

## Preparation of Isotactic Polypropylene/Fibrous Cellulose Composite Oxo-Biodegradation Induced by Poly(ethylene oxide)/TiO<sub>2</sub> Initiator and Accelerator System

Kensuke Miyazaki, Kazuto Shibata, Hisayuki Nakatani

Department of Biotechnology and Environmental Chemistry, Kitami Institute of Technology 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan

Correspondence to: H. Nakatani (E-mail: nakatani@chem.kitami-it.ac.jp)

**ABSTRACT:** In this work, a novel isotactic polypropylene (PP)/fibrous cellulose (FC) composite containing a poly(ethylene oxide) (PEO)/TiO<sub>2</sub> was prepared, and its oxo-biodegradation behavior was studied. FC loading of 5 and 1% resulted in an opaque film and relatively good transparency, respectively. Fourier transform infrared (FTIR) spectra of the nonphotodegraded composite samples revealed little PP auto-oxidation under the melt-mixing condition. Ultraviolet irradiation enhanced the auto-oxidation of the composite. FTIR analyses of the composite indicated that TiO<sub>2</sub> and PEO functioned as the initiator and accelerator of PP auto-oxidation, respectively. In addition, even with 1% PEO, the accelerator effect was enhanced by the spreading of the degraded PEO component from other areas when the film thickness was increased. All PP/PEO/TiO<sub>2</sub>/FC composites with a PEO content varying from 0.3 to 5% showed a Young's modulus value of ~ 180% higher than that of pristine PP. Biodegradability of the photodegraded composite was confirmed by a soil burial test. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** biodegradable; poly(propylene); composites; degradation

Received 1 May 2011; accepted 28 March 2012; published online

DOI: 10.1002/app.37808

### INTRODUCTION

Cellulose is a highly popular polymeric material worldwide and is used as a raw material for building materials and paper. Cellulose is a low-cost, high-modulus, renewable, and biodegradable material. Cellulose has recently attracted much attention as a filler material for polypropylene (PP),<sup>1–6</sup> because of its great potential for the production of composite materials with a high-modulus and biodegradability.

PP is a typical nonbiodegradable polymer because large molecules such as PP cannot enter into the cells of microorganisms, making it difficult for microorganisms to metabolize. PP can be degraded to low-molecular weight compounds; however, by a pro-oxidant that converts it to a biodegradable polymer. This method is called “oxo-biodegradation,”<sup>7–11</sup> and the mechanism comprises two stages: abiotic and microbial oxidation. Oxo-biodegradation also renders PP/cellulose composites biodegradable. There is a major obstacle, however, for the application of oxo-biodegradation to PP/cellulose composites, which is the opacity of the PP/cellulose composite. Opacity disturbs the photoabiotic

oxidation (auto-oxidation) stage inside the composite, which leads to an extreme decrease in the microbial oxidation rate. Commercial application of the PP/cellulose composite requires biodegradability under sunshine irradiation as well as a high modulus. Thus, the design of a novel pro-oxidant system by which auto-oxidation proceeds in this composite is needed. In our previous studies,<sup>12–14</sup> we succeeded in preparing an oxo-biodegradable PP using a novel pro-oxidant system. The pro-oxidant system was composed of TiO<sub>2</sub> and poly(ethylene oxide) (PEO) compounds. In this system, the TiO<sub>2</sub> worked as a radical initiator for both PP auto-oxidation and PEO degradation.<sup>12</sup> PEO was photocatalytically degraded by TiO<sub>2</sub>, producing acid and aldehyde compounds. These products accelerated hydroperoxide decomposition, which is the rate-determining step in PP auto-oxidation.<sup>15,16</sup> PEO acted to accelerate PP auto-oxidation.<sup>12</sup> PEO accelerates hydroperoxide decomposition even inside the PP/cellulose composite. Because the acid and aldehyde compounds produced by PEO photodegradation spontaneously spread inside the PP/cellulose composite, the

Additional Supporting Information may be found in the online version of this article.

© 2012 Wiley Periodicals, Inc.

hydroperoxide is rendered decomposable even by irradiation with a common light source such as sunlight or a mercury lamp.

In this study, we prepared a PP/PEO/TiO<sub>2</sub>/fibrous cellulose (FC) composite and studied its oxo-biodegradation behavior with Fourier transform infrared (FTIR) spectra. The effects of FC loading on the tensile properties of the PP/PEO/TiO<sub>2</sub> composite were studied with tensile testing. In addition, the PP/PEO/TiO<sub>2</sub>/FC composite film retrieved from the soil burial test was stained with lactophenol cotton blue, and then attached fungal morphologies were observed by optical microscopy to identify the species.

## EXPERIMENTAL

### Materials

PP (meso pentad fraction = 98%) was supplied by Japan Polypropylene. The number-average molecular weight ( $M_n$ ) and the polydispersity ( $M_w/M_n$ ) of the PP were  $4.6 \times 10^4$  and 5.7, respectively.

PEO was purchased from Wako Pure Chemical Industries. The average molecular weight was  $5.0 \times 10^5$ .

TiO<sub>2</sub> was purchased from Wako Pure Chemical Industries. The crystal structure was anatase (more than 98.5%), and the surface area was about 6 m<sup>2</sup>/g. The TiO<sub>2</sub> was used without pretreatment.

Fibrous cellulose (W-100GK) was donated by Nippon Paper Chemicals. The FC was dried in desiccator for 7 days before preparation. The moisture of the FC was below 0.7%. The FC dimensions are more than 90% pass 100 mesh (below 150  $\mu\text{m}$ ), and the average length was about 37  $\mu\text{m}$ .

### Preparation of PEO/TiO<sub>2</sub>/FC Blend

Mixing of pure water solution (40 mL/g-PEO) of the PEO/TiO<sub>2</sub>/FC was performed using a 0.1-L glass equipped with a stirrer at 23°C for 24 h. The water solvent was evaporated using a rotary evaporator. The sample obtained was dried at 50°C for 24 h in a vacuum oven and was used as the PEO/TiO<sub>2</sub>/FC blend.

