

# Natural Weathering of Polypropylene in a Tropical Zone

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**ABSTRACT:** Natural weathering of isotactic polypropylene (PP) plates (2 mm in thickness) was conducted for 15 months in the Philippines. Optical microscopy, scanning electron microscopy, and atomic force microscopy revealed that the surface layer (200–300 nm in thickness) was affected in the first month, and cracks are formed toward the deeper layer. On the basis of the microscopic observations along with FTIR, DSC, GPC, and tensile strength measurements, the following degradation mechanism of PP was proposed. At first, through oxygen introduced into the PP, only the surface layer seems to be affected. Gradually, the surface layer may be removed, exposing the inner layer. Then, mo-

lecular chains of the inner layer start to be degraded, accompanying a significant loss of tensile properties. Part of the degraded materials seems to be eroded, leading to the formation of cracks on the surface of the uncovered inner layer. Finally, the original surface layer may be totally eroded, making the structure of the inner layer (which should reflect the spherulitic texture) evident. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 931–938, 2003

**Key words:** polypropylene; weathering; degradation; surface structure; crystallinity

## INTRODUCTION

Polypropylene (PP) is one of the most widely used materials in plastic industries. During product use, its performance will be affected by atmospheric factors such as exposure to sunlight, temperature, humidity, and seasonal variations, as well as by environmental pollutants (e.g., dust particles of corrosive chemical agents).<sup>1–3</sup> As a major process, photooxidation leads to discoloration, loss of the mechanical properties, and embrittlement.

Natural weathering gives the most practical and the faithful data regarding the variation of the performance of the products in use. Sometimes, interesting and unpredictable results are obtained by carrying out this experiment. For example, Tidjani<sup>2</sup> reported on the effect of the degree of crystallinity on the deterioration of the mechanical properties of PP. He found that the low crystalline PP retained its physical properties for a longer time than did the high crystalline PP, despite the fact that the formation of photoproducts is quantitatively and qualitatively similar.

Although natural weathering experiments take a long time, as is known from the example mentioned above, the results are essential to obtain a fundamen-

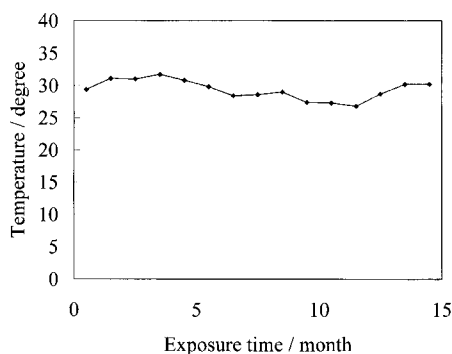
tal basis of the service life of PP, which is commonly estimated through, for example, simulation using the regional experimental data together with those obtained in a laboratory machine under an accelerated condition. Because weathering conditions differ from place to place, ideally the natural weathering experiments should be performed in each region where the materials are used. However, in a tropical zone, few reports have been made on the natural weathering of PP. As one of these few examples, Uzomah et al.<sup>3,4</sup> investigated the mechanical properties of aged PP films during the rainy season (September to October) in Nigeria. The major changes of the yield stress, initial modulus, plastic strain, and work of yield were explained on the basis of the physicochemical reactions, chemocrystallization, chain scission, and leaching. Because their samples were film-shaped and the length of exposure was less than 1 month, there still remain requirements to perform a prolonged natural weathering experiment for thicker samples.

In this study, the results of natural weathering of PP plates exposed for 15 months in the Philippines are reported. Along with the usual analytical methods for weathered plastic materials, the surface was studied in detail by atomic force microscopy (AFM).

## EXPERIMENTAL

Injection-grade PP (code No. 1100N) was supplied by Petrochemicals Corp. of Asia Pacific (PETROCORP). This sample does not contain any ultraviolet light absorbent. The PP was introduced into a Shinto com-

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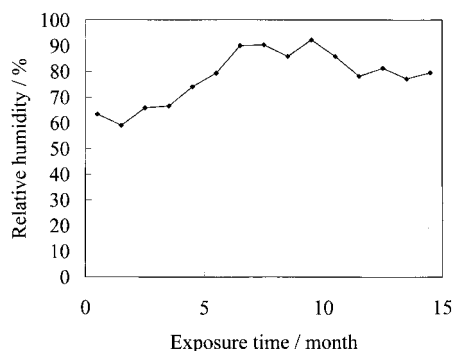


**Figure 1** Variation of average temperature at Bicutan exposure site during the experiment.

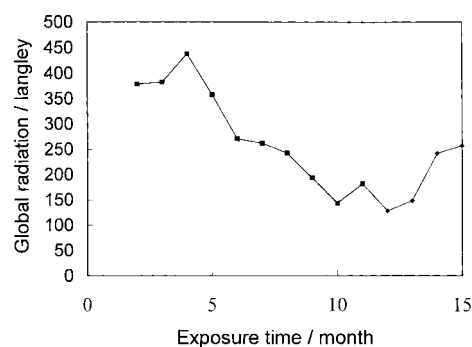
pression-molding machine (model WFA-37; Shinto, Japan). After being heated to 190°C at a pressure of 50 kg/cm<sup>2</sup>, the melted resin was slowly cooled for 20 min at the same pressure. Finally, a plate of 2 mm thickness was produced.

