Photooxidation of Polypropylene/Montmorillonite Nanocomposites. 2. Interactions with Antioxidants

Sandrine Morlat-Therias, Bénédicte Mailhot, David Gonzalez, and Jean-Luc Gardette*

Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS-UBP 6505,
Université Blaise Pascal (Clermont-Ferrand), F-63177 Aubiere Cedex, France

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The influence of stabilizing additives on the photooxidation of polypropylene/montmorillonite (PP/MMt) nanocomposites exposed to UV light was studied. Two different stabilizers were used, a phenolic antioxidant and a redox antioxidant. A significant reduction in the induction period of oxidation was observed in the presence of MMt. This is believed to arise from interactions between the additives and the nanoclay. The interactions could involve the adsorption of additives onto the clay, the degradation of the alkylammonium cations exchanged in MMt, and the catalytic effect of iron impurities of the organomontmorillonite. Iron could catalyze the decomposition of the primary hydroperoxides formed by photooxidation of PP, which would in turn accelerate the additive consumption and decrease the length of the period before the permanent regime of oxidation is reached.

Introduction

Polymer−clay nanocomposites are a new class of filled polymers in which clay platelets at the nanometer scale are dispersed in a polymer matrix. These nanocomposites exhibit enhanced properties at very low amount of filler, usually less than 5 wt %, such as increased Young's modulus and storage modulus, increase in thermal stability and gas barrier properties, and also good flame retardancy.[1] Polypropylene (PP) nanocomposites[2] are obtained by melt compounding PP and organophilic clays (such as montmorillonite (MMt)) in the presence of maleic anhydride grafted polypropylene. Elementary clay platelets consist of a 1-nm thick layer made of two tetrahedral sheets of silica fused to an edge-shared octahedral sheet of alumina or magnesia. Isomorphic cation substitution results in an excess of negative charges within the layer. Inorganic cations (e.g. Ca^{2+}, Na^+) can be exchanged with organic cations, rendering the silicate surface organophilic.

This work on the photooxidation of polypropylene/montmorillonite nanocomposites is part of a general study dealing with the influence of the nanofiller on the behavior of nanocomposite materials in conditions of photolytic oxidation. A first paper[3] reported a detailed study on the mechanism of photooxidation of these PP nanocomposites. This article compared the oxidation mechanisms of both the pristine polypropylene and the polypropylene/montmorillonite nanocomposites. The influence of the compatibilizing agent was also examined. The data indicated that the photooxidation mechanism of polypropylene was not modified. However, a dramatic shortening of the induction period of the oxidation was observed in the presence of the nanofiller, leading to a decrease of the durability of the nanocomposite. This unexpected result was attributed to the inhibition of the activity of the residual phenolic processing antioxidant. Among the numerous literature related to nanocomposite materials, only three other papers deal with photodegradation of polymer/clay nanocomposites, but surprisingly these important results are not mentioned.[4−6]

The aim of the present paper is to study this peculiar point which has considerable consequences in terms of both fundamental aspects of the photooxidation of nanocomposites and durability of these materials. One has then to characterize and to understand the interactions between the antioxidant, the clay (montmorillonite), and the compatibilizing agent (maleic anhydride). Special attention has to be given to the influence of each component on the rate of oxidation of the polymeric matrix. Two kinds of stabilizers were tested: a phenolic antioxidant generally used to process polypropylene and a redox antioxidant of the hindered amine light stabilizer (HALS) class, which is used as long-term stabilizer for polypropylene.

Experimental Section

Materials. The organo-modified clay used here was supplied by Süd-Chemie, with the trade name EXM948 (abbreviated MMt). This clay is a natural montmorillonite exchanged with dimethyltallowammonium cations, and its interlayer spacing is 1.8 nm.

The polypropylene matrix (PP) was obtained from Solvay; the trade name is HV001P. The melt flow index (MFI) is 10 g/(10 min). The maleic anhydride modified PP (termed PPgMA) is a copolymer of ethylene−polypropylene grafted with maleic anhydride (MA; MA content, 1.4 wt %; $M_w = 84\,000$ g/mol; Fusabond MD353D, Dupont; polydispersity $Ip = 6.4$).

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* To whom correspondence should be addressed. E-mail: luc.gardette@univ-bpclermont.fr.

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Chart 1. Chemical Structure of the Phenolic Antioxidant (AO)

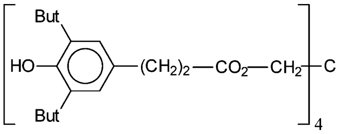

Chart 2. Chemical Structure of the Redox Antioxidant (HALS)

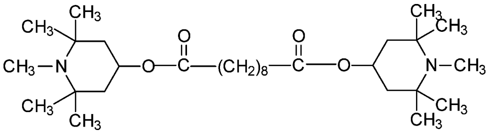

Table 1. Composition of the Samples

sample	PP (%)	PPgMA (%)	MMt (%)	AO (%)	HALS (%)
virgin PP	100				
PP	99.9	–	–	0.1	
PP/MMt	94.9	–	5	0.1	
PP/PPgMA	79.9	20	–	0.1	
PP/PPgMA/MMt	74.9	20	5	0.1	
PP/AO	99.4			0.6	
PP/MMt/AO	94.4		5	0.6	
PP/HALS	98.8			0.6	0.6
PP/MMt/HALS	93.8		5	0.6	0.6
PP/PPgMA/HALS	78.8	20		0.6	0.6
PP/PPgMA/MMt/HALS	73.8	20	5	0.6	0.6

Samples were processed using a phenolic processing stabilizer (Irganox 1010 from Ciba-Geigy; Chart 1). The concentrations used here are given later in the text.