### Preparation of PP/PEO/TiO<sub>2</sub>/FC Composite

Loading of the PEO/TiO<sub>2</sub>/FC blend into PP was prepared by an Imoto Seisakusyo IMC-1884 melting mixer. After a small amount of the phosphite antioxidant (ADK STAB PEP-36, ca. 0.1%) was added, the mixing was performed at 180°C at 100 rpm for 5 min.

### Photodegradation Test

The sample was molded into a thin film (50 or 100  $\mu\text{m}$ ) by compression molding at 190°C under 5 MPa for 5 min. The film was cut into the 20  $\times$  20  $\times$  0.05 mm<sup>3</sup> or 20  $\times$  20  $\times$  0.1 mm<sup>3</sup>, and put into a vial (Pyrex reactor). The photodegradation test 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 mW/cm<sup>2</sup>; Riko-Kagaku Sangyo). The test was performed at 30°C in air.

### Fourier Transform Infrared Analysis and Estimation of Carbonyl Group Concentration

The IR spectra of 16 scans were measured with an FTIR spectrometer (Perkin-Elmer Spectrum One) at a resolution of 2 cm<sup>-1</sup> over the full mid-IR range (400–4000 cm<sup>-1</sup>).

Carbonyl group (methylketone) is a main product of auto-oxidation of PP.<sup>17</sup> The corresponded IR peak appears at around 1720 cm<sup>-1</sup>, and its average molar absorptivity is 330 mol L<sup>-1</sup> cm<sup>-1</sup>.<sup>17</sup> The carbonyl group concentration of the photodegraded PP was estimated by Lambert–Beer law using the average molar absorptivity and the pristine PP density (0.900 g/mL).

### 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 mm<sup>3</sup> 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 tensile testing were performed at 20°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 10 measurements.

### Biodegradation Test

A soil burial test was performed for biosusceptibility. The film samples (20  $\times$  20  $\times$  0.05 mm<sup>3</sup>) put into containers with the soil of the flowerbed in our institute (Kitami Institute of Technology). The pH of the soil was 7.7, and the soil was used without addition of nutrients and micronutrients. To avoid the soil dryness, the containers were treated with water spray every day. The biodegradation test had been performed for 28 days at 20°C.

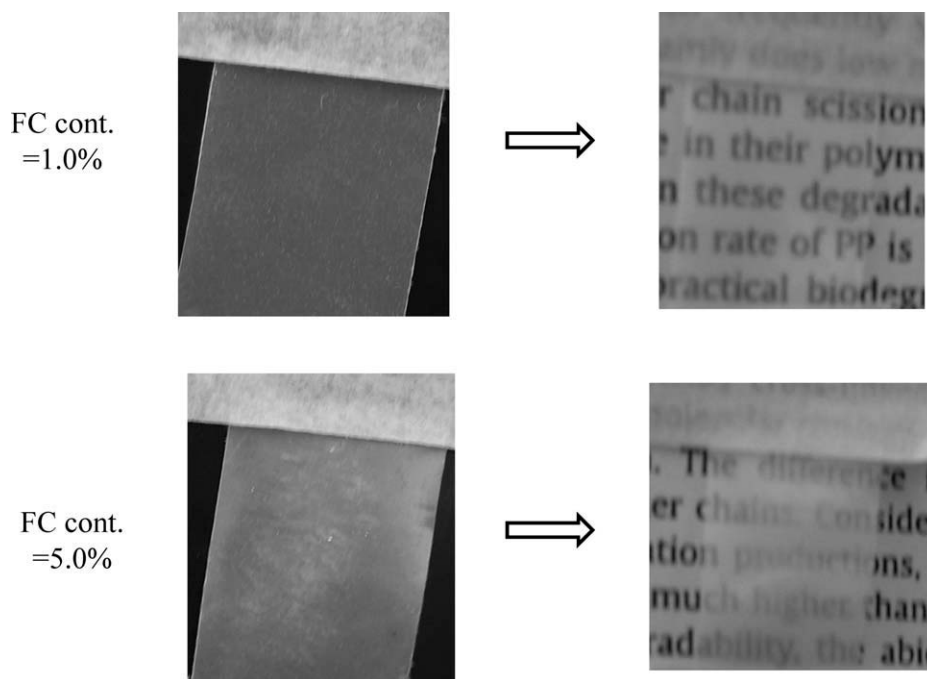
### Optical Microscope Observation

Optical microscope observation was performed with a Nikon ECLIPSE 50/POL optical microscope (Nikon, Tokyo, Japan). The samples were stained with lactophenol cotton blue (purchased from Kanto Chemical) before optical microscope imaging.

## RESULTS AND DISCUSSION

FC is hydrophilic and tends to aggregate, showing incompatibility with hydrophobic PP. In addition, loading of opaque FC decreases the transparency of PP, thus FC directly interferes with PP photodegradation. Figure 1 shows photographs of the PP(98.2%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) and PP(94.2%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(5.0%) films. Although 5% FC loading considerably increases the film opacity, transparency is still relatively maintained following 1% loading. Therefore, a small FC loading keeps the PP transparent at some level.

