Quantitative Study of Photocatalyzed Oxidation of Ethylene–Propylene Rubber and Atactic Polypropylene

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ABSTRACT: The effect of photoactive pigments such as ZnO, CdS, and TiO_2 on the photooxidation (with and without water vapor) of ethylene–propylene rubber and atactic polypropylene were examined. The effects of surface treatment (passivation) and low granulometry (nanopigments) were also studied for TiO_2. A drastic increase of ketone and an inhibition of carboxylic acid formation for ZnO filled polymers were revealed and quantitatively measured by using derivatization reactions. Such a phenomenon, as well as a small decrease of average molecular weight, were explained by a modification of the ZnO decomposition mechanism of tertiary hydroperoxides. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1681–1689, 1998

Key words: photocatalyzed oxidation; ethylene–propylene rubber; atactic polypropylene

INTRODUCTION

Photoactive pigments like ZnO or TiO_2 play an interesting role in the photo- or thermal oxidation[1-4] of polymers, particularly when these are "transparent" in the solar spectral region reaching the earth surface ($\lambda \geq 295$ nm). In usual conditions, these polymers, among which we find most of the materials of industrial interest (polyolefines, poly(vinyl chloride), polyamide, elastomers, etc.), are oxidized via extrinsic chromophoric impurities (hydroperoxides from processes, catalyst residues, etc.)[5] or via the absorption of complexes of oxygen and polymers.[6] The presence of photoactive pigment affords the control of the absorbed light (filter effect; most of them absorb intensively at $\lambda \leq 405$ nm) and the control of the oxidation because very active forms of oxygen are generated by electron photoejection from the pigment surface[7-17] (photocatalytic effect).

$$\text{Pigment} + O_2 + H_2O \cdots \xrightarrow{h\nu} {}^1O_2, {}^\bullet OH, {}^\bullet OOH \cdots$$
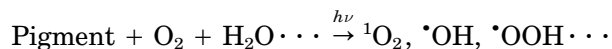
These pigments, particularly TiO_2, are extensively used in plastic and paint formulations because of their high hiding power (diffusion of visible light). White, as well colored polymers, contain significant amounts (a few percent) of these pigments; this is why the study of their influence in polymer photoaging is of practical and fundamental interest.

The diffusing properties of visible light (white polymer) and the photocatalytic (prodegradant) effect of photoactive pigments can be canceled by using microparticular and surface treated (coated) TiO_2, respectively. The combination of both effects can ensure the development of transparent inorganic UV absorbers usable in films, cosmetics, and other products.