Natural weathering was conducted for 15 months, from February 1998 to June 1999, at the Bicutan exposure site of the Industrial Technology Development Institute, (Metro-Manila, Philippines), located at latitude 14°29'N and longitude 121°02'E. The weather conditions during the exposure are shown in Figures 1–3. The temperature and relative humidity were measured at the exposure site (Figs. 1 and 2), whereas the global radiation (Fig. 3) was determined by PAG-ASA, Weather Bureau<sup>5–7</sup> in Quezon City, situated at latitude 14°36'N and longitude 121°04'E. The PP plates were clipped onto the exposure racks at a 5° angle of inclination. Test samples were collected after 1, 2, 3, 6, 9, 12, and 15 months of exposure. Hereafter, the length of exposure (months) is denoted as  $t_e$ . The samples were washed with distilled water, dried, wrapped with clean paper, and stored in a dark room at 23°C and 65% relative humidity.

The average molecular weights were determined by use of a GPC SSC 7100 (Senshu Scientific Co. Ltd., Tokyo, Japan). The sample was dissolved in *o*-dichlorobenzene, to give a 0.1 wt % solution. The analysis



**Figure 2** Variation of average relative humidity at Bicutan exposure site during the experiment.



**Figure 3** Variation of average global radiation reported by PAG-ASA during the experiment.

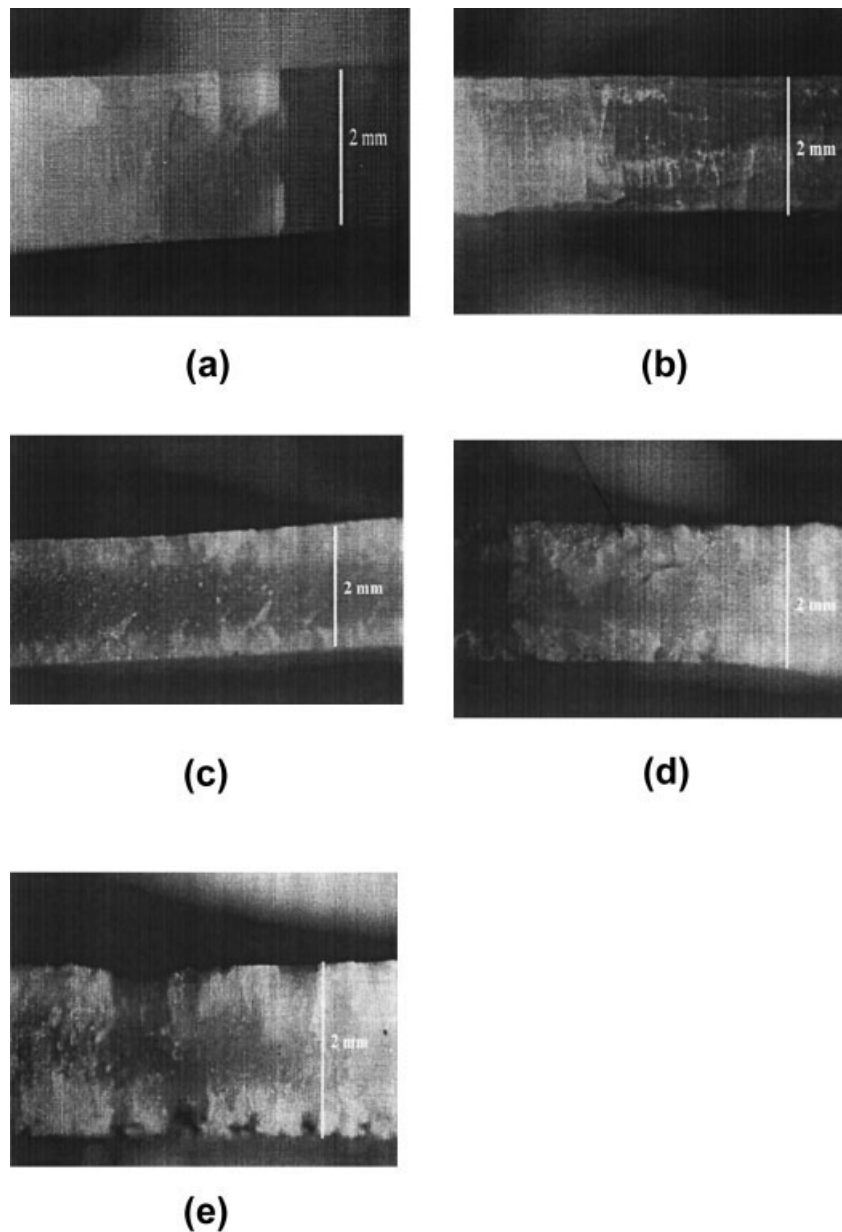
was conducted for the solution at 145°C and a flow rate of 1.0 mL/min. The column and reference material for calibration were Shodex UT and polystyrene, respectively.