The FTIR spectra around ethylenic unsaturated and carbonyl group peaked before and after photodegradation (Figure 2). Broad peaks (at 1642 cm<sup>-1</sup>) assigned to the ethylenic unsaturated group were also observed. The amount of the ethylenic unsaturated group was hardly dependent on the FC content or the presence of PEO. Thus, a small amount of the ethylenic unsaturated group was spontaneously produced during the melt-mixing process. In addition, there was no carbonyl peak. These

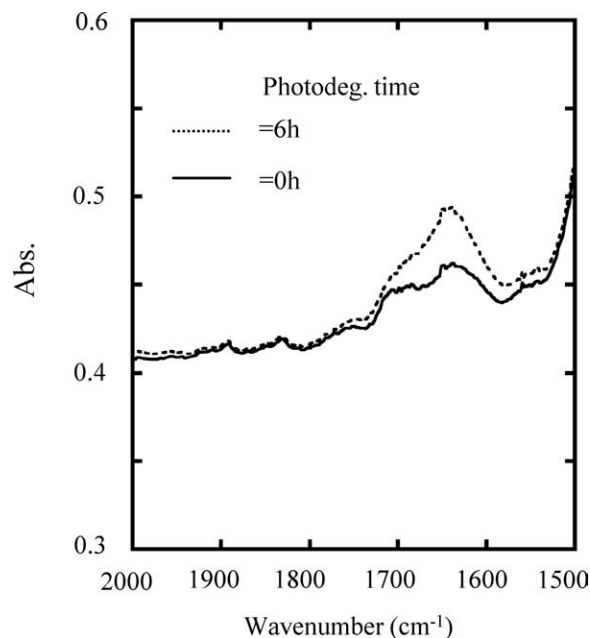


**Figure 1.** Photographs of the PP(99.2-x%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(x%) films: Film thickness = 50  $\mu$ m.

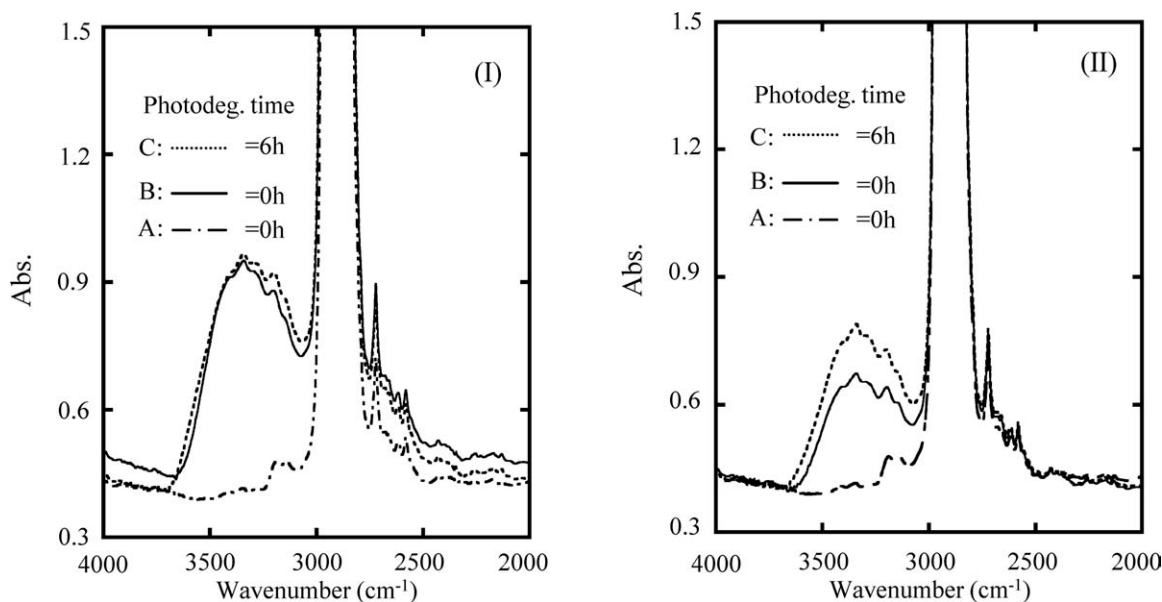
findings suggest that little PP auto-oxidation occurs under the melt-mixing condition. In the sample with a higher FC content (5.0%), the rate of the ethylenic unsaturated group increase was higher after 6 h photodegradation compared with the sample with a lower FC content (1.0%). Thus, FC appears to act as the photodegradation initiator.<sup>18</sup>

FTIR spectra were observed around 2000–4000  $\text{cm}^{-1}$  of the pristine PP, PP/FC, and PP/PEO/TiO<sub>2</sub>/FC samples, respectively (Figure 3). In the PP/FC sample, the peak intensity of the OH group (around ca. 3350  $\text{cm}^{-1}$ ) of PP(90.0%)/FC(10.0%) was quite high. In addition, no change in the peak intensity was observed in the photodegraded sample [see Figure 3(I)]. This behavior suggests that the OH group originating from hydroperoxide is not contained in these peaks. Thus, auto-oxidation does not occur in these PP/FC samples under photodegradation conditions. Interestingly, the OH group peak intensity of PP(98.2%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) was considerably higher than that of PP(95.0%)/FC(5.0%), although the FC content was lower. The OH group peak shape was sharper than that of the other samples, and the peak intensity was hardly changed before or after photodegradation. This finding suggests that the OH group originating from hydroperoxide is absorbed by the PP(98.2%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(1.0%). Considering the good transparency of the PP(98.2%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) film (see Figure 1), it is likely that auto-oxidation easily occurred in these PP/FC samples under a low-intensity light source such as interior light. In the PP(94.2%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(5.0%) film as well as in the PP(95.0%)/FC(5.0%) film, the OH group peak intensity was weaker. In the PP(94.2%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(5.0%) sample, however, both the OH group peak intensity and the ethylenic unsaturated group intensity were higher after 6 h pho-

todegradation treatment [see Figure 3(II)]. This finding suggests that auto-oxidation occurs by irradiation with a high-pressure mercury vapor lamp. Because the film is highly opaque, the auto-oxidation process requires a much stronger light source compared with the PP(98.2%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) film. These results reveal that the presence of PEO



**Figure 2.** FTIR spectra of undegraded and photodegraded PP(94.2%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(5.0%) around ethylenic unsaturated and carbonyl group peaks. Film thickness = 50  $\mu$ m.