Past studies by our group[18-21] revealed that a "pure" (without any direct oxidation) photocatalytic effect can occur for oxidation of low molecular compounds or of polyolefins in particular conditions. The blending of zinc oxide with amorphous polyolefins such as ethylene–polypropylene rub-
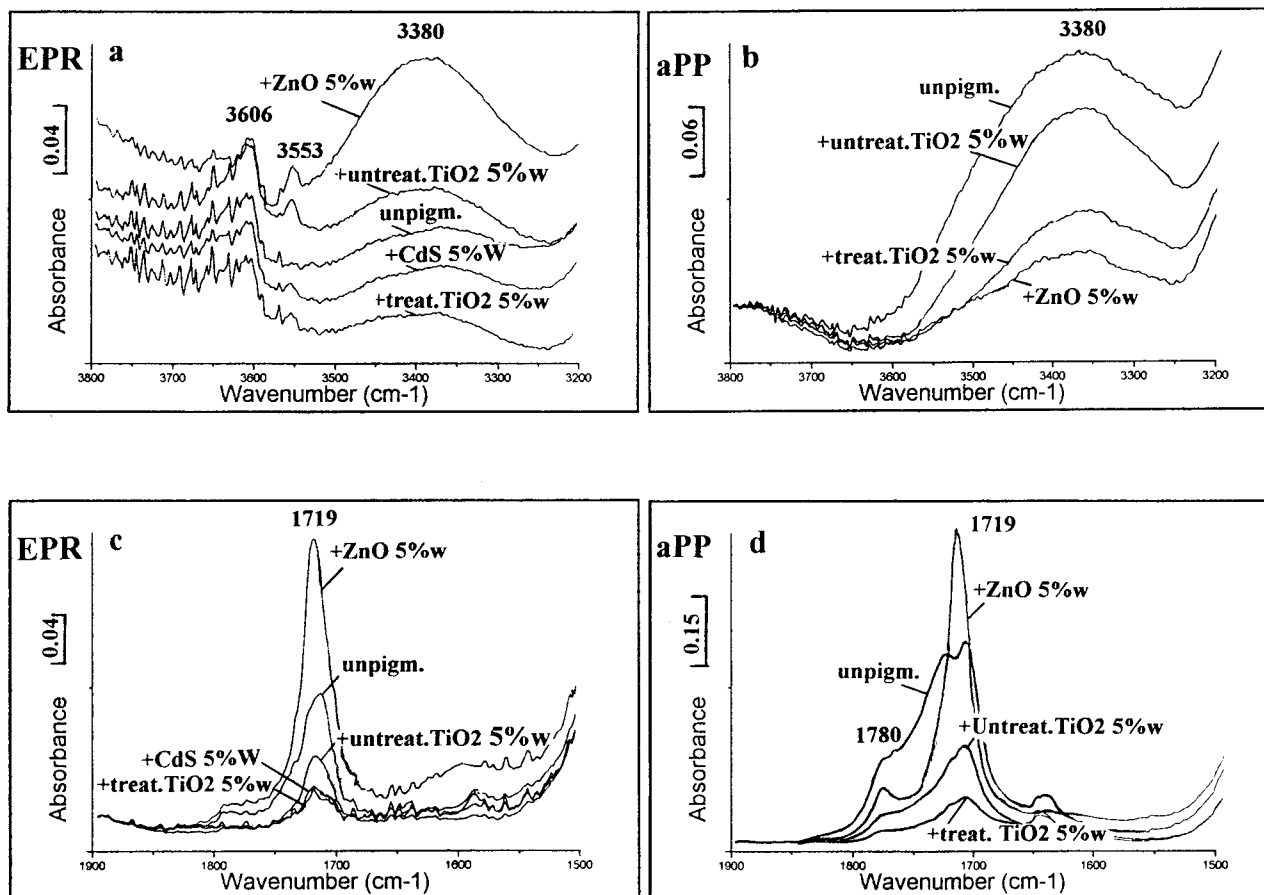
Figure 1 IR changes upon NO treatment (96 h at −20°C) of photooxidized (a) EPR and (b) EPR + ZnO 5% (exposure times 100 h).

bers (EPRs) or atactic polypropylene (aPP) showed a unique behavior because the photooxidation (fast) was characterized by narrow carbonyl absorption bands assigned mainly to ketones and γ lactones. These carbonyl groups were photoprotected by the pigment (filter effect), avoiding the formation of secondary products such as those resulting from Norrish reactions on ketones (chain breaking products, carboxylic acids, unsaturations, etc.). The effect of photoactive pigments on hydroperoxide groups was revealed to be more complex because the pigment can act as both a promotor and specific decomposer of hydroperoxides.[22]

The present article reports on the systematic evaluation of ketones, acids, and hydroperoxides along the photooxidation of aPP and EPR containing or not containing photoactive pigments such as ZnO, CdS, and TiO$_2$ (surface passivated or not, normal and low granulometries). The role of water in paint (chalking)[23] is also examined.

EXPERIMENTAL

EPR (VISTALON MD 84/2, 75 wt % ethylene, Exxon-F) containing 0.05 wt % of a processing antioxidant and a few percent of zinc stearate (antiacid) was mixed for 5 min at 160°C with the family of pigments ZnO A (Vieille Montagne-Bel), TiO$_2$ RL11A and RL90 (surface treated) (Thann & Mulhouse-Fr.) and ultrafine TiO$_2$ UF01 and UF10 (surface treated) (Tioxide-Fr.) and CdS (Bayer-Ger.) and pressed into films (ca. 100 μm) at 210°C for 5 min. Before photooxidation each film was Soxhlet extracted for 48 h with acetone (removing of processing antioxidant).

