Photooxidation of Polypropylene Under Natural and Accelerated Weathering Conditions

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ABSTRACT: The environmental and accelerated photodegradation of two polypropylene (PP) films (high and low crystallinity) were investigated. FT–IR measurements coupled with derivatization reactions (NO and SF_4), elongation at break tests and gel permeation chromatography technique were used to monitor the degree of oxidation during the UV exposure. No stoichiometry changes were observed under both UV conditions for the PP films. The dominant photoproduct, i.e., ketone, was suggested to be produced from peroxy radicals. The low concentration of *tert*-alcohol detected questioned the validity of its formation from hydroperoxide decomposition as suggested by several authors. Under natural exposure, the effect of degradation on mechanical property was different for high and low PP. High PP was useless after a short exposure time; low PP retained its physical property for a longer period of time. In the latter case, the analysis of the changes in elongation at break, the polydispersity $P = M_w/M_n$, the number of chain scissions N_t, and the kinetic accumulation of photoproducts provided strong indications on the mechanisms of acid and ester production and shed some light on the competition between crosslinking and chain scission reactions. The estimated acceleration factors were 7.5 and 8.5 for high and low PP, respectively, values that were much lower than those obtained for linear low-density polyethylene. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64**: 2497–2503, 1997

INTRODUCTION

A common drawback of large-scale polymers is their tendency to oxidize when exposed to UV radiations. In most laboratories throughout the world the degradation of polymers by UV light is generally induced in relatively short times by using an appropriate artificial system. As a result, with the help of new technologies and methods of analysis, a good understanding of the photo-oxidation process of polymers has been achieved. The comprehension of the oxidation mechanisms from laboratory tests is supposed to help research-

ers in their prediction of service life of polymers under natural conditions. This turned out to be more complicated than was expected. The reason is that under natural conditions, external factors such as exposure to sunlight, day and night temperatures, seasonal variations, humidity, or atmospheric contamination by highly corrosive agents are all both important and difficult to control or even record. In addition, study of natural photodegradation is time consuming; it may take several years to obtain any result, particularly for stabilized polymers. The direct consequence is a lack of basic information on natural weathering of polymers. To bridge this gap, we have been performing studies of photodegradation of polymers in the natural environment. Recently, we have compared the oxidation of stabilized and unstabilized linear low-density polyethylene and the decomposition of polyethylene hydroperoxides un-

der natural and accelerated conditions on the line of other authors.[1–11]

Herein, the outdoors and artificial weathering of one of the most studied polymers, polypropylene, is reported. Two different polypropylene (PP) films were experienced: high and low crystallinity samples. Quantitative and qualitative evaluations of oxidation products have been conducted with FT–IR technique combined with chemical derivatization (SF$_4$ and NO treatments). To gain some insights on how to correlate loss of mechanical property with chemical changes, we have followed the molecular weight changes during the natural exposure by Gel Permeation Chromatography (GPC).

EXPERIMENTAL

Materials

Polypropylene pellets were melted under pressure at 200°C to produce 0.1 mm thick films and then quenched in a bath. Rapid quenching to 0°C lead to low crystallinity PP films, while films with high crystallinity were obtained by performing a slow cooling down to 20°C. The molecular weight of the virgin films was estimated (the experimental conditions are described below): low crystallinity PP film: $M_n = 30,899$, $M_w = 197,895$; high crystallinity PP: $M_n = 31,738$, $M_w = 192,110$.

Irradiation Conditions

The accelerated weathering tests were performed in a Weather-O-meter with an incident light corresponding to an average of 161 kJ/m^2 per hour. The silver panel temperature was set at 40°C. The outdoor exposure tests were carried out during summer time in Tsukuba City (Japan), located at 140° E longitude and 36° N latitude. No stress was applied to the films during exposure. The intensity of the light was collected from the national meteorological station under outdoor conditions.

Evaluation of Degradability

Immediately after UV exposure, the degradation of PP films was evaluated. Whenever the evaluation was not possible, the exposed samples were frozen to avoid further degradation before analysis.