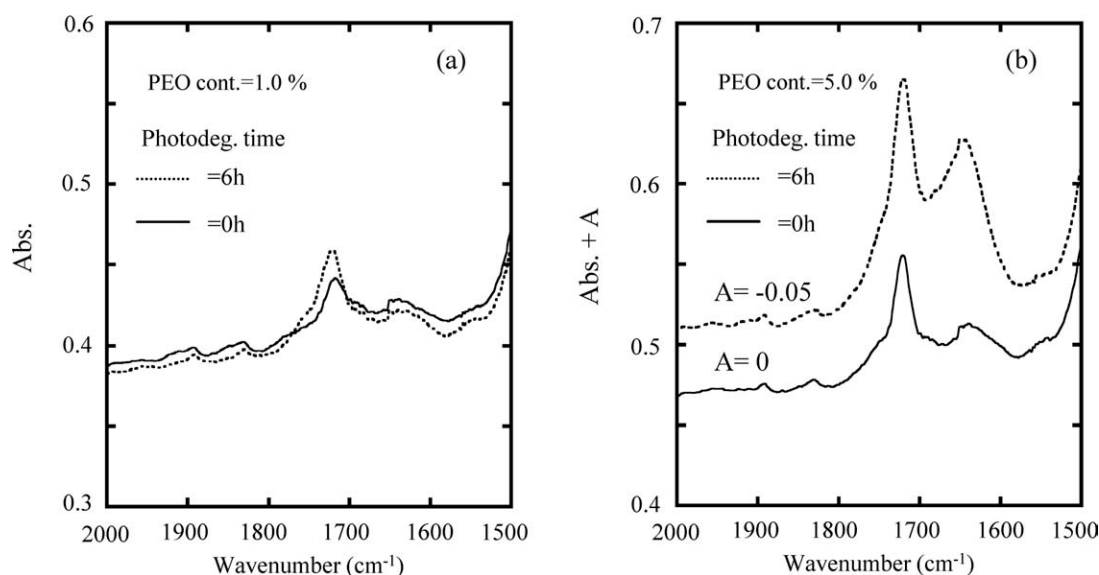


**Figure 3.** FTIR spectra of various samples around OH group peak. Film thickness = 50  $\mu\text{m}$ . (I): A = pristine PP, B and C = PP(90.0%)/FC(10.0%). (II): A = pristine PP, B and C = PP(94.2%)/PEO(0.3%)/TiO<sub>2</sub>(0.5%)/FC(5.0%).

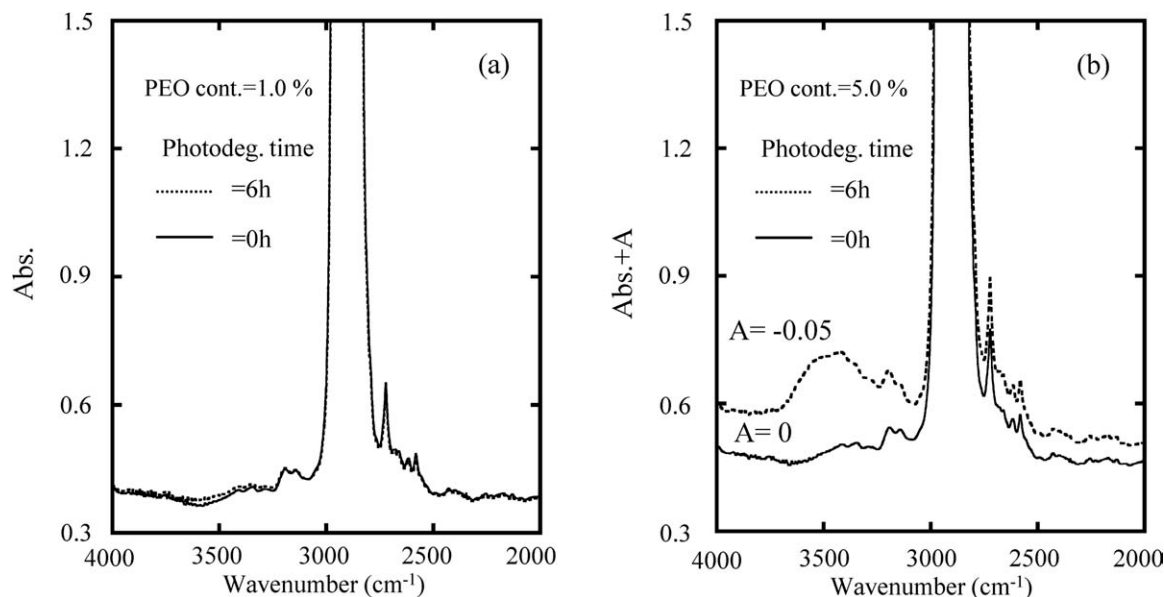
and TiO<sub>2</sub> allows for auto-oxidation to proceed in the PP/FC composite.

Figure 4 shows the FTIR spectra of PP(98.5- $x\%$ )/PEO( $x\%$ )/TiO<sub>2</sub>(0.5%)/FC(1.0%) film samples containing two different amounts of PEO around the ethylenic unsaturated and carbonyl group peaks before and after photodegradation. An increase in the PEO content increases the peak intensity of both groups after photodegradation. Figure 5 shows the FTIR spectra of these samples around the OH group peak. Samples with a 1.0% PEO content show an increase in the ethylenic unsaturated and carbonyl group peak intensities after photodegradation, but the OH group peak intensity is almost zero, and the increase can

hardly be detected. In samples with 5% PEO, however, there is an observable increase in the OH group peak intensity after photodegradation. Figure 6 shows the increases in the ethylenic unsaturated and carbonyl group peak intensities for the pristine PP and the PP(98.5- $x\%$ )/PEO( $x\%$ )/TiO<sub>2</sub>(0.5%)/FC(1.0%) films during photodegradation. The intensities of both peaks increased with an increase in the PEO content, whereas the peak intensities of the pristine PP were zero (no degradation) until after 6 h photodegradation. The photodegradation time-dependence was considerably different, however, between these samples. The maximum peak intensity of the ethylenic unsaturated group occurred after  $\sim 1$  h of photodegradation,



**Figure 4.** FTIR spectra of various samples around ethylenic unsaturated and carbonyl peaks. Film thickness = 50  $\mu\text{m}$ . (a) = PP(97.5%)/PEO(1.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%). (b) = PP(93.5%)/PEO(5.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%).