The FTIR spectra were obtained through use of a Vector 22 FTIR spectrophotometer (Vector Laboratories, Burlingame, CA). The samples were dissolved in hot xylene. A solution-cast film was prepared in a petri dish for each of the samples of  $t_e = 0$  and  $t_e = 1$ , and the detached film was used for the measurement. On the other hand, the KBr method was adopted for samples of  $t_e \geq 2$ . The difference in the sample preparation was attributed to their rigidity and brittleness.

DSC curves were obtained through use of a Seiko DSC Model 220 (Seiko Instruments, Japan). Samples of about 10 mg were cut and cramp-sealed in an aluminum cell. Both the sample and the reference material were heated from 25 to 200°C at 10°C/min under N<sub>2</sub> atmosphere to obtain the heat of fusion.

The tensile properties of PP plates were measured by use of an Instron tensile tester (Canton, MA) (Model 8872). The crosshead speed of the equipment was set at 5 mm/min. The dimension of the test piece, cut from the sample plate, was 80 × 15 × 2 mm. The tensile strength and strain were calculated on the basis of the maximum load and the break point, respectively. An average value of five samples was recorded.

Optical microscopy (OM) was done by use of a Nikon stereomicroscope (Nikon, Tokyo, Japan). Scanning electron microscopy (SEM) at higher resolution was done by use of a JEOL T-330 (JEOL, Peabody, MA). The sample was coated with gold (~ 200 μm thickness). Atomic force microscopy (AFM) was carried out by use of a Shimadzu SPM-9500-J2 (Shimadzu, Kyoto, Japan) in the “dynamic mode,” where the silicone cantilever is oscillated close to its resonance. The change of the vertical cantilever oscillation amplitude is detected, which is caused by the interaction of the tip with the surface. The height signal was recorded for a smaller region at the higher resolution.



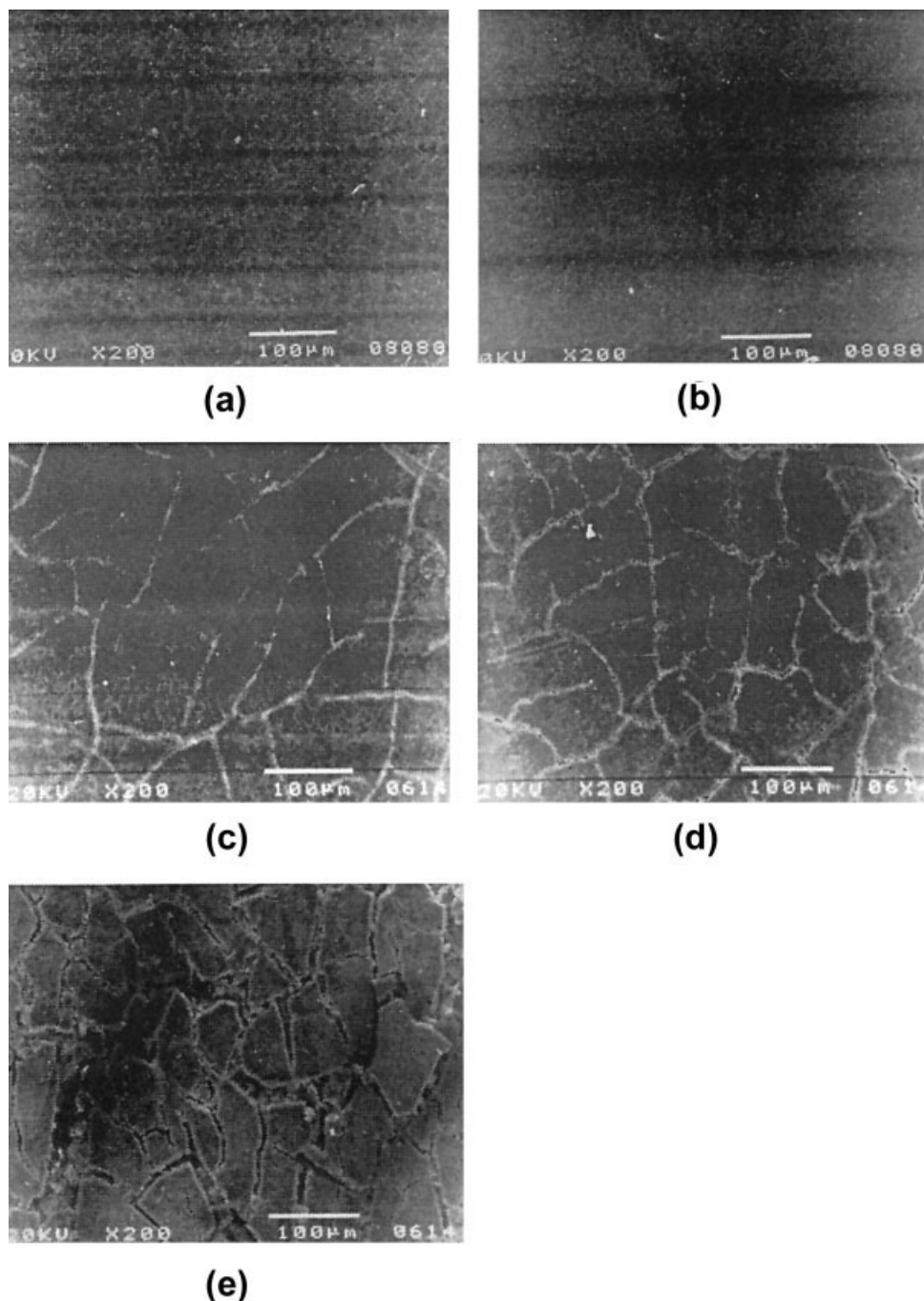
**Figure 4** Cross-sectional view of the samples taken by OM: (a) unexposed ( $t_e = 0$ ) and exposed for (b)  $t_e = 3$ , (c)  $t_e = 6$ , (d)  $t_e = 12$ , and (e)  $t_e = 15$ .