The aPP (softening point 121°C, Scientific Polymer Products) was first purified by dissolution in n-hexane and reprecipitation in methanol. Blends with pigments (ZnO A, TiO$_2$ RL11A, TiO$_2$ RL90, and ultrafine TiO$_2$ UF01 and UF10 were made by a new dissolution of the polymer in n-hexane, stirring with pigment, and final precipitation of
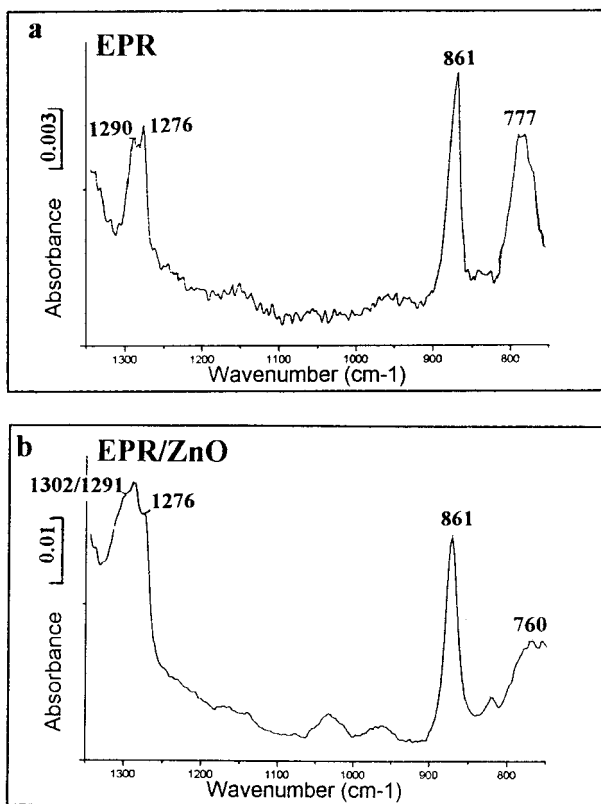
Other pigments showed an intermediate behavior that was probably due to an insufficient dispersion in the polymer matrix; the phenomena were interpreted as a superposition of normal oxidation in nonpigmented zones and a photocatalyzed oxidation in pigmented zones.

The lower contribution of carboxylic acids in the presence of ZnO can be checked by using specific derivatization reactions. Both ammonia and sulfur tetrafluoride are known to convert, at the solid state, carboxylic acids into acid fluorides and ammonium carboxylates, respectively. Because of large IR wave number shifts for the new groups ($-COF$, $-CO_2^-$), the carboxylic acid contribution can also be derived from spectrum substractions (after–before treatment) as seen in Figure 3.

Both SF_4 and NH_3 treatments indicate a very small contribution of carboxylic acids in ZnO filled samples (EPR and aPP). SF_4 results in acid fluoride bands at 1846 (EPR) (residual antiacid zinc stereate is also converted into acid fluoride; its contribution was taken into account for calculations) and 1839 (aPP) cm^{-1} while NH_3 leads to a broad carboxylate band at $1560-1580$ cm^{-1}.

For NH_3 treatment, differential spectra show the disappearance of carboxylic acids (negative band at $1705-1710$ cm^{-1}) and the conversion of esters ($1730-1735$ cm^{-1}) into amides (1680 cm^{-1}). In the case of SF_4 treatment, an unexpected additional positive band can be seen at 1722 cm^{-1} [Fig. 3(c)] for ZnO filled EPR. This phenomenon derives from an increase of the ketone band because of the destruction of associations between hydroperoxide–alcohols and ketones (SF_4 reacts with ROH and ROOH, too). The ketone band becomes less broad and more intense, but this phenomenon is only revealed when the contribution of carboxylic acids is very low. The determination of carboxylic acid and ketone contributions (ketone contribution derived from the residual carbonyl band at 1723 cm^{-1} after treatments) were done for most of the samples; results are shown in Figure 4 for EPR and aPP.

The presence of zinc oxide inhibits the formation of acids and favors the formation of ketones for EPR and aPP. Untreated titanium dioxide seems to have a similar effect in aPP but not in EPR. Treated TiO_2 shows the expected filter effect (UV absorber) in both polymers. Cadmium sulfide also shows a filter effect, probably because of weak photocatalytic activity (already reported elsewhere[20]).