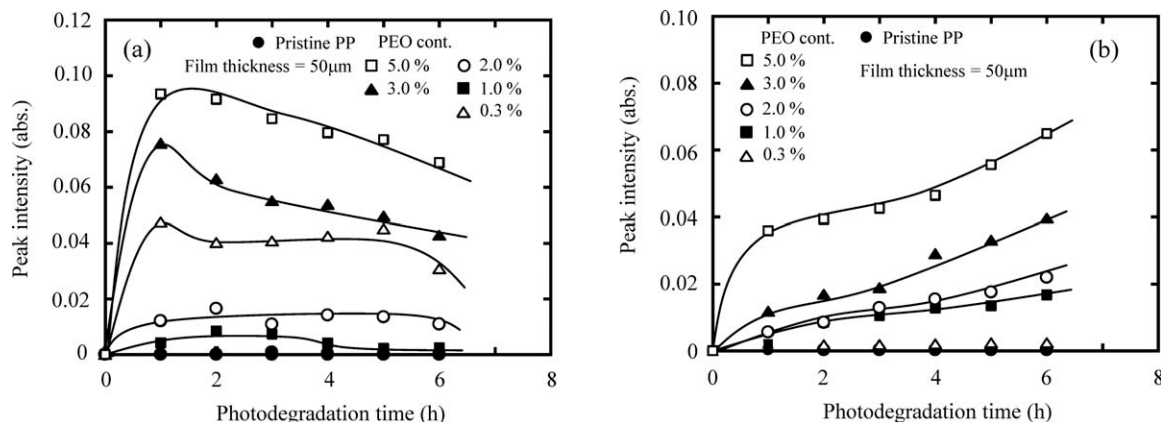
**Figure 5.** FTIR spectra of various samples around OH group peak. Film thickness = 50  $\mu\text{m}$ . (a) = PP(97.5%)/PEO(1.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%). (b) = PP(93.5%)/PEO(5.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%).

regardless of the PEO content, whereas that of the carbonyl group logarithmically increased with an increase in the photodegradation time, also regardless of the PEO content.

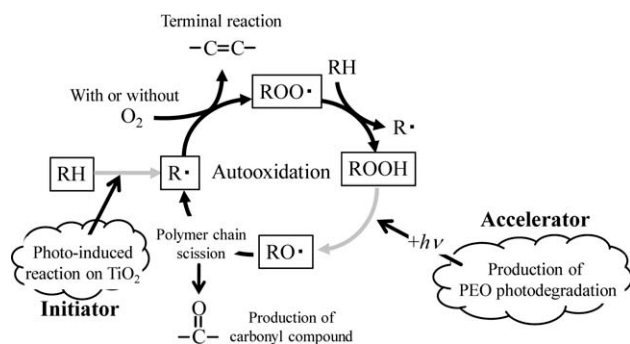
TiO<sub>2</sub> initiates PP auto-oxidation (Figure 7).<sup>12,13,19</sup> PEO acts to produce an acid and an aldehyde, which accelerate auto-oxidation.<sup>12,13,15,16</sup> In other words, TiO<sub>2</sub> and PEO work as the “initiator” and the “accelerator,” respectively. In auto-oxidation of the PP/PEO/TiO<sub>2</sub>/FC composite, in particular, the presence of PEO appears to be important for development. As mentioned earlier, it is likely FC acts as the auto-oxidation initiator as well as TiO<sub>2</sub>. Therefore, the auto-oxidation initiation readily occurs in the composite. Some of the generated alkyl radicals affect the ethylenic unsaturated group (terminal reaction), and others affect the hydroperoxide group. The radical species (OH $\cdot$ ) generated by TiO<sub>2</sub> photocatalysis spreads and initiates the auto-oxidation inside the composite films. Hydroperoxide decomposition requires light and cannot easily occur inside the composite

films. In fact, the hydroperoxide accumulates, and the auto-oxidation hardly proceeds in the composite films with a small amount (0.3%) of PEO (Figure 3). In composite films with higher amounts (>1%) of PEO, there is little accumulation of hydroperoxide and auto-oxidation proceeds. PEO is photocatalytically decomposed in the presence of TiO<sub>2</sub> and generates acid and aldehyde compounds, which accelerate the hydroperoxide decomposition.<sup>12,13</sup> This PEO accelerator effect supports the auto-oxidation process inside the composite films. The generated acid and aldehyde compounds make the films degradable under lower light intensity. Therefore, the degree of auto-oxidation process depends on the amount of PEO amount.

Figure 8 shows the carbonyl peak intensity increases of thicker PP/PEO/TiO<sub>2</sub>/FC films (100  $\mu\text{m}$ ) during photodegradation. The intensity increase samples with a 1% PEO content was distinct and was greater than that in samples with a 5% PEO content more than 3 h of photodegradation. The dependence on the

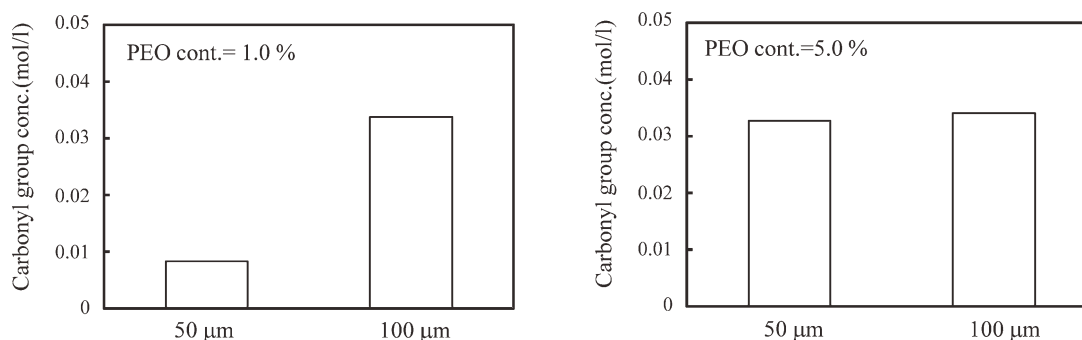


**Figure 6.** Increments of peak intensities in pristine PP and PP([98.5-x]%/PEO(x%)/TiO<sub>2</sub>(0.5%)/FC(1.0%)) during photodegradation. (a) Ethylenic unsaturated group. (b) Carbonyl group.