## RESULTS AND DISCUSSION

The PP plates before the exposure were translucent white. Exposed samples of  $t_e = 1$  and  $t_e = 2$  exhibited only slight changes in appearance. After 3 months of exposure, however, a light yellow color started to develop on the surface. OM images of the cross section revealed that the samples of  $t_e \geq 3$  are composed of two types of layers: one is opaque and the other, translucent [Fig. 4(b)]. The thickness of the opaque layer increased with the length of exposure. About 60% of the cross section became opaque in the samples exposed for 15 months [Fig. 4(e)]. In the SEM images of the surface, development of cracks with the increase in  $t_e$  was observed (Fig. 5). On the basis of these

observations, the opaque surface layer and the translucent inner layer in the OM images were attributed to the eroded and the noneroded parts, respectively.

Figure 5 seems to indicate that the surface of the sample of  $t_e = 1$  is not affected. However, the AFM image revealed that the surface of this sample was affected. Figure 6 shows the AFM images of the samples of  $t_e \leq 3$ . The surface of the unexposed sample is rough in this height scale [Fig. 6(a)]. The distribution of the height (i.e., height histogram) is indicated on the right side of the color bar. It should be noted that the histogram shows a single peak for the unexposed sample. On the other hand, the surface of exposed samples ( $t_e \geq 1$ ) appears to be partly eroded, resulting



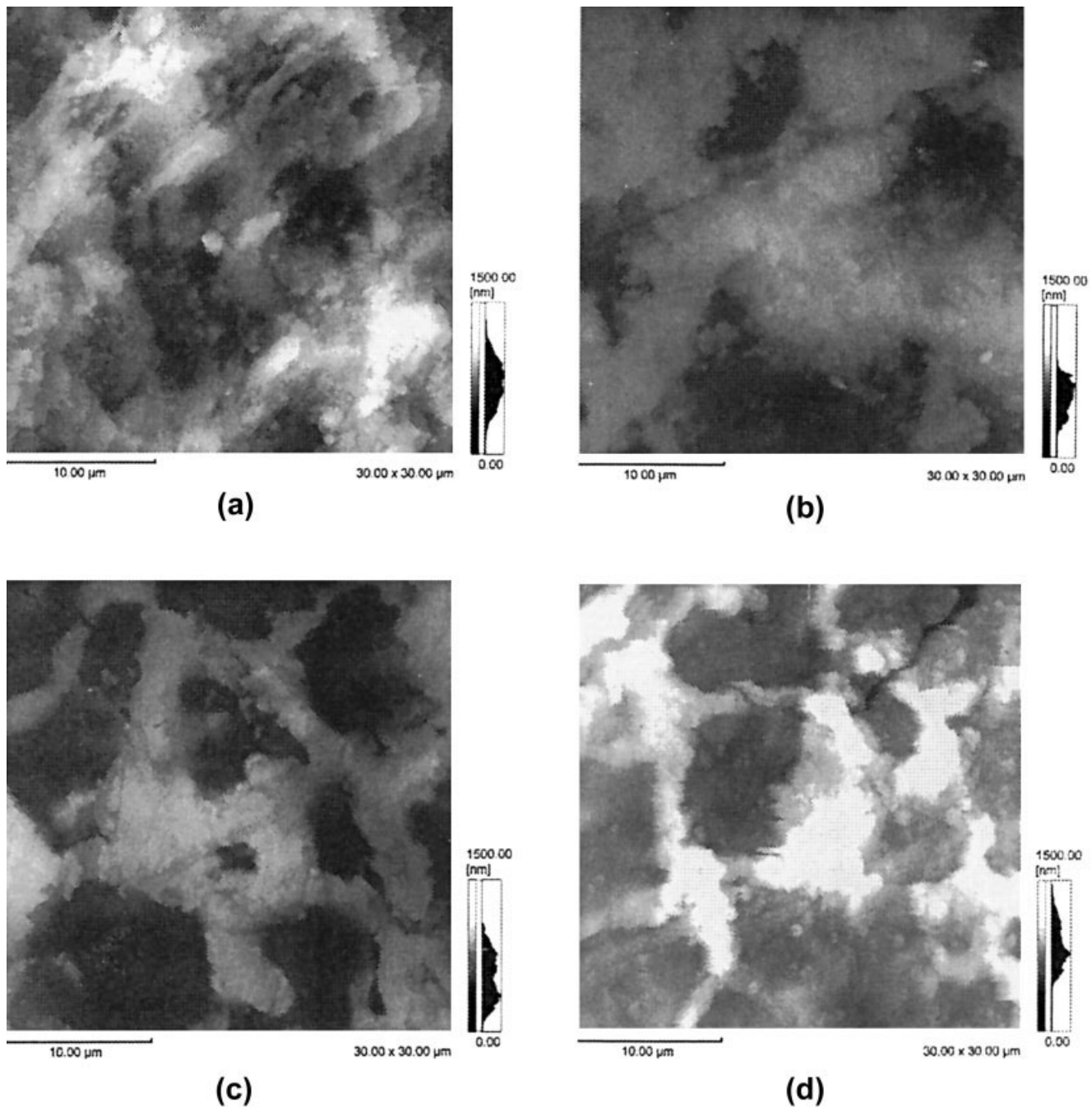
**Figure 5** SEM images of the surface of the samples: (a) unexposed ( $t_e = 0$ ) and exposed for (b)  $t_e = 1$ , (c)  $t_e = 2$ , (d)  $t_e = 3$ , and (e)  $t_e = 15$ .