For pigments other than ZnO, in comparison with unpigmented polymers, the contribution of

carboxylic acids seems to be reduced in EPR but not in aPP ([ketone] $\approx$ [acids]).

This similar contribution of ketones and acids in photooxidized aPP was already demonstrated in the case of isotactic PP[32] and complementary experiments suggested that carboxylic acids and ketones were mainly methylated. A mechanism based on the β scission of tertiary hydroperoxides (present in large concentration, see below) has been suggested.
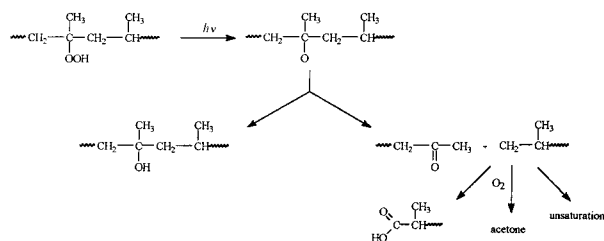
Such a mechanism implies that ketones and acids would both derive from tertiary hydroperoxide after chain breaking. Another implication would be the decrease of molecular weight.

Table I contains the molecular weight changes upon photooxidation of aPP filled or unfilled with zinc oxide.

A very small decrease is observed for the ZnO filled sample, in spite of a much higher oxidation level (see Figure 1 and below). Such a result can be correlated with former results: the weak decrease of mechanical properties for photooxidized pigmented samples[33] or the absence of chain scission products and carboxylic acids after the ZnO photocatalyzed oxidation of low molecular compound models of PP such as 2,4-dimethyl pentane, 2,2,4-trimethyl pentane, and 1,3,5-trimethylcyclohexane.[34]