Identification and Quantification of Oxidation Products

Oxidation products were identified and quantified by FT–IR spectroscopy (Perkin–Elmer model 1750) coupled with derivatization reactions (NO and SF$_4$; for more details on these treatments see ref. 12). It is worth mentioning the complexity of NO treatment of PP. It must be performed at low temperature (≈ -20°C). In addition, besides an overlap of the IR bands of nitrates and nitrites—issued from the NO reaction with hydroperoxides and alcohol, respectively—these products were unstable. This makes difficult a quantification of hydroperoxide and alcohol species. In a recent investigation, we reported a way out to overcome this difficulty.[13]

Mechanical Tests

The elongation at break was monitored using a TENSILON model UCT-1T (Orientec, Japan) apparatus with a traction speed of 100 mm/min. The samples used for the elongation tests were cut into dumbbell shapes (70 mm long with a 15 × 3 mm neck). The results reported here are the average of five tests.

Gel Permeation Chromatography (GPC)

The molecular weight analysis of the virgin and UV-irradiated samples was carried out using a WATERS model 150-C GPC (AT-80 M/S Shodex, Showa Denko, Japan). The working temperature was set at 135°C. The samples were dissolved in 1,2,3-trichlorobenzene. The solvents used all contained the antioxidant [4,4-thiobis(2-*tert*-butyl-6-methyl phenol)] to prevent any further degradation. Polystyrene was used for calibration. Measurements of the molecular weight were performed in duplicate. The average deviation of M_w expressed as a percentage of the mean value is 5%, whereas the one for M_n is 8%.

EXPERIMENTAL RESULTS

Kinetic Accumulation of Photoproducts

Natural and accelerated weathering of PP lead to the formation of different photoproducts as stated changes in the hydroxyl and carbonyl regions of the recorded FT–IR spectra. In the carbonyl region, a sharp band appears at 1715 cm^{-1} (ascribed to carboxylic acid and ketone species) with several shoulders and bands attributed to ester, perester,

and γ-lactone entities. To facilitate their quantification, UV-irradiated samples were submitted to SF$_4$ gas. After this treatment, the resulting FT–IR spectrum showed the formation of acid fluorides at 1841 cm^{-1} issued from the conversion of carboxylic acids present in the polymer. It also clearly displayed ketone groups at 1720 cm^{-1}, perester at 1770 cm^{-1}, ester at 1740 cm^{-1} and a γ-lactone band at 1795 cm^{-1}. In the hydroxyl region, it is well known that the IR bands of hydroperoxide and alcohol groups interfere; the NO treatment helps to characterize and quantify these photoproducts. The FT–IR spectrum of the NO-treated piece of degraded PP allowed us to distinguish tertiary hydroperoxides (at 1293 cm^{-1}) from secondary ones (at 1276 cm^{-1}).[13] Only tertiary alcohol entities at 756 cm^{-1} were detected in our investigations on PP. It is worth noting that no unsaturation products, no free and primary hydroperoxide species were detected under natural and artificial conditions.