in the doubled peaks in the histogram [Fig. 6(b)–(d)]. The difference of the heights between the corresponding peaks in the histogram is 200 to 300 nm. Further exposure ( $t_e \geq 2$ ) resulted in an increase in area of the eroded surface layer, which is known from the increased fraction of the peak attributed to the lower height in the height histogram. At the same time, development of cracks toward the inner layer was observed [Fig. 6(c), (d)].

Figure 7 shows the surfaces of  $t_e = 3$  and  $t_e = 6$  taken by AFM at higher magnification. The surface of the

inner layer is comparatively flat except for the existence of very small cracks in the case of  $t_e = 3$ , whereas the surface of the sample of  $t_e = 6$  is rough, with a globular texture of about 500 nm in diameter.

The microscopic observation mentioned earlier suggests three steps of degradation of PP sample plates, as illustrated in Figure 8. Figure 8(a) schematically represents the cross section of the sample. The surface layer of 200–300 nm thickness is thought to have been chemically or mechanically degraded during the process of sample preparation. (Because the samples were



**Figure 6** AFM images of the surface of the samples: (a) unexposed ( $t_e = 0$ ) and exposed for (b)  $t_e = 1$ , (c)  $t_e = 2$ , and (d)  $t_e = 3$ .

prepared by slow cooling in the molding machine, the surface may not be the amorphous skin layer that is commonly found in injection-molded pieces.) The circles represent large spherulites. These large spherulites may be surrounded by amorphous and small crystallites. In the first step of degradation, the surface layer (200–300 nm in thickness as revealed from AFM) is eroded, creating “holes” in the surface layer [Fig. 8(a), (b)]. The area of the “holes” increases with exposure length. The formation of small cracks on the

surface of the uncovered layer may follow as the second step [Fig. 8(c)]. Finally, the original surface layer may be totally eroded, showing the structure of the inner layer (which should reflect the spherulitic texture) [Fig. 8(d)]. The following data support this model and give us further information about the degradation mechanism of PP.

Figure 9 shows the FTIR spectra of the specimens. The absorption peaks, which appeared at approximately 1715 and 2365  $\text{cm}^{-1}$  ( $t_e = 12$  and  $t_e = 15$ ),