However, according to the mechanism reported previously, an efficient protection of ketones by zinc oxide may not inhibit the formation of carboxylic acids and a decrease of the molecular weight. Zinc oxide probably plays a specific role in the oxidation mechanism by favoring reactions without chain breakings such as the β scission of the methyl group (instead of CH_2) and the formation or decomposition of secondary hydroperoxides:
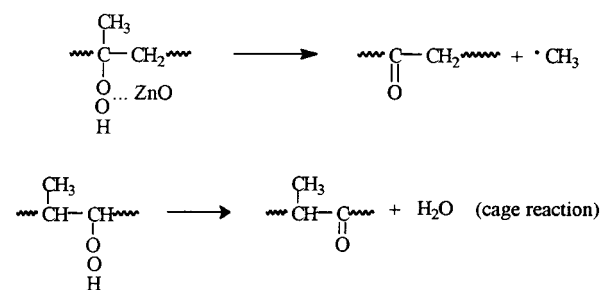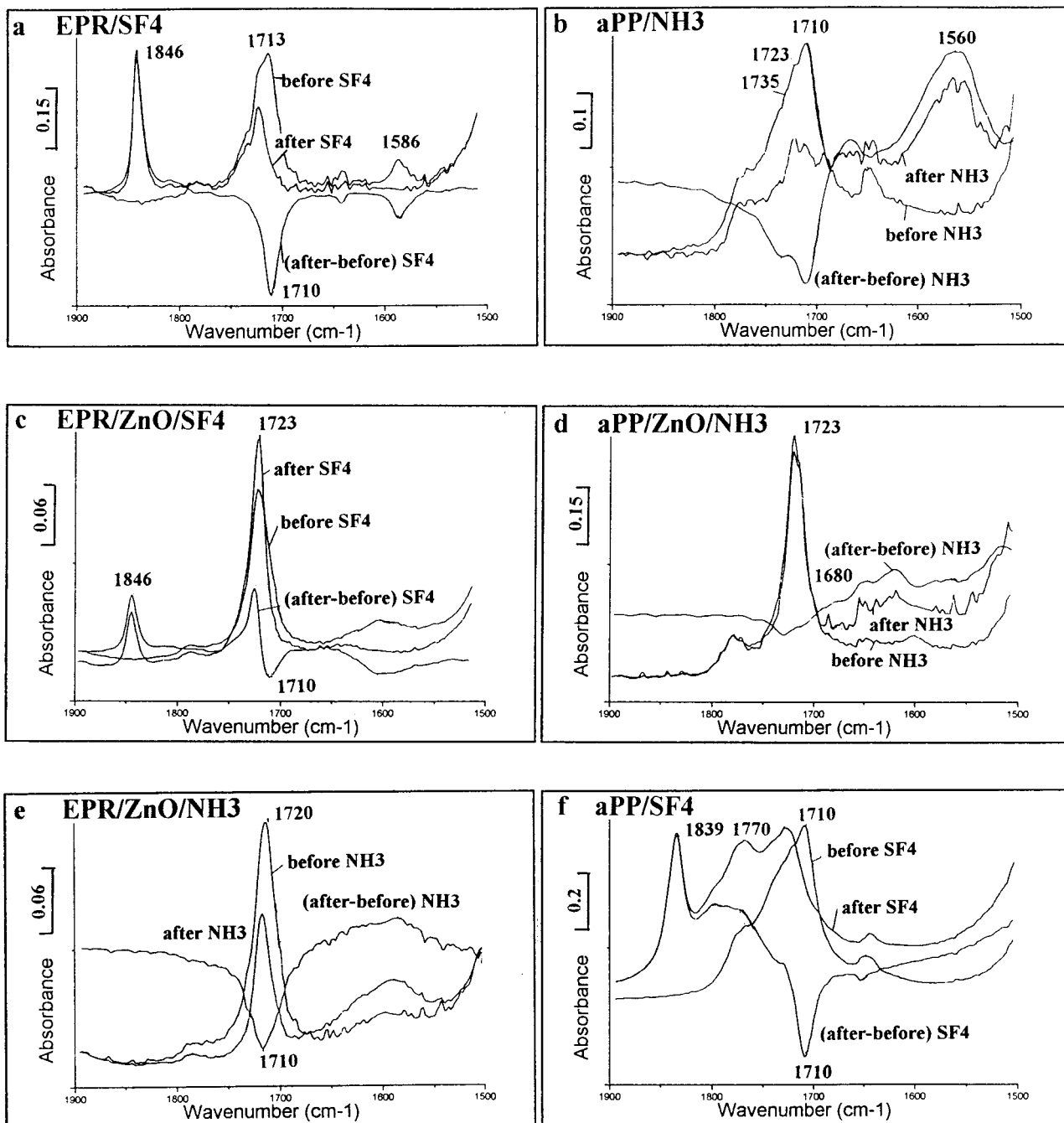
Figure 3 IR changes upon SF_4 and NH_3 treatments of photooxidized EPR, EPR + ZnO 5%, aPP, and aPP + ZnO 5%.

In the absence of pigment the methyl scission is generally considered as unprobable,[35] but recently this reaction was proposed to account for the low formation of methanol in isotactic PP.[36,37] In our case, a specific interaction between ZnO (base) and hydroperoxide groups may have changed the chemical properties of hydroperoxide.[38]

Kinetic Approach

Evolutions of hydroperoxide (iodometry) and carboxylic acids (NH_3 derivatization) are plotted in Figure 5.

Surprisingly enough, hydroperoxidation rates are very similar for EPR and aPP, in spite of the