Figures 1 and 2 exhibit the kinetic accumulation of all photoproducts quantified. Note that Figure 1 is quite similar to the one obtained by other authors.[14] In both exposure conditions, the increase in most photoproducts (except tertiary hydroperoxides and tertiary alcohol) shows an induction period. This induction period varies from one photoproduct to the other; it is followed by a reasonably rapid acceleration according to photoproduct. The production of tertiary alcohols is negligible, a result that is quite surprising. As for tertiary hydroperoxide, its plot displays a significant increase all over the induction time. Afterwards, the increase rate becomes less important, and shows even a tendency to a plateau under accelerated conditions. Secondary hydroperoxides also plateau under accelerated conditions. Whatever the exposure mode, ketone groups appear to be the dominant photoproducts. It is followed by acid and esters that are produced to roughly the same extent (except for PP high crystallinity under accelerated conditions, see Table I). The slower build up in γ-lactones concentration is observed in both figures. More information about the evolution of the functional group concentrations can be obtained by determining the extent of oxidation. The results are given in Table I. Remember that the extent is taken in first approximation as the slope of the exponential part of the plot; it is estimated by the ratio of the tangent axis to the x-axis expressed in unit of length. The interesting point to note is that under accelerated conditions the rate of oxidation of PP low crys-
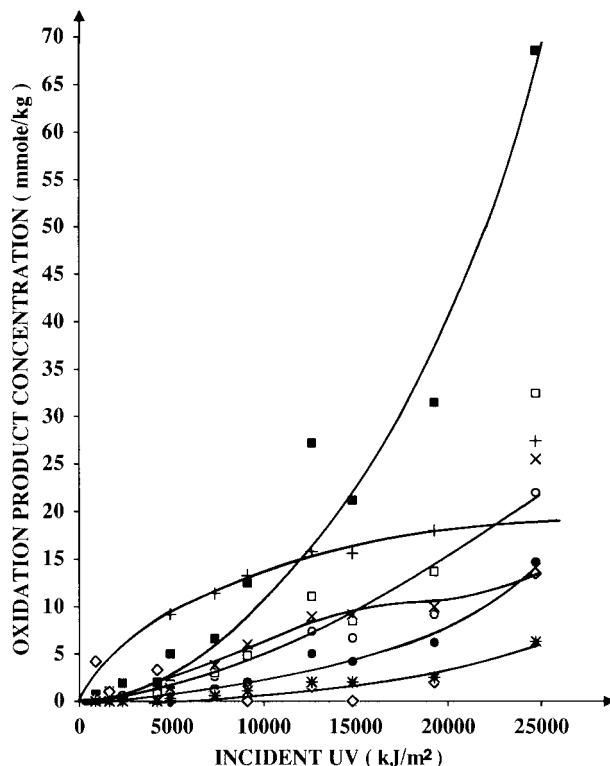

Figure 1 Evolution of the oxidation products vs. the intensity of UV light during the accelerated photodegradation of PP (low crystallinity): ($\bigcirc$) acid, ($\blacksquare$) ketone, ($\square$) ester, ($\times$) secondary hydroperoxide, ($+$) tertiary hydroperoxide, ($\diamond$) tertiary alcohol, ($*$) γ-lactone, ($\bullet$) perester.

tallinity is found to be higher than that of PP high crystallinity; on the other hand, under natural conditions, the evolution of the functional groups did not differ between low and high PP, taking into account experimental errors. It was also observed that the extent of tertiary hydroperoxide was twofold higher than the one of secondary hydroperoxide under natural photo aging; this was no longer true under accelerated conditions where secondary hydroperoxides were produced at a higher extent.

Mechanical Properties

The oxidation of polymers results in numerous chain scissions under UV exposure. This leads to physical deterioration of the polymers. Elongation at break and molecular weight tests are suitable methods for measuring the small physical modifications that occur. For PP high crystallinity, failure of the elongation at break occurred after only 10 days of natural exposure. Its value went from
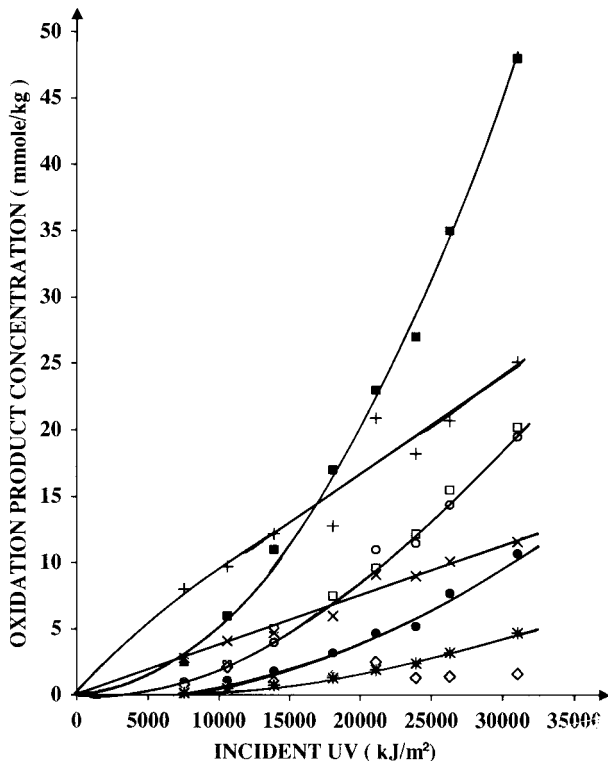
Figure 2 Evolution of the oxidation products with the intensity of UV light during the outdoor photodegradation of PP (low crystallinity). Symbols as in Figure 1.

