophilicity. It seems that the $\text{OH}\cdot$ produced by the normal- TiO_2/PEO paint can hardly penetrate inside the PP having hydrophobicity. To perform PP photodegradation with TiO_2/PEO photocatalyst paint, the production of new radical species having ability to penetrate is required. Linoleic acid derivative such ML is known to be a nonpolar lipid model and has been widely used in antioxidant activity testing.^{33–35} Linoleic acid has allyl hydrogens and becomes a stable radical due to its radical resonance structure. Linoleic acid is suitable as source of such radical species since it has compatibility to penetrate inside PP. Commercial plant oil (canola oil) contains linoleic acid and is a kind of low cost oil. The plant oil addition would improve the permeability by the photocatalyst paint.

Figure 1 shows the FTIR spectra of the control and PP samples painted by the normal- $\text{TiO}_2/\text{PEO}/\text{plant oil}$ with 24 h- and 48 h-photodegradation times. The 24 h-photodegraded PP shows a high intensity peak (at 1745 cm^{-1}) assigned to linoleic acid group, suggesting that the linoleic acid component grafts on the PP. In addition, a low intensity peak appears at 1713 cm^{-1} . The peak position coincides with that of carbonyl (methyl ketone) group produced by PP degradation.⁷ The 48 h-photodegraded PP shows a decrease of the linoleic acid group peak intensity and increase of the carbonyl one. The result suggests that the grafted linoleic acid group is decomposed, and then the PP degradation occurs.

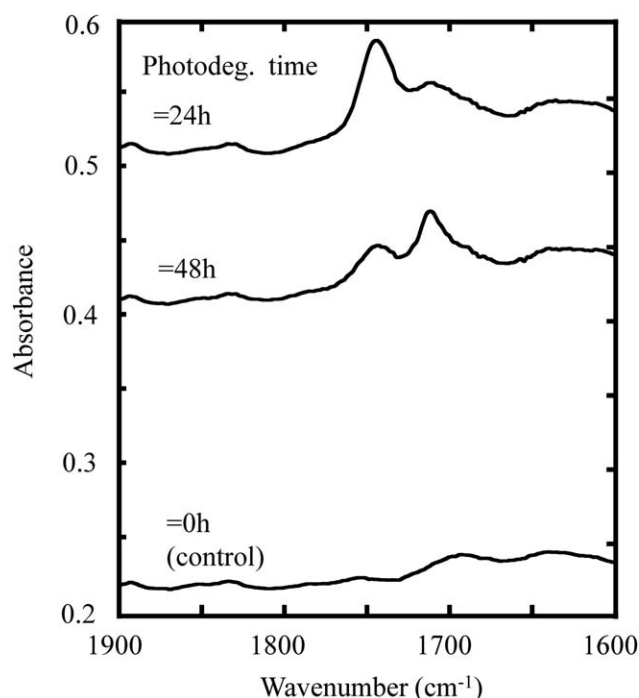


Figure 1. FTIR spectra of control and PP samples painted by normal-TiO₂/PEO/plant oil with various photodegradation time.

Figure 2 shows the comparison of FTIR spectra of the 48 h-photodegraded PP samples with the normal-TiO₂/PEO/plant oil and nano-TiO₂/PEO/plant oil paints. Nano size effect frequently brings about higher catalyst activity and leads to a decrease in catalyst use. As shown in Figure 2,