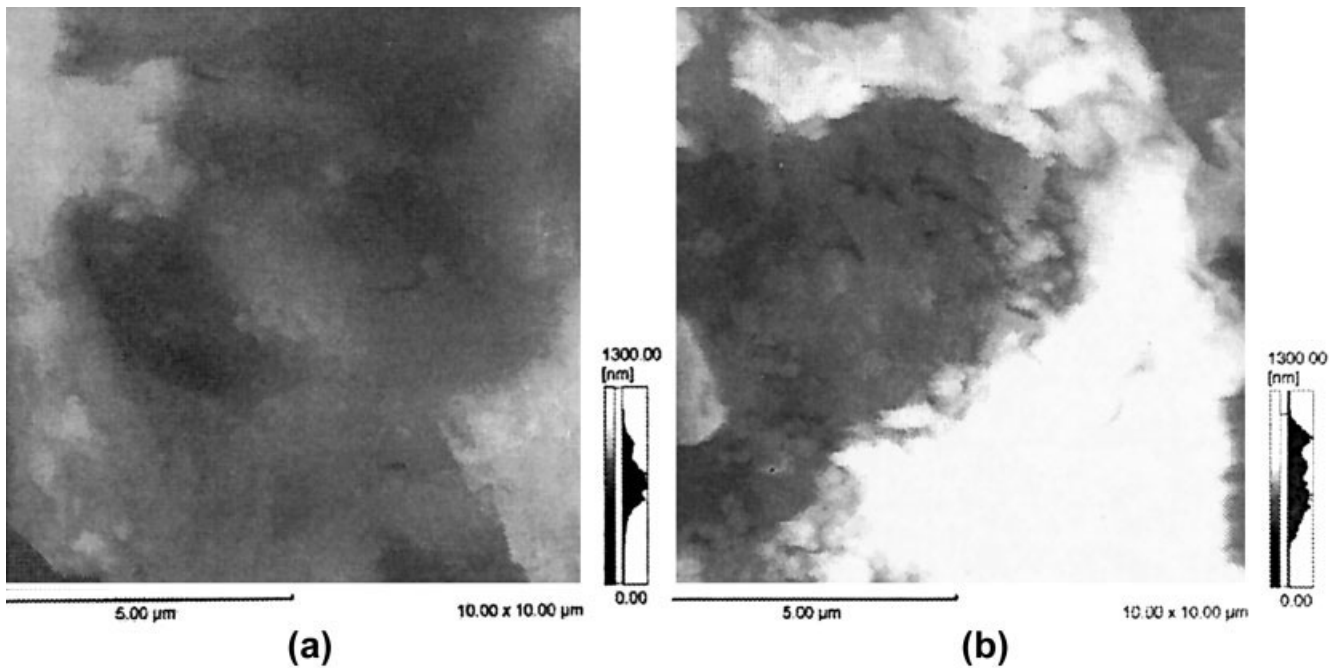


Figure 7 AFM images of the surface of the samples: (a)  $t_e = 3$  and (b)  $t_e = 6$ .

indicate the occurrence of carbonyl and methyl groups,<sup>8</sup> respectively. The FTIR spectrum of the unexposed PP showed traces of carbonyl groups, probably attributable to thermal oxidation during processing of the virgin resin into plates. (This supports our assumption that the surface layer may have been degraded during the preparation process.) On the basis of these peaks, the accumulated carbonyl index of the samples was calculated by use of the following formula<sup>8</sup>:

$$CI = D_{1715}/D_{2365}$$

where  $CI$  is the carbonyl index and  $D_{1715}$  and  $D_{2365}$  represent the optical densities [=  $\log(I_0/I)$ ], which

were estimated by the baseline method; that is,  $I_0$  is the intensity of the incident beam determined for the baseline and  $I$  is the intensity of the transmitted beam from the sample; both are at the wavenumber in question. Figure 10 shows the variation of the accumulated carbonyl index. It is interesting that the  $CI$  value increases almost linearly with time until it saturates.

Figure 11 shows the DSC traces. It is apparent that, as the exposure time is prolonged, the melting peak temperature is lowered. In the first 3 months, the exposure resulted in broadening of the melting peaks. Another melting peak at the lower temperature side was evident for samples of  $t_e \geq 6$ . The lower melting peak temperature was almost constant for the samples exposed longer than 9 months.

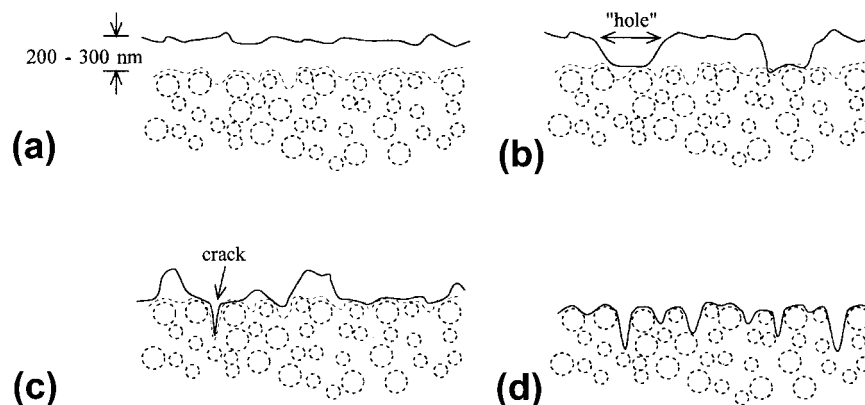


Figure 8 Schematic representation of the degradation mechanism of PP plates proposed in this study: (a) cross-sectional view of the original structure, (b) formation of "holes" on the surface layer ( $t_e \sim 1-2$ ), (c) formation of small cracks ( $t_e \sim 2-3$ ), and (d) total removal of the original surface layer.