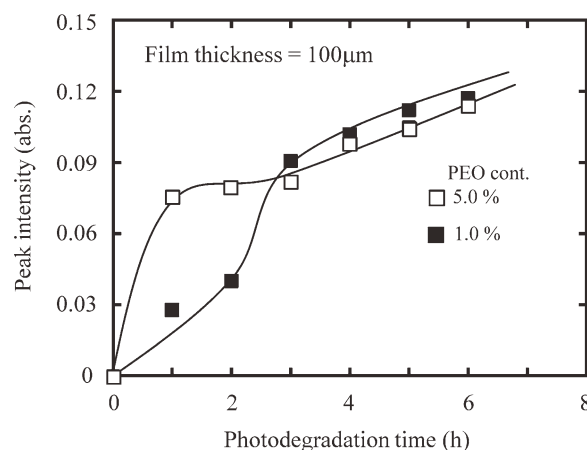


**Figure 7.** Degradation induced by PEO/TiO<sub>2</sub> initiator and accelerator system.

PEO content was different from that of the 50- $\mu\text{m}$  films. Figure 9 shows the increases in the carbonyl group concentration (estimated as methylketone) before and after photodegradation in the PP(97.5%)/PEO(1.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) and PP(93.5%)/PEO(5.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) films with thicknesses of 50 and 100  $\mu\text{m}$ , respectively. Interestingly, in PP(97.5%)/PEO(1.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%), the carbonyl group concentration increase in the 100- $\mu\text{m}$  film was approximately four times higher than that of the 50  $\mu\text{m}$  film. The concentration increase was not different, however, between the 50 and 100- $\mu\text{m}$  PP(93.5%)/PEO(5.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) films. The difference in the increase was due to the PEO content. As mentioned earlier, the acid and aldehyde compounds, which are generated by PEO photodegradation, accelerate hydroperoxide decomposition. The generated accelerators (acid and aldehyde compounds) spread throughout the composite film. As shown in Figure 10, at some point distant from each of the PEO/TiO<sub>2</sub>/FC domains, the accelerator, which spreads from other PEO/TiO<sub>2</sub>/FC domains, fills in the gaps. The complementary effect would be amplified to a suitable level by an increase in the film thickness, resulting in acceleration of the hydroperoxide decomposition, even in films with a PEO content as low as 1%. In fact, as shown in Figure 8, the carbonyl peak intensity of the sample with a 1% PEO content exponentially increases between 2 and 3 h of photodegradation, suggesting that the accelerator reaches the requisite concentration to accelerate the hydroperoxide decomposition by spreading. Composite film with a low PEO content is similarly affected when the film thickness is enhanced.



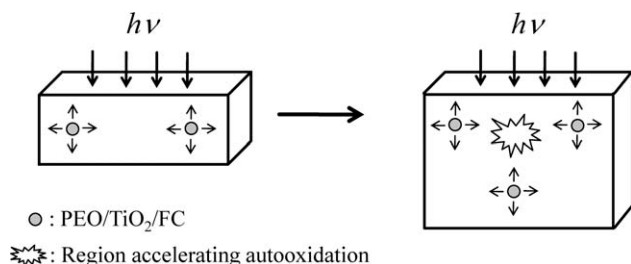
**Figure 9.** Increments of carbonyl group concentration between before and after photodegradation in PP(97.5%)/PEO(1.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) and PP(93.5%)/PEO(5.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) having 50 and 100 mm film thickness, respectively. Photodegradation time = 5 h.



**Figure 8.** Increments of carbonyl peak intensity in PP(97.5%)/PEO(1.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) and PP(93.5%)/PEO(5.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) during photodegradation.

Figure 11 shows a comparison of Young's modulus, tensile strength, and elongation at break values of the pristine PP and the PP/PEO/TiO<sub>2</sub>/FC films. In our previous reports,<sup>20,21</sup> we studied the effects of FC and PEO loadings on PP tensile properties and revealed the following: (1) FC loading increases Young's modulus and tensile strength, and rapidly decreases elongation at break; (2) PEO loading decreases Young's modulus and tensile strength, but hardly affects elongation at break; (3) loading the PEO/FC blend into the PP weakens the interface strength between the PEO/FC and PP and increases the PEO content. The tendencies of the tensile properties were the same in PP/PEO/TiO<sub>2</sub>/FC. Notably, all the composites showed a Young's modulus of about 180% higher than that of pristine PP. This finding indicates that PP/PEO/TiO<sub>2</sub>/FC has good photodegradability with a higher Young's modulus.

After the soil burial test for 28 days with incubation at 20°C, microorganisms (fungi) were observed on the surface of the photodegraded PP(97.5%)/PEO(1.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) sample. Figure 12 shows the FTIR spectra of the samples before and after the soil burial test. In the nonphotodegraded sample, the carbonyl peak intensity was considerably lower and hardly changes between before and after the soil burial test, indicating that the microorganisms do not metabolize the composite. In contrast, the photodegraded sample shows that the carbonyl