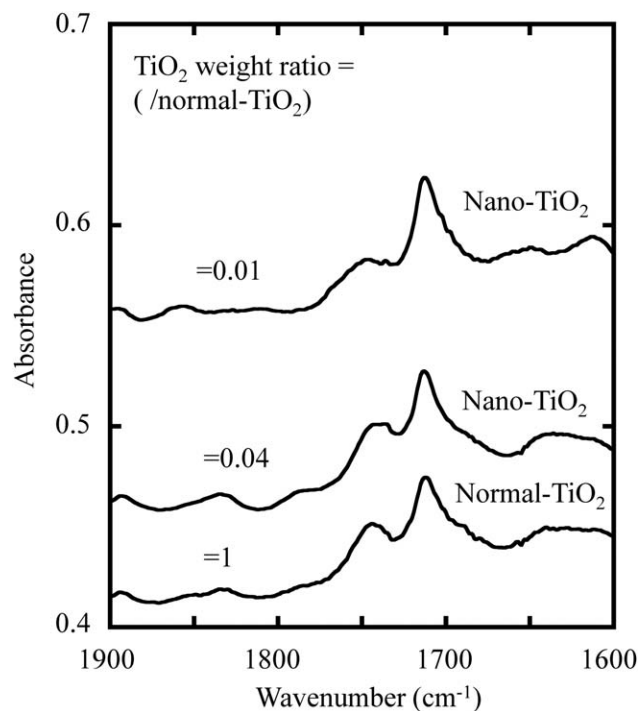


Figure 2. Comparison of FTIR spectra of 48h-photodegraded PP samples with normal-TiO₂/PEO/plant oil and nano-TiO₂/PEO/plant oil paints.

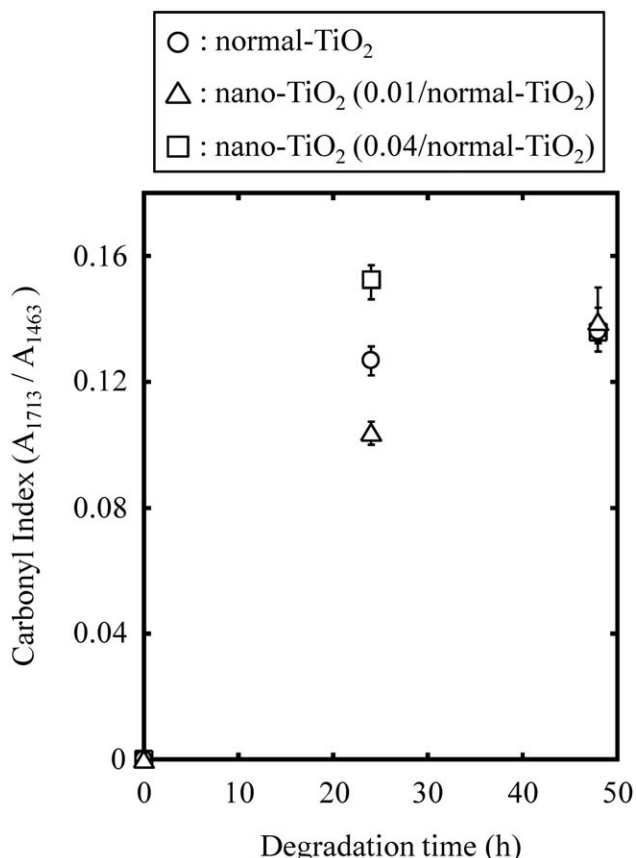


Figure 3. Carbonyl index versus photodegradation time for normal-TiO₂/PEO/plant oil and nano-TiO₂/PEO/plant oil paint samples: Average value, measurement times = 5.

the linoleic acid and methyl ketone group peak intensities of the nano-TiO₂ paint with the TiO₂ weight ratio=0.04/normal-TiO₂ are almost the same as those of the normal-TiO₂ one. In addition, the sample by the nano-TiO₂ paint with the lower weight ratio (0.01/normal-TiO₂) shows that the linoleic acid group peak intensity decreases, and methyl ketone one increases. The intensity of the methyl ketone group peak was normalized by carbonyl index calculated from the absorbance ratio at 1713 and 1463 cm⁻¹ (CH₂ scissoring peak in PP main chain).³⁶ As shown in Figure 3, although the value of the nano-TiO₂ paint sample with the TiO₂ weight ratio=0.01/normal-TiO₂ is lower than those of others at the 24 h, it becomes almost equal to them at the 48 h. These results show that there exists the nanosized (large surface area) effect in the PP photodegradation process. The TiO₂ photocatalytic reaction plays in an important role for the process, and the superiority of nano-TiO₂ use is obvious.