Figure 3 Changes of the polydispersity P ($\bullet$), the elongation at break ($\circ$), and the number of chain scissions N_t (mol/mg) ($+$) with the intensity of UV light during the outdoor photodegradation of PP (low crystallinity).

508 ± 41 to 11 ± 5; this corresponds to 48 and 88% decrease in the values of the molecular weight M_w and the number-average molecular weight M_n, respectively. PP low crystallinity kept its valuable mechanical property for about 21 days of exposure corresponding to 14000 kJ/m^2 (Fig. 3). Afterwards, the elongation at break decreases sharply. On the same figure, we observe a rapid increase
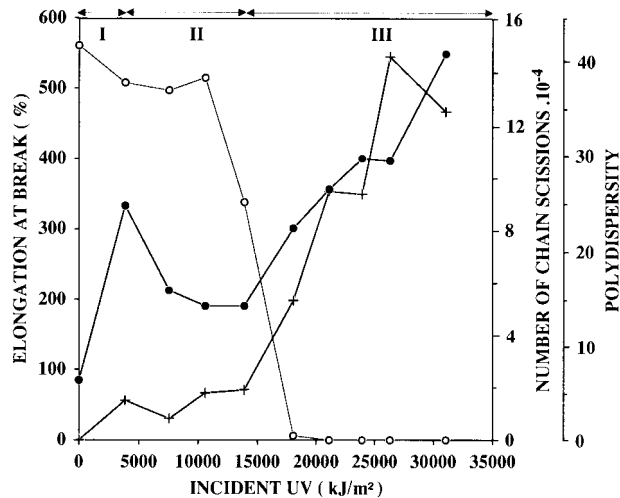
of the polydispersity ratio P $= M_w/M_n$ at the very beginning of the UV exposure (Phase I) followed by a decrease (Phase II). The film lost its physical property at the end of this decreasing phase. From this point, another increase of P happened during the remaining period (Phase III).

Changes of mechanical properties during UV exposure are essentially caused by chain scission reactions. According to Hoekstra et al.,[15] the conversion of chain scission reactions can be expressed in terms of the number of scission events per gram of material $N_t = 1/M_{nt} - 1/M_{no}$, where M_{nt} and M_{no} are the values of the number-average molecular weight at time t and before exposure,

Table I Extents of the Evolution of Oxidation Products Quantified Under Natural and Artificial UV Exposures for Both PP Films

UV Irradiation Conditions	PP Low Cristallinity		PP High Cristallinity	
	Weather-O-Meter	Outdoor	Weather-O-Meter	Outdoor
Ketone	1.77 ± 0.13	2.06 ± 0.19	1.41 ± 0.11	1.78 ± 0.17
Acid	0.51 ± 0.07	0.84 ± 0.11	0.27 ± 0.06	0.69 ± 0.11
Peresters	0.37 ± 0.06	0.44 ± 0.09	0.27 ± 0.06	0.44 ± 0.09
Ester	0.51 ± 0.07	0.84 ± 0.11	0.68 ± 0.08	0.69 ± 0.11
tertiary Hydroperoxide	0.37 ± 0.06	0.69 ± 0.11	0.14 ± 0.05	0.66 ± 0.10
secondary Hydroperoxide	0.51 ± 0.07	0.31 ± 0.08	0.27 ± 0.06	0.28 ± 0.08
γ-Lactones	0.13 ± 0.05	0.22 ± 0.08	0.09 ± 0.05	0.16 ± 0.07

Remind that the extent is taken in first approximation as the slope of the exponential part of the plots; it is estimated by the ratio of the tangent axis to the x-axis, both expressed in unit of length.

respectively. The variation of N_t with the light intensity (Fig. 3) displays a slight increase at the first sampling. This increase remains almost constant up to 14,000 kJ/m^2 (Phase I and II) followed by a fairly rapid increase (Phase III). One can notice a net correlation between the drastic loss of the elongation at break and the starting point of the significant increase of N_t.