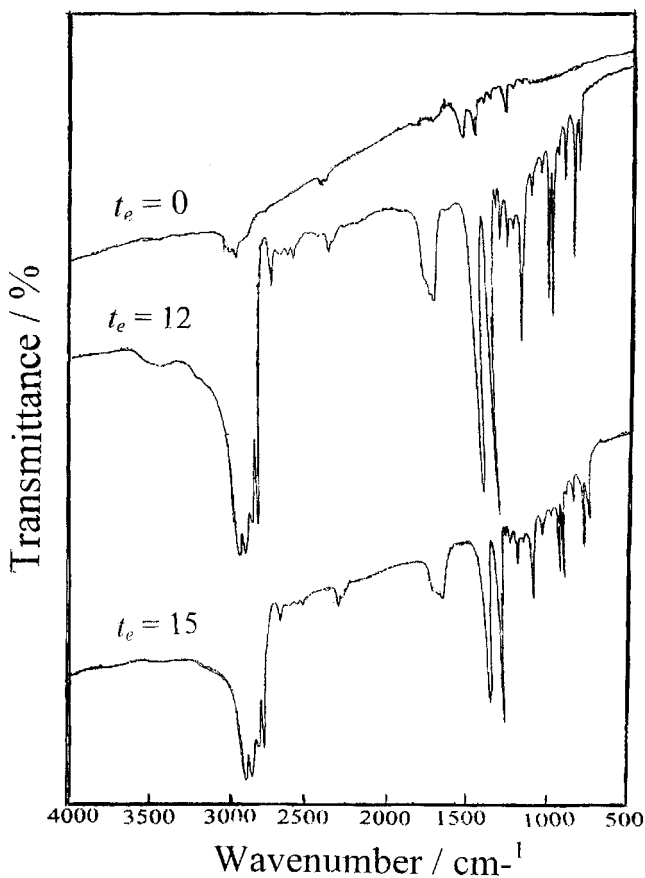


Figure 9 FTIR charts of the samples.

Through use of the results of the DSC experiments, the crystallinity of each sample was calculated as<sup>9,10</sup>

$$\text{Crystallinity (\%)} = \frac{\Delta H}{\Delta H_0} \times 100$$

where  $\Delta H$  is the heat of fusion obtained from the experimental work and  $\Delta H_0$  is the heat of fusion of perfectly crystalline PP, which is 209 J/g.<sup>11</sup> Figure 12 shows the variation of crystallinity thus calculated. In the first month, the crystallinity increased and the

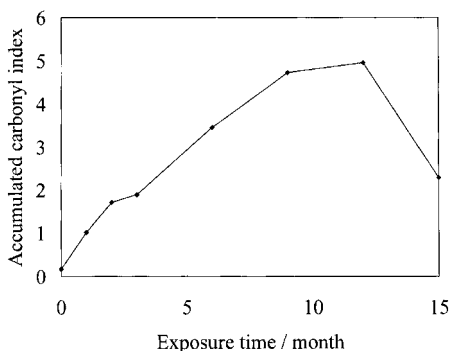


Figure 10 Variation of the accumulated carbonyl index with exposure time.

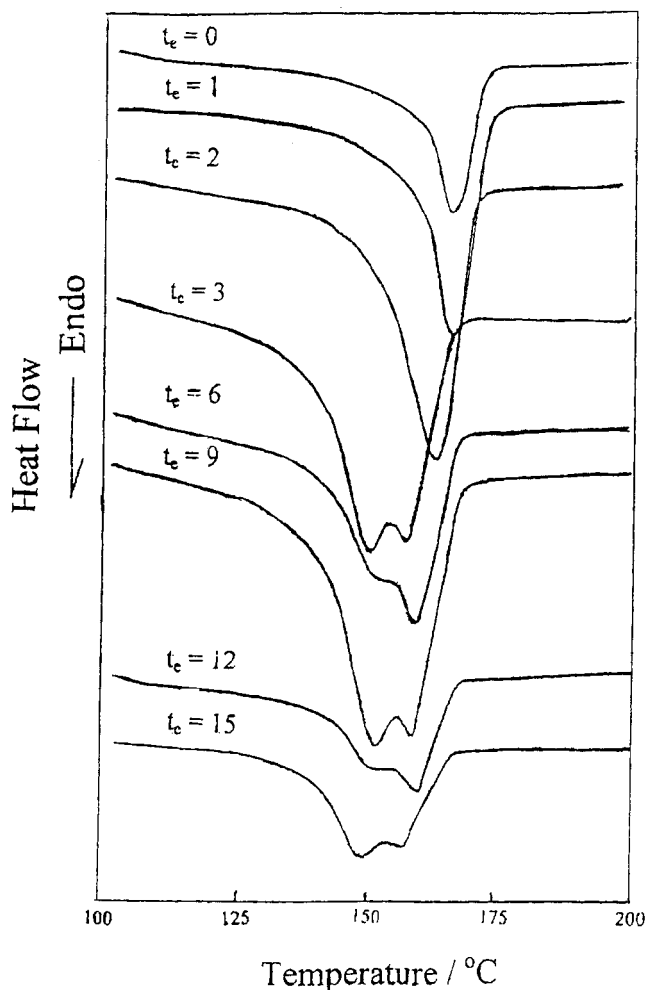


Figure 11 DSC charts of the samples.