Figure 4 shows the SEM microphotographs of the 96 h-photodegraded surface of PP with the nano-TiO₂/PEO/plant oil paint. Many streaks can be observed on the PP surface. The magnified photograph shows that the streaks are composed of reticulation. The reticulation would be composed of the linoleic acid graft-polymer. As other possibility, it would be a recrystal part produced by chemi-crystallization because

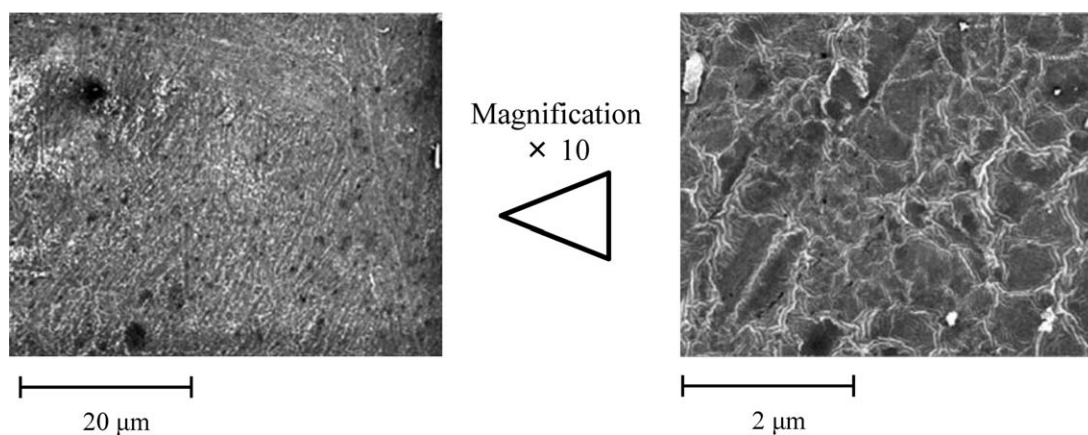


Figure 4. SEM microphotographs of 96h-photodegraded PP surface with nano-TiO₂/PEO/plant oil paint: Nano-TiO₂ concentration ratio = 0.04/normal-TiO₂.

reorganization of PP crystal part (chemi-crystallization) is caused by photodegradation process.^{26–31}

Figure 5 shows the thermal treatment dependences of FT-IR spectra of the 24 h-photodegraded PP samples with the nano-TiO₂/PEO/plant oil paint. The 1745 cm⁻¹ peak intensity rapidly decreases during the 2 h-thermal treatment at 100°C. Interestingly, the resonance between at 1720 and 1710 cm⁻¹ becomes flatness as compared with that of the no thermal treatment sample. This behavior suggests that the methyl ketone group on the PP chain grows up during the thermal treatment. The decrease of the linoleic acid peak intensity and increase of the methyl ketone one can be observed as