DISCUSSION

Natural and accelerated weathering of PP in air involve oxidation of the polymer chain. According to our results, the dissociation of a C—H bond, resulting in the formation of secondary or tertiary alkyl radicals is predominant. These radicals, after a combination with oxygen followed by a hydrogen abstraction from the polymer chain, generate secondary and tertiary hydroperoxides. Figures 1 and 2 showed that tertiary hydroperoxides outnumbered secondary hydroperoxides in the time scale of our experiments. Under natural exposure, this observation was confirmed by a much higher extent of *tert*-hydroperoxide. Under accelerated conditions, though *sec*-hydroperoxides were produced at a higher extent, our observation remained valid. Indeed, both plots of *sec*- and *tert*-hydroperoxides showed a plateau, with a higher concentration of the latter. The higher formation of hydroperoxides during the induction period, particularly *tert*-hydroperoxide, confirmed their role as the primary photoproducts of oxidation. Methyl-ketone, end-ketone, or alcohol have been proposed to be produced at the expense of hydroperoxide species.[14] This interpretation cannot be set apart, but we believe that their formation from peroxy radicals can be a contender. As suggested by the group of Russel[16,17] the interaction of peroxy radicals may lead to alkoxy radicals or inactive products.
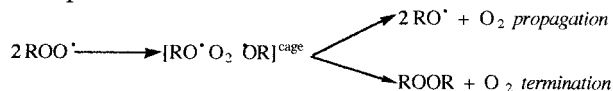

These reactions are more likely to happen because the dissociation energy of the O—O bond is lower in peroxy radical than in hydroperoxide (154.8 kJ/mol compared to 175.7 kJ/mol). The alkoxy radicals created can lead to different photoproducts following Scheme 1.

Because no free, primary hydroperoxides and unsaturations were detected, it can be reasonably assumed that primary alkyl radicals, created through pathway 1b and 1c, will recombine in the cage leading to crosslinking reactions. This recombination may be also valid for primary alkyl radicals generated in the initiation step. The results obtained in the changes of physical property of PP low crystallinity confirm this assumption. Indeed, in phase I and part of phase II, the elongation at break remained unchanged from its initial value, the number of chain scissions N_t stayed low, the polydispersity increased only in phase I. These observations are all consistent with the fact that the probability of crosslinking was larger than that of chain scission. However, the decrease of P in phase II did not corroborate such a behavior; its increase in phase III also contradicted the changes observed in N_t and the elongation at break. We reach the conclusion that the variations of P have to be interpreted with caution. This conclusion is in agreement with that of O'Donnell et al.,[18] who found out that inaccuracies are inevitable in M_n and M_w measurements, especially for highly degraded polymers. In contrast, the variations of N_t did provide a sensitive means for monitoring the tensile properties during UV exposure. Recently, Hoekstra et al.[15] found a remarkable correlation between the number of chain scissions and the number of carbonyls. Looking more closely Figures 2 and 3, it is also relevant to notice that the curves of N_t, ketone, acid, and ester formation show a similar trend. This suggests the production of acid and ester species from scission reactions and confirms the formation of ketones following Scheme 1. Acid and ester species can be derived following scheme 2.[19] These reactions corroborate the similar trend observed in the evolution of ketone, acid, and ester groups.

The surprising result is the low concentration of *tert*-alcohol recorded. Several authors have proposed its formation from hydroperoxide decomposition. Therefore, the negligible concentration of alcohol detected challenges the validity of the proposed mechanisms. Indeed, the significant concentration of hydroperoxides recorded should have led to a nonnegligible concentration of alcohol on the ground that these last species are stable under our experimental conditions. On the other hand, the formation of *tert*-alcohol as proposed from route 1a of Scheme 1 does not seem to be favored; this may explain its low concentration.

Under natural exposure it was mentioned that PP high crystallinity met a rapid loss of the elongation at break, suggesting a rapid destruction of tie molecules responsible for the mechanical
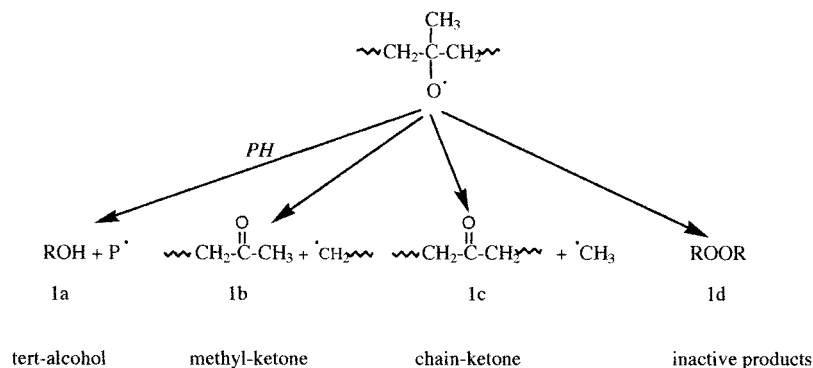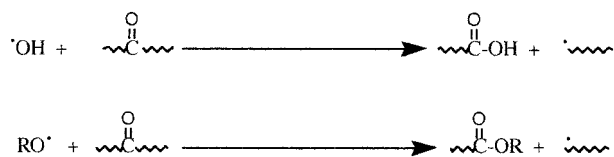
Scheme 1

properties. Despite the difference in mechanical changes, the chemical formation of photoproducts did not differ either quantitatively or qualitatively in both PP films under natural exposure. This is surprising, because the amorphous part in which the oxidation process takes place is larger in PP low crystallinity than in PP high crystallinity films. This must presumably result to a higher rate of oxidation in the former film than in the latter as observed under accelerated conditions. Such contrasting results illustrate how the degradation rate can depend heavily on the method chosen to assess the behavior of polymers under UV light. Here, we can speculate on the flux of photons, the temperature, and the diffusion of oxygen to be the major causes of such discrepancies. However, all these discrepancies did not have a great influence on the acceleration factor. The latter was determined from the time required to obtain a value of 0.1 absorbance at 1715 cm^{-1}. It matched 8.5 and 7.5 for low and high PP, respectively. These values are much lower than those obtained previously for linear low-density polyethylene (average value = 29 ± 3).[6] This supports and extends our previous conclusions that each type of polymer and even formulation has a specific acceleration factor.

Another point of interest was to check whether the stoichiometry of oxidation was identical under both experimental conditions. Even if we could note some differences in the extent of oxidation

Scheme 2

outcomes—which were generally higher under natural conditions than under accelerated ones—the stoichiometry remained unchanged in proportion for both polymers, taking experimental errors into account.

CONCLUSION

In this article, comparative photo-oxidation of two PP films (high and low crystallinity) under natural and accelerated conditions was reported. In both conditions, hydroperoxides were the primary photoproducts and ketones were the dominant oxidation products. Besides its formation from hydroperoxide, the production of ketone species can be reasonably issued from peroxy radicals (Scheme 1). Under natural exposure, the consequence of the oxidation on mechanical properties differed drastically from high PP to low PP. The former was useless after the first sampling, performed after 10 days of UV exposure. Low PP kept its valuable property for 21 days. In this case, the combination of the elongation at break changes, the polydispersity P and the number of chain scission N_t provided a clear picture on how physical properties might strongly depend on the balance between crosslinking and chain scission reactions. It gave us strong indications that ester and acid species were probably issued from scission reactions (Scheme 2). The low concentration of *tert*-alcohol recorded challenged the validity of its formation from hydroperoxide decomposition. Its formation from alkoxy radical suggested was not favored—a point that needs to be clarified. Though some inconsistencies appeared in the extent of some functional group concentrations under both UV exposure conditions, the acceleration factors of the PP films tested were quite close (7.5 for high

PP, 8.5 for low PP). In terms of stoichiometry, the degradation of PP, low, and high crystallinity, appeared to proceed in the same way under both UV-exposure modes.

In conclusion, we can say that all these results added to previous ones prove that investigation of the natural photo aging of polymers is a necessity to minimize errors in the prediction of polymers life service, even if it is time consuming.

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