value was almost unchanged until the ninth month. The increased crystallinity could be attributed to the higher ordering of the amorphous region,<sup>3</sup> to the recombination of the alkyl and alkoxy radicals in the more ordered forms,<sup>3,10</sup> to chemicrystallization,<sup>11-13</sup> and to the annealing effect arising from the increased temperature of the specimens in the strong sunshine. More prolonged exposure of the PP plates decreased

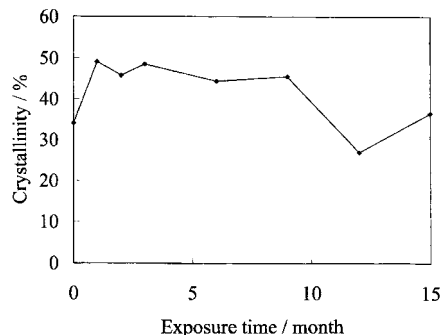


Figure 12 Variation of crystallinity of the samples with exposure time.

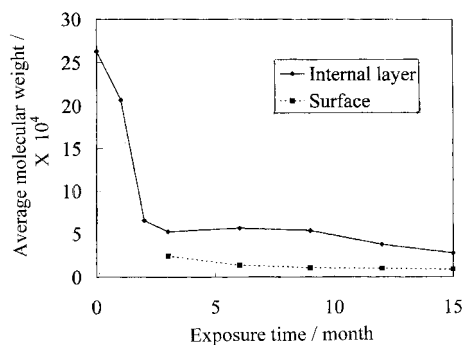
the crystallinity and the sample of  $t_e = 12$  showed a minimum in crystallinity. This may be attributed to the further increase of photooxidation products such as the carbonyls and hydroperoxides that act as chemical irregularities and limit the crystallinity.<sup>12</sup> The crystallinity apparently increased again as exposure was continued to  $t_e = 15$ . However, this could be attributable to the partial detachment of the surface layer [see Fig. 4(e)]: strong rains and typhoons may have washed the severely degraded part of the surface layer away, leaving the inner part that still possessed relatively high crystallinity. This also explains the decrease of the accumulated carbonyl index after 12 months' exposure (Fig. 10).

Figure 13 shows the weight-average molecular weight of the samples. The molecular weight strongly decreased in the first 2 months. The prolonged exposure of the samples after 3 months gradually decreased the average molecular weight. When separated, the average molecular weight of the opaque surface layer (Fig. 4) was lower than that of the translucent inner layer.

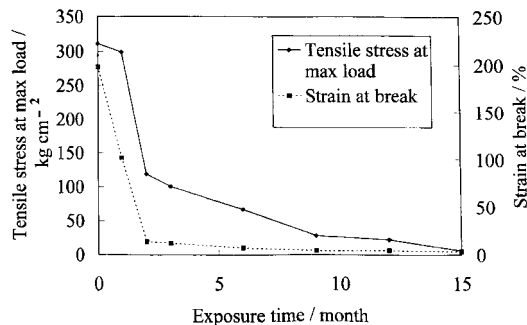
The variation of tensile properties of the unexposed and exposed PP plates is shown in Figure 14. The sample exposed for 1 month showed only a slight decrease of the maximal tensile stress, whereas the strain value at the breaking point exhibited a remarkable decrease, to about half the value of the unexposed PP. After 2 months' exposure, both of the tensile property values decreased significantly.

## CONCLUSIONS

On the basis of FTIR, DSC, GPC, and tensile strength measurements along with morphological observations (Figs. 4–7), the degradation mechanism of PP may be described as follows. According to Figure 10, oxygen is introduced into PP at an almost constant rate until it saturates. At first, however, the introduction of oxygen may not be directly related to the scission of molecular chain, and only the surface layer may be



**Figure 13** Variation of weight-average molecular weight with exposure time.



**Figure 14** Variation of tensile properties as a function of exposure time.

affected. After 2 months of exposure, molecular chains of the inner layer start to be degraded [Fig. 8(b), (c)], accompanying the significant loss of tensile properties (Fig. 14). Part of the degraded materials may be eroded, leading to the formation of cracks on the surface of the inner layer. The degradation may progress faster in the amorphous part of the PP plate and a spherulitic texture may show up on the surface after prolonged exposure [Fig. 8(d)].

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