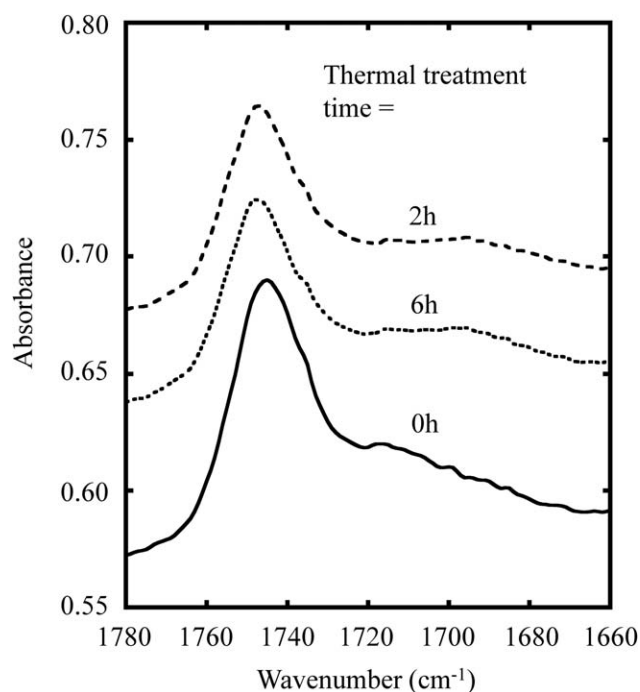
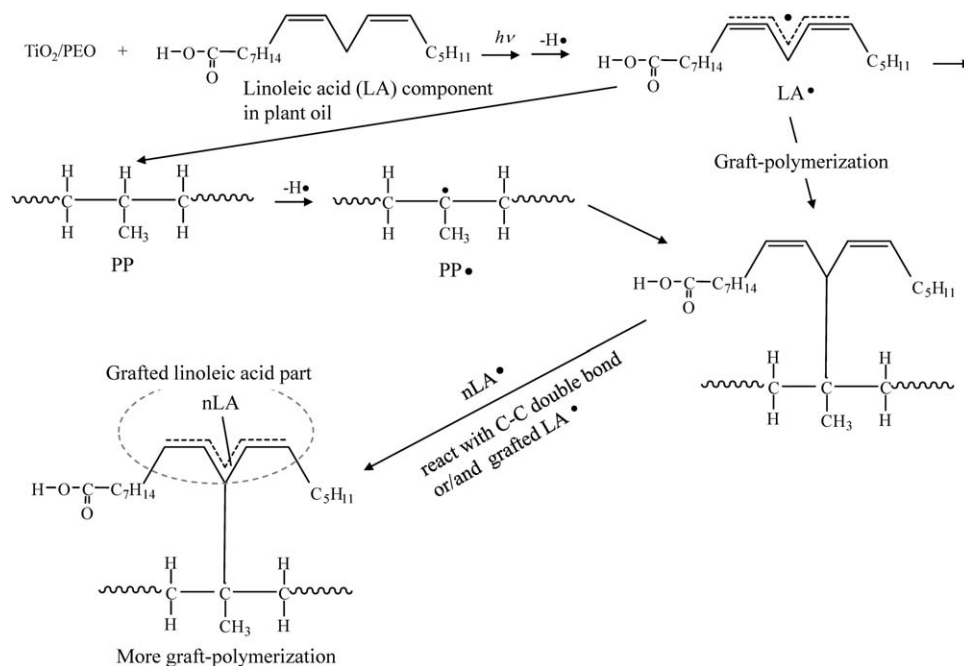


Figure 5. Thermal treatment dependences of FT-IR spectra of 24 h-photodegraded PP samples with nano-TiO₂/PEO/plant oil paint. Thermal treatment temperature = 100°C. Nano-TiO₂ concentration ratio = 0.04/normal-TiO₂.

well as those of the longer photodegraded PP. In addition, the longer thermal treatment pushes forward the behavior. As shown in Scheme 2, the linoleic acid becomes a stable radical and reacts with the PP radical, and then the graft-polymerization occurs. As shown in Scheme 3, the grafted linoleic acid part contains many allyl protons serving as a sensitive agent of degradation (autooxidation).³⁷ Therefore, the grafted part must be frequently decomposed by photo- or thermal-degradation. When the autooxidation occurs, the PP chain scission is inevitably accompanied, and then the methyl ketone, vinylidene, tri-substituted double bond (isobutenyl), and vinylene groups are produced as shown in Scheme 3.