Some samples contained a redox antioxidant (Tinuvin 765 from Ciba-Geigy; Chart 2).

Preparation of Polypropylene Nanocomposites. The nanocomposites were prepared by melt intercalation process in a twin-screw extruder (co-rotative screws). Details on processing conditions and characterization of dispersion of nanoplatelets have been given in a previous paper.[2] When the PPgMA copolymer is used as compatibilizing agent, the clay platelets are better dispersed, as shown by characterization of nanocomposites with transmission electron microscopy and X-ray diffraction.[2] It was shown that the use of PPgMA was efficient to push apart the clay layers which form tactoids of three to five platelets. The polymers studied here were extruded in order to obtain films with a thickness around 100 μm. Such thin films are required for two main reasons: the first one is that this permits performing UV irradiations of the materials in conditions where the oxidation is not limited by the diffusion of oxygen.[7] The second one is that it facilitates the chemical analysis of the oxidized samples by infrared spectrometry in transmission mode.

Eleven different formulations of PP polymer and stabilizers were studied, which are described in Table 1. The following abbreviations are used in this article. The composition is expressed in weight percent. The pristine matrix is named PP, the blend of PP and organomontmorillonite (5%) PP/MMt, the blend of PP and PPgMA (20%) PP/PPgMA, and the nanocomposite of PP, MMt (5%), and the compatibilizant PPgMA (20%) PP/PPgMA/MMt**.** The stabilizers are denoted by AO for Irganox 1010 and HALS for Tinuvin 765.

Irradiation and Characterization of the Oxidation. Irradiations were performed at $\lambda > 300$ nm in the presence of oxygen in a SEPAP 12.24 unit at a temperature of 60 °C. This apparatus has been designed in order to accelerate the photodegradation of polymers in artificial conditions which are relevant to natural aging.[8] The device SEPAP 12.24 is equipped with four medium-pressure mercury lamps. A borosilicate envelope filters wavelengths below 300 nm.

Infrared spectra were recorded with a Nicolet 5SX-FTIR spectrometer, working with OMNIC software. Spectra were obtained using 32 scan summations and a 4 cm^{-1} resolution. To compare the spectra of different formulations of nanocomposites, an internal calibration of the thickness (e, μm) of each sample was performed by measuring the absorbance at 2722 cm^{-1} (stretching band ν(C−H) of polypropylene).[3]

UV−visible spectra were recorded on a Shimadzu UV-2101 PC spectrometer equipped with an integrating sphere.

The behavior of the polymer without antioxidant was also studied, which necessitates an extraction of the additive; it was carried out for 24 h in a Soxhlet with hexane or ethyl acetate.

Results and Discussion

Infrared Analysis of Nanocomposites. The IR spectra recorded during photooxidation for each sample showed notable changes. The main modifications of the IR spectra of films of nanocomposites PP/MMt upon irradiation in the presence of oxygen are an increase of absorbance in two domains of the infrared, which correspond to the hydroxyl and carbonyl regions (Figure 1).

In the case of samples containing montmorillonite, the shape of the oxidation bands and the relative intensities of each carbonyl band are the same as in the case of pure polypropylene. This indicates that polypropylene/montmorillonite nanocomposites and PP develop the same photoproducts. This result suggests, as reported previously, that the mechanism of oxidation of the polymer is not modified by the presence of the clay.[3]

Rates of Photooxidation. In the case of the formulations containing maleic anhydride, the IR spectra of the unexposed samples present an absorption band at 1715 cm^{-1}. This absorption band results from a partial hydrolysis of the anhydride functions that produces carboxylic acids. This band overlaps with the bands of the acids coming from the oxidation of polypropylene, which prevents one from comparing the kinetics of oxidation by the measurement of the carbonyl absorption at 1713 cm^{-1}, as is usually done.[9] The kinetic curves presented here were then determined by plotting the variation of absorbance in the hydroxyl region at 3400 cm^{-1}.

Polymer processing makes it difficult to obtain films with exactly the same thickness. The films that were irradiated had a thickness in the range of 95−100 μm. The measured values of the absorbance were multiplied by a correcting factor in order to fit the thickness to a value arbitrarily fixed at 100 μm, as already reported in the previous paper.[3] It is worth noting that the correcting factors remain rather weak, since the differences in thickness are less than 5% from one film to another. Such corrections can be made because no heterogeneous oxidation resulting from a limitation of the

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