**Figure 10.** A schematic image of complementary auto-oxidation induced by enhancement of film thickness.

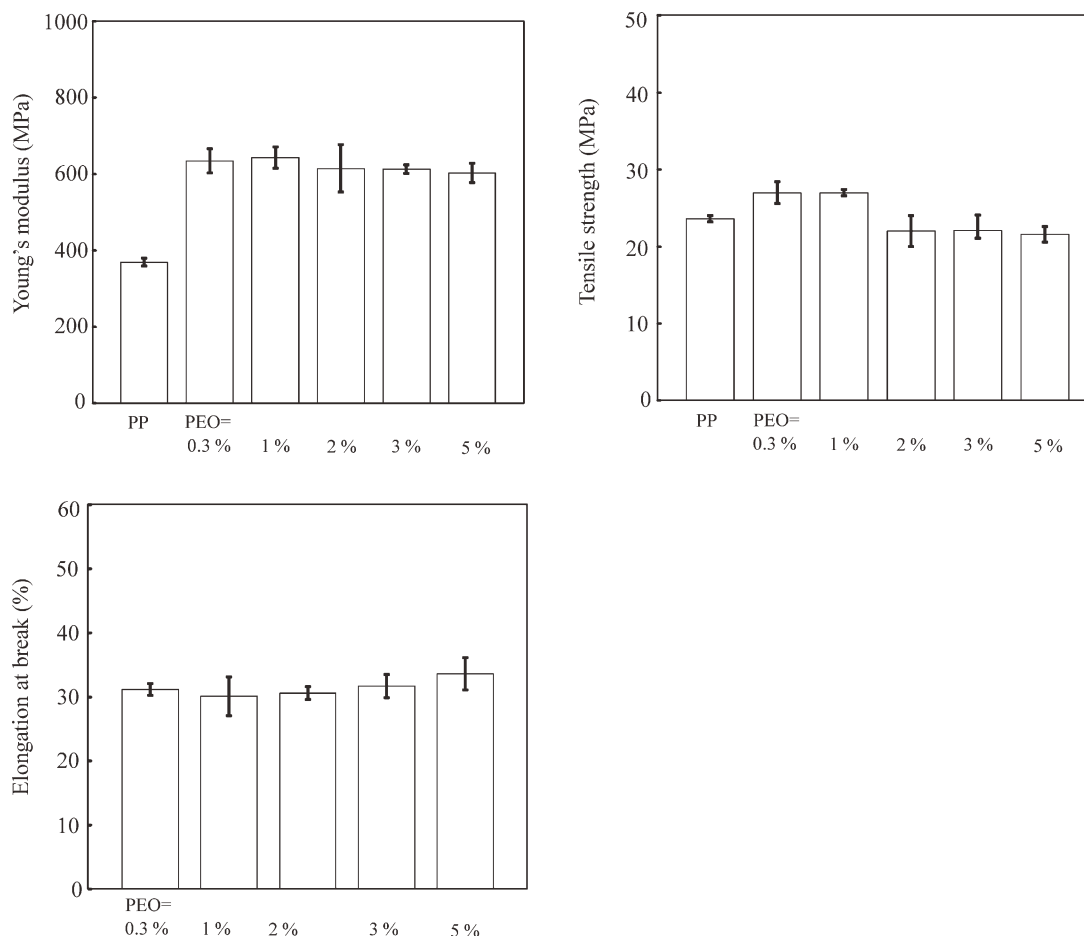
peak intensity was much higher than that of the nonphoto-degraded sample. The higher carbonyl peak almost disappeared after the soil burial test, which is typical biodegradation behavior by metabolism of the microorganism.<sup>14,22–24</sup> To investigate the microorganism morphology, the film retrieved from the soil burial test was stained with lactophenol cotton blue and then examined by optical microscopy. A long and short filamentous fungus with septate hypha was observed. Motta et al.<sup>25</sup> observed colonization and adhesion of *Curvularia* sp. on an oxidized polystyrene surface and this phenomenon implied its biodegradation (metabolism) by the fungus. The observed filamentous fungus would be an identical species, that is, *Curvularia* sp.

because it exhibits a characteristic appearance, that is, a ribbon-like shape and septate structure. This type of fungus has the ability to degrade lignocellulosic materials due to its highly efficient enzymatic system.<sup>26</sup> Therefore, the filamentous fungus has the potential to degrade FC as well as PP. Attachment of the fungus suggests biodegradation of the PP/FC composite. Although examination of the fungus gene is necessary for identification, it appears that this fungus is able to biodegrade the photodegraded PP/PEO/TiO<sub>2</sub>/FC composite.

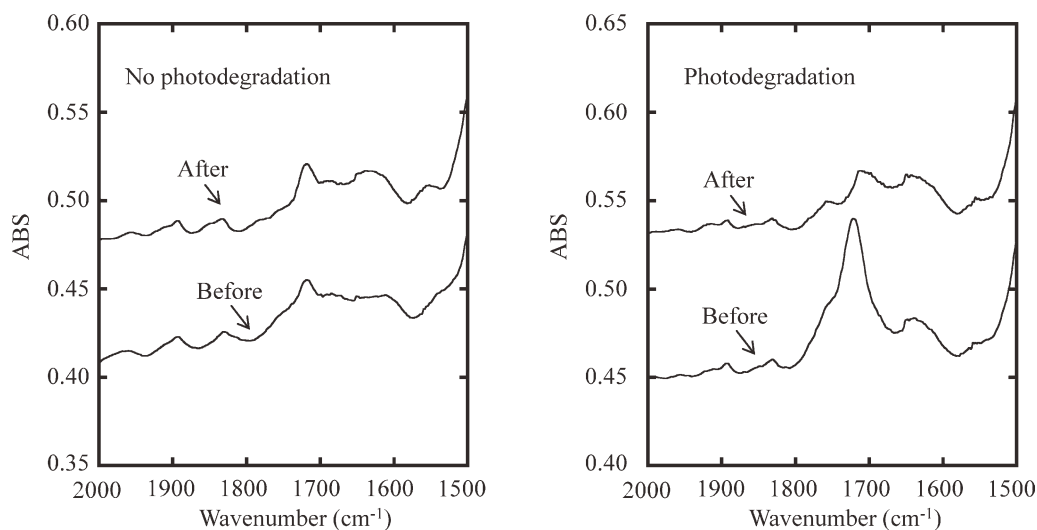
There are several reports of biodegradable polyethylene (PE)/starch composites.<sup>27–29</sup> The PP/PEO/TiO<sub>2</sub>/FC composite is similar to the PE/starch composite in terms of the biodegradable components it contains, such as FC. The biodegradable portion of the PE/starch composite, however, is confined to the starch component. The PP/PEO/TiO<sub>2</sub>/FC composite shows different biodegradation behavior, although the biodegradation rate is not very high. Complete biodegradation is possible, however, by inducing the oxo-biodegradation mechanism.