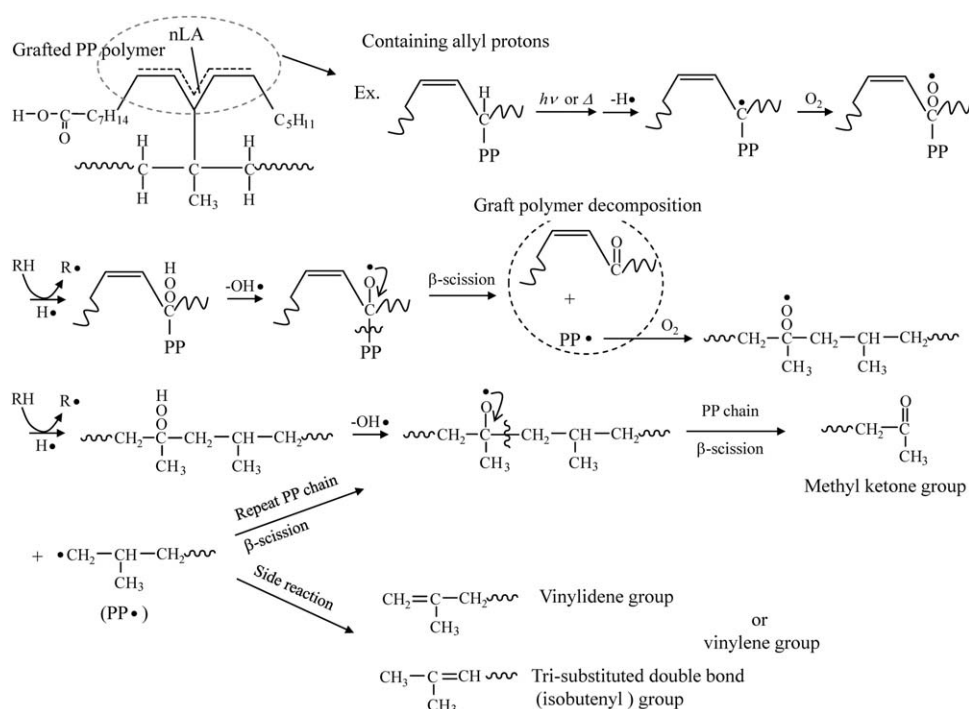
ML is a kind of linoleic acid derivative and can produce a stable radical.²⁰ Instead of the plant oil, the ML addition leads to a simplification of the paint system, leading to elucidation of the degradation mechanism of the linoleic acid component in the plant oil. Figure 6 shows the thermal treatment dependence of FTIR spectra of the 24 h-photodegraded PP samples with the normal-TiO₂/PEO/ML paint. The 1745 cm⁻¹ peak shows higher intensity as compared with that of the 24 h-photodegraded PP with the normal-TiO₂/PEO/plant oil (see Figure 1). After the 5 h-thermal treatment, the peak intensity considerably decreases, and the 1713 cm⁻¹ peak appears. The behavior shows that the ML graft-polymerization, decomposition and then PP degradation successively occur. The photodegradation time dependences of melting behavior of the photodegraded PP samples with the nano-TiO₂/PEO/ML paint were studied by the DSC measurements. These T_m , ΔH , and χ_c values were summarized in Table I. The T_m value of the 24 h-photodegraded PP slightly decreases, and those of the 48 and 96 h-ones considerably do as that of the pristine PP. The ΔH and χ_c values of these samples decrease up to the 48 h and drastically increase at the 96 h. The decreases of these values are due to the ML graft-polymerization. The ML penetrates among the PP lamellae and graft-polymerizes. The disorder of lamella crystal part occurs, leading to the decreases of the T_m and χ_c values. The 96 h-photodegraded sample shows the lower T_m and higher χ_c , respectively. The χ_c increase is explainable in terms of the



Scheme 2. Schematical reaction path of graft-polymerization with TiO₂/PEO/plant oil photocatalyst system.

chemi-crystallization.³⁰ The ML graft-polymer decomposition and PP chain scission occur between at the 48 and 96 h photodegradation time. The parts of the grafted PP chains can be preferentially broken, and the crystallization (chemi-crystallization) occurs by the rearrangement of these disconnected PP chains. Such chemi-crystallization brings about the increase of the crystalline part. The tensile properties of the photode-

graded PP samples with nano-TiO₂/PEO/ML paint were studied by the tensile testing. The Young's modulus, tensile strength and strain at break values obtained were summarized in Table II. The 24 h-photodegraded PP shows the 77% Young's modulus, 88% tensile strength and 103% strain at break values as compared with those of the pristine PP. In addition, the yield region became broader than that of the



Scheme 3. Decomposition step of grafted PP polymer and plausible productions.

Methyl linoleate (ML)=

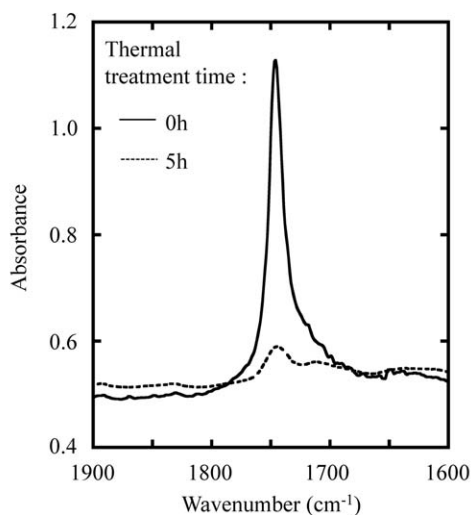
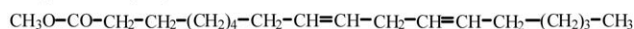


Figure 6. Thermal treatment dependence of FT-IR spectra of photodegraded PP samples painted by normal-TiO₂/PEO/ML for 24 h photodegradation time. Thermal treatment temperature = 100°C.

pristine PP. The change of the tensile properties suggests that the PP plasticizing occurs by the ML graft-polymerization. In contrast, the 96 h-photodegraded PP shows the 85% Young's modulus, 80% tensile strength and 1% strain at break values to those of the pristine PP. The typical brittle behavior supports that the PP chain scission and chemi-crystallization occur during the 96 h-photodegradation. Figures 7 and 8 show the ¹H-NMR spectra of ML and 96 h-photodegraded PP with nano-TiO₂/PEO/ML paint, respectively. As shown in Figure 8, the photodegraded PP spectrum contains resonances of ML. However, the three resonances assigned to vinyl (f: δ 5.3 ppm), methyl ester (a: δ 3.6 ppm) and allyl (g: δ 2.7 ppm) protons become much smaller. Instead, new resonances

Table I. Melting Temperature (*T_m*), Fusion Enthalpy (ΔH), and Crystallinity (χ_c) of Photodegraded PP Samples with Nano-TiO₂/PEO/ML Paint

Photodegradation time (h)	<i>T_m</i> (°C)	ΔH (J/g)	χ_c (%)
0	165.0	70.1	34
24	163.7	37.2	17
48	161.1	30.2	14
96	161.4	89.1	42

Table II. Tensile Properties of Photodegraded PP Samples with Nano-TiO₂/PEO/ML Paint

Photodegradation time (h)	Young's modulus (MPa)	Tensile strength (MPa)	Strain at break (%)
0	524 ± 76	25 ± 2	1472 ± 149
24	406 ± 28	22 ± 3	1509 ± 106
96	446 ± 24	20 ± 2	16 ± 4

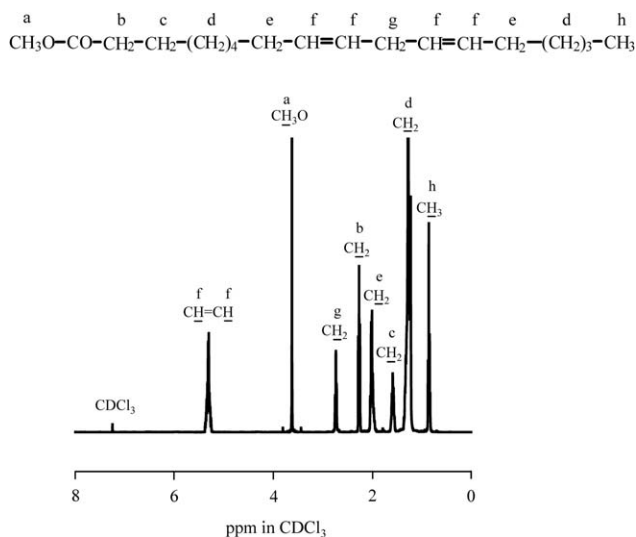


Figure 7. ¹H-NMR spectrum of ML.

appear. The expanded spectrum distinctly shows the resonance assigned to the methyl ketone group (δ 2.15 ppm, integral ratio = 0.03). The group is originated from the PP chain scission by the autooxidation (see Figure 8). The NMR spectrum as well as the FT-IR shows that the PP was certainly photodegraded by the paint photocatalyst system. When the PP chain scission occurs by the autooxidation, the production amount of the isobutenyl group (δ 5.24 ppm) must be lower than that of the methyl ketone one. In fact, the integral ratio (= 0.14) of the isobutenyl group is much higher. The behavior suggests that the group is also produced by other reaction. Although the production mechanisms are not clarified, several resonances assigned to ester group can be observed as

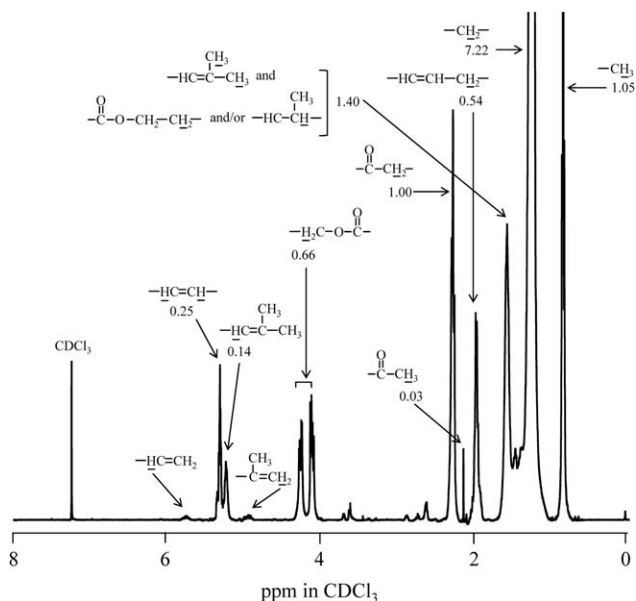


Figure 8. ¹H-NMR spectrum of 96 h-photodegraded PP with nano-TiO₂/PEO/ML paint: Numerical value represents integral ratio of each resonance.

well. These results suggest that the PP photodegradation is accompanied by side reactions.

CONCLUSIONS

The photodegradation of the PP film was performed by painting of the TiO₂/PEO/plant oil photocatalyst system. The photodegradation underwent two stages of development as follows: Initially PP reacted with linoleic acid radical originated from the photoreaction of plant oil component. Secondly the linoleic acid graft-polymer was decomposed, and then PP chain scission was caused. The process was studied using ML in detail. It was found that the grafted ML was readily decomposed using the 100°C-thermal treatment. The DSC measurement and tensile testing showed that the ML graft-polymerization and the decomposition brought about the PP plasticizing and chemi-crystallization, respectively. The ¹H-NMR spectrum of the photodegraded PP as well as that of the FT-IR showed the resonance assigned to the methyl ketone group, demonstrating that the PP was certainly photodegraded by the paint photocatalyst system.

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