EPR

aPP
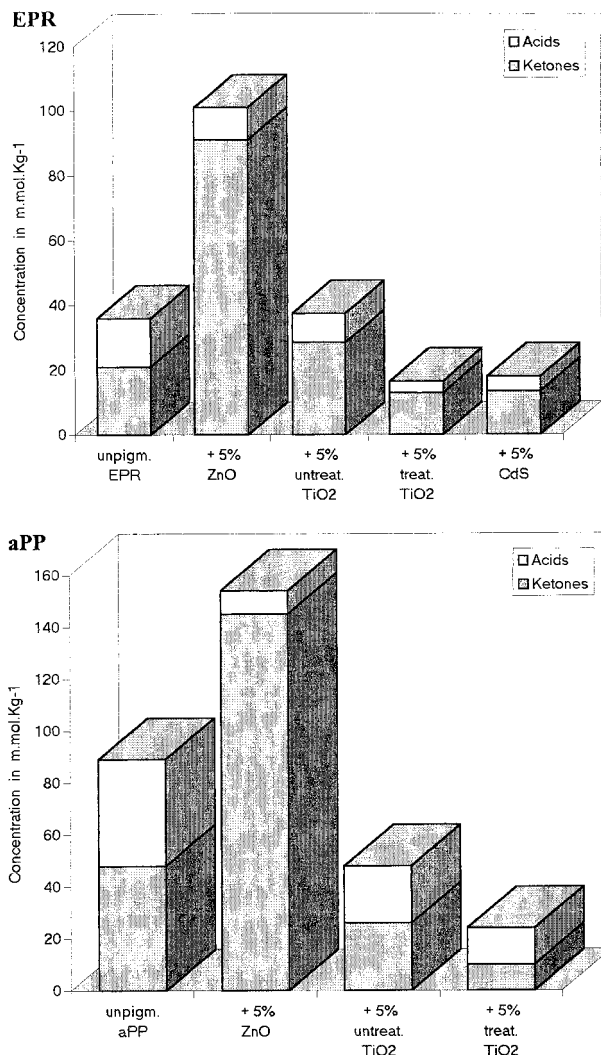
Figure 4 Contribution of carboxylic acids and ketones upon photooxidation of (a) EPR and (b) aPP. Influence of photoactive pigments; exposure times: EPR, 250 h; and aPP, 180 h.

high content of ethylene in the EPR. Hydroperoxides accumulate in the matrix and reach very high concentrations compared to other oxidation products like ketones or acids.

The increase of carboxylic acids in the ZnO filled EPR and aPP is also shown in Figure 5. Their formation is autoaccelerated, particularly in the case of aPP. Such a phenomenon can be explained by the competition between ZnO and oxidation products for the light absorption. For short exposures, all the light is absorbed by the pigment and both hydroperoxides and ketones are protected (no carboxylic acid, no Norrish reactions[20]), but as the oxidation progresses ketones and hydroperoxides reach sufficient concentra-

Table I   Viscocity Average Molecular Weights (g mol^{-1}) of aPP upon Photooxidation

	Before Irradiation	After Irradiation (150 h)
aPP	6450	3430 (−47%)
aPP + ZnO, 5 wt %	10880[a]	8655 (−20%)

[a] The presence of ZnO probably involves a small change in Mark–Houwink–Sakurada parameters.

tions to absorb UV light directly, leading to the products expected from direct photooxidation (acids, vinyl (EPR), etc.).

The effect of pigments and the role of water can be derived from the carbonyl evolution followed by IR spectroscopy (see Fig. 6). Both for EPR and aPP, zinc oxide and untreated TiO$_2$ significantly increase the oxidation rate according to the photocatalytic effect. Treated TiO$_2$ and CdS are mainly characterized by their filter effect (UV absorber), and the oxidation rate is
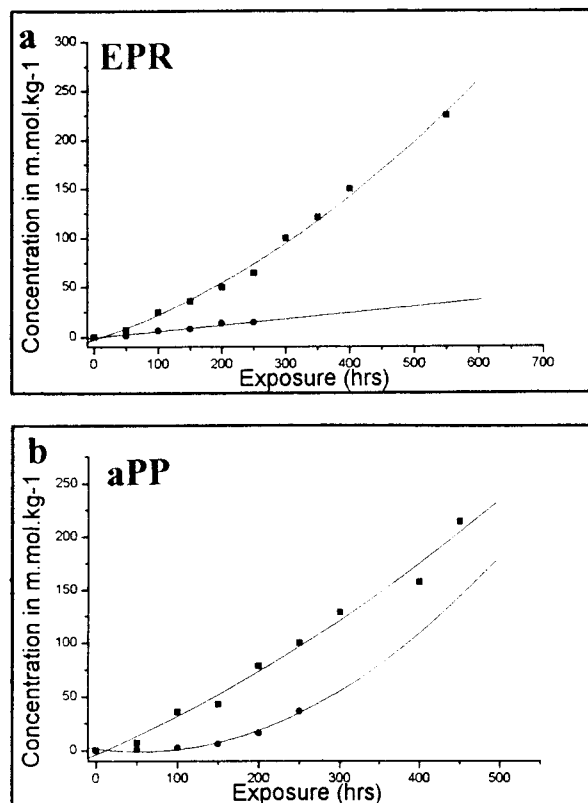

Figure 5 Formation rates of (■) hydroperoxides and (●) carboxylic acids upon photooxidation of (a) EPR and (b) aPP pigmented with 5 wt % ZnO.
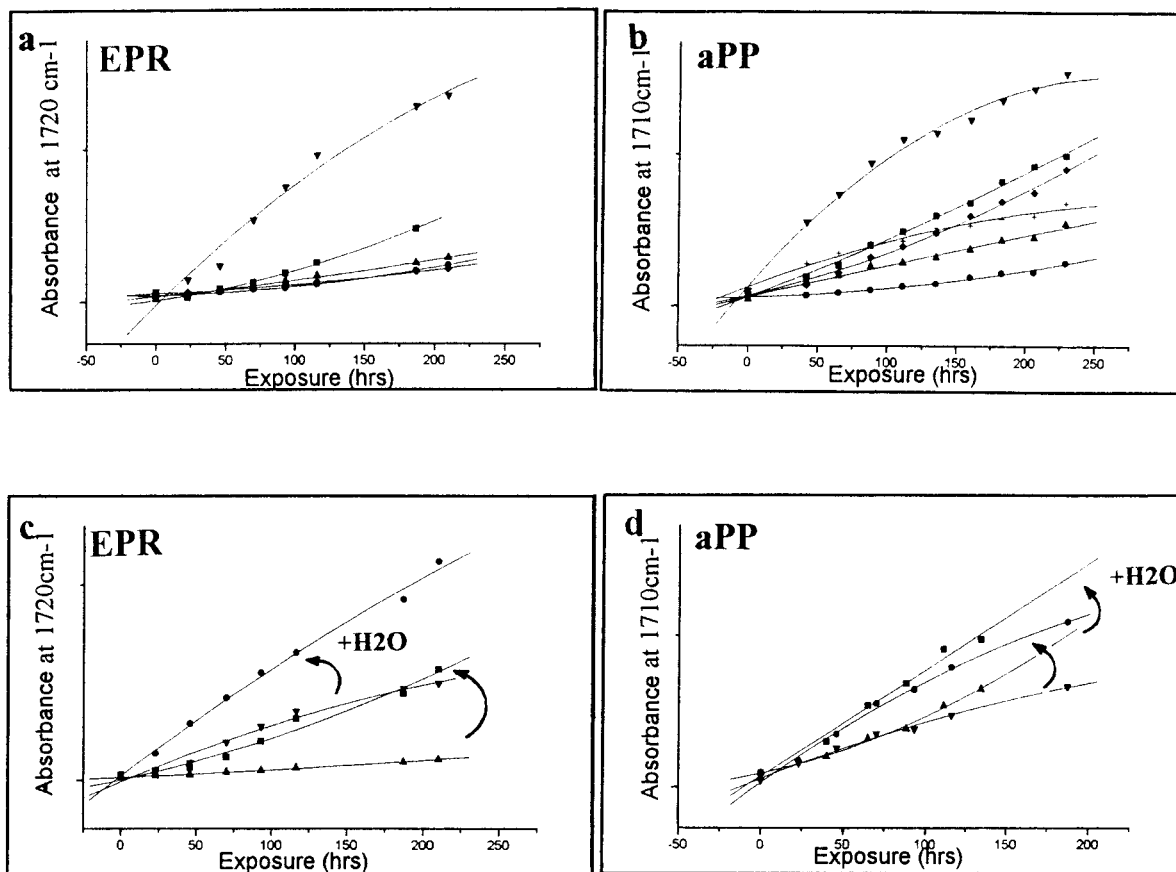
Figure 6 Carbonyl group formation upon photooxidation of EPR and aPP. (a,b) Influence of photoactive pigments. (c,d) Influence of water vapor on samples pigmented with ZnO and untreated TiO_2 (no changes observed for other samples). (a) (■) unpigmented EPR; (▼) + ZnO 5 wt %; (▲) + untreated TiO_2 5 wt %; (●) + treated TiO_2 5 wt %; (♦) + CdS wt %. (b) (■) unpigmented aPP; (▼) + ZnO 5 wt %; (▲) + untreated TiO_2 5 wt %; (●) + treated TiO_2 5 wt %; (♦) + ultrafine TiO_2; (+) + treated ultrafine TiO_2. (c) (▲) (dry), (■) (water vapor) EPR + untreated TiO_2 5 wt %; (▼) (dry), (●) (water vapor) EPR + ZnO 5%. (d) (▲) (dry), (■) (water vapor) aPP + untreated TiO_2 5 wt %; (▼) (dry), (●) (water vapor) aPP + ZnO 5%.
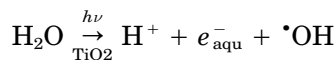
much slower than that for unpigmented polymers. Ultrafine pigments were tested in aPP only. Their effect is comparable to that observed for unpigmented polymer; in particular, the surface treated pigment (UF10) seems to present an unexpected photocatalytic effect. Such a result was also received in photoaging studies of isotactic PP[39] and may have resulted from insufficient passivation by the surface treatment (silica + alumina + lauric acid).

The effect of water is seen in Figure 6(c,d). A neat increase of the oxidation rate is observed in EPR and aPP filled with untreated TiO_2 and ZnO (the shape of the spectra is not modified by the presence of water; i.e., with pigments presenting a photocatalytic effect). Water adsorbed on the pigment surface is involved in most photocatalysis mechanisms[7–17]; in particular, it acts as a promotor of ·OH (and ·OOH) radicals, which are very active oxidizing species. The presence of water increases the oxidation rate sufficiently enough to be seen by IR spectroscopy, in spite of the probable elimination of low molecular weight polar compounds by washing.

Adsorbed water (together with surface hydroxyl groups) is involved in most mechanisms describing the photocatalytic phenomena. Its main effect is the generation of hydroxyl radicals; then the increase of its concentration by addition of water vapor may result in an increase of the oxidation rate of polymers and paints,[23,40] even if an opposite result was reported by Irick[41] when

he studied the photocatalyzed conversion of isopropanol into acetone.

$$H_2O \overset{h\nu}{\underset{TiO_2}{\rightarrow}} H^+ + e^-_{aqu} + {}^{\bullet}OH$$

from Voeltz et al.,[9]

$$TiO_2 \rightarrow e^- + p$$

$$^-OH + p \rightarrow {}^{\bullet}OH$$

from Voeltz et al.,[10] and

$$TiO_2 + O_2 \overset{h\nu}{\longrightarrow} TiO_2^{+\bullet} + O_2^{-\bullet}$$

$$HO^{\bullet} + HOO^{\bullet} + TiO_2 \overset{H_2O}{\longleftarrow} \qquad \longrightarrow TiO_2 + {}^1O_2$$
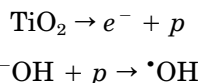
from Sullivan.[7]
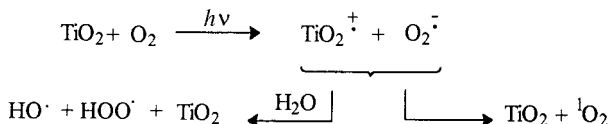
CONCLUSION

Titration of carboxylic acids by derivatization with NH_3 or SF_4 confirms that the ZnO photocatalyzed oxidation involves mainly hydroperoxides and ketones. The acid formation is inhibited particularly at the beginning of oxidation when ZnO absorbs all the photons of $\lambda > 300$ nm. This absence of acids, as well as the small drop of molecular weight of aPP upon ZnO photocatalyzed oxidation, can be explained by a specific photocatalytic decomposition of tertiary hydroperoxide located on propylene sites (β scission of CH_3). Among other pigments, only untreated TiO_2 or its ultrafine homologue present a certain photocatalytic effect, but no inhibition of carboxylic acid is observed. The presence of water vapor significantly increases the oxidation rate for polymers filled with ZnO and untreated TiO_2 (i.e., significantly increases the photocatalyzed oxidations).

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