### CONCLUSION

In this study, the PP/PEO/TiO<sub>2</sub>/FC composite was prepared, and its oxo-biodegradation behavior was studied. The FC loading of 5 and 1% resulted in opaque film and relatively good transparency,



**Figure 11.** Comparisons of Young's moduli, tensile strengths, and elongation at break values of pristine PP and PP((98.5-x%)/PEO(x%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) films: Pristine PP elongation at break = more than 200%.



**Figure 12.** FTIR spectra of undegraded and photodegraded PP(97.5%)/PEO(1.0%)/TiO<sub>2</sub>(0.5%)/FC(1.0%) samples before and after soil burial test for 28 days of incubation at 20°C. Film thickness = 50 μm. Photodegradation treatment for 24 h at 30°C.

respectively. The FTIR spectra of the nonphotodegraded composite samples indicated that the PP auto-oxidation hardly occurred under the melt-mixing condition. After the ultraviolet irradiation, the auto-oxidation smoothly advanced in the composite. The FTIR analyses of the composite revealed that the TiO<sub>2</sub> and the PEO played the roles of the initiator and the accelerator of PP auto-oxidation, respectively. In addition, even at a lower PEO content, the accelerator effect was found to be supplemented with the spreading of the degraded PEO component from other place by the enhancement of the film thickness. The PP/PEO/TiO<sub>2</sub>/FC composite showed the higher Young's modulus. The biodegradability of the photodegraded composite was confirmed by the soil burial test, and the attachment of the filamentous fungus was observed on the surface.

#### ACKNOWLEDGMENTS

A part of this work was supported by the Grant-in-Aid for Scientific Research, No. 22510097 and 226529 from Japan Society for the Promotion of Science.

#### REFERENCES

- Takase, S.; Shiraishi, N. *J. Appl. Polym. Sci.* **1989**, *37*, 645.
- Felix, J. M.; Gatenholm, P. *J. Appl. Polym. Sci.* **1991**, *42*, 609.
- Qiu, W.; Zhang, F.; Endo, T.; Hirotsu, T. *J. Appl. Polym. Sci.* **2003**, *87*, 337.
- Qiu, W.; Zhang, F.; Endo, T.; Hirotsu, T. *J. Appl. Polym. Sci.* **2004**, *91*, 1703.
- Qiu, W.; Zhang, F.; Endo, T.; Hirotsu, T. *J. Appl. Polym. Sci.* **2004**, *94*, 1326.
- Hristov, V. N.; Vasileva, S. T.; Krumova, M.; Lach, R.; Michler, G. H. *Polym. Compos.* **2004**, *25*, 521.
- Albertsson, A. C.; Andresson, S. O.; Karlsson, S. *Polym. Degrad. Stab.* **1987**, *18*, 73.
- Albertsson, A. C.; Barenstedt, C.; Karlsson, S. *Polym. Degrad. Stab.* **1992**, *37*, 163.
- Weiland, M.; Daro, A.; Dacid, C. *Polym. Degrad. Stab.* **1995**, *48*, 275.
- Jakubowicz, I. *Polym. Degrad. Stab.* **2003**, *80*, 39.
- Reddy, M. M.; Gupta, R. K.; Gupta, R. K.; Bhattacharya, S. N.; Parthasarathy, R. *J. Polym. Environ.* **2008**, *16*, 27.
- Miyazaki, K.; Nakatani, H. *Polym. Degrad. Stab.* **2009**, *94*, 2114.
- Miyazaki, K.; Nakatani, H. *Polym. Degrad. Stab.* **2010**, *95*, 1557.
- Miyazaki, K.; Shibata, K.; Nakatani, H. *Polym. Degrad. Stab.* **2011**, *96*, 1039.
- Broska, R.; Rychlý, J.; Csomorová, K. *Polym. Degrad. Stab.* **1999**, *63*, 231.
- Eriksson, P.; Reiberger, T.; Stanberg, B. *Polym. Degrad. Stab.* **2002**, *78*, 183.
- Adams, J. J. *Polym. Sci. A-1*, **1970**, *8*, 1077.
- Seldén, R.; Nyström, B.; Långström, R. *Polym. Comp.* **2004**, *25*, 543.
- Blakey, I.; George, G. A. *Polym. Degrad. Stab.* **2000**, *70*, 269.
- Nakatani, H.; Miyazaki, K. *J. Appl. Polym. Sci.* **2009**, *112*, 3362.
- Miyazaki, K.; Nakatani, H. *J. Appl. Polym. Sci.* **2009**, *114*, 1656.
- Koutny, M.; Sancelme, M.; Dabin, C.; Pichon, N.; Delort, A. -M.; Lemaire, J. *Polym. Degrad. Stab.* **2006**, *91*, 1495.
- Chiellini, E.; Corti, A.; D'Antone, S. *Polym. Degrad. Stab.* **2007**, *92*, 1378.
- Hadad, D.; Geresh, S.; Sivan, A. *J. Appl. Microbiol.* **2005**, *98*, 1093.
- Motta, O.; Protob, A.; Carlob, F. D.; Caroa, F. D.; Santoroa, E.; Brunnetta, L.; Capunzo, M. *Int. Hyg. Environ. Health* **2009**, *212*, 61.
- Sánchez, C. *Biotechnol. Adv.* **2009**, *27*, 185.
- El-Shafei, H. A.; El-Nasser, N. H. A.; Kansoh, A. L.; Ali, A. M. *Polym. Degrad. Stab.* **1998**, *62*, 361.
- Albertsson, A. -C.; Erlandsson, B.; Hakkarainen, M.; Karlsson, S. *J. Polym. Environ.* **1998**, *6*, 187.
- Koutny, M.; Lemaire, J.; Delort, A. M. *Chemosphere* **2006**, *64*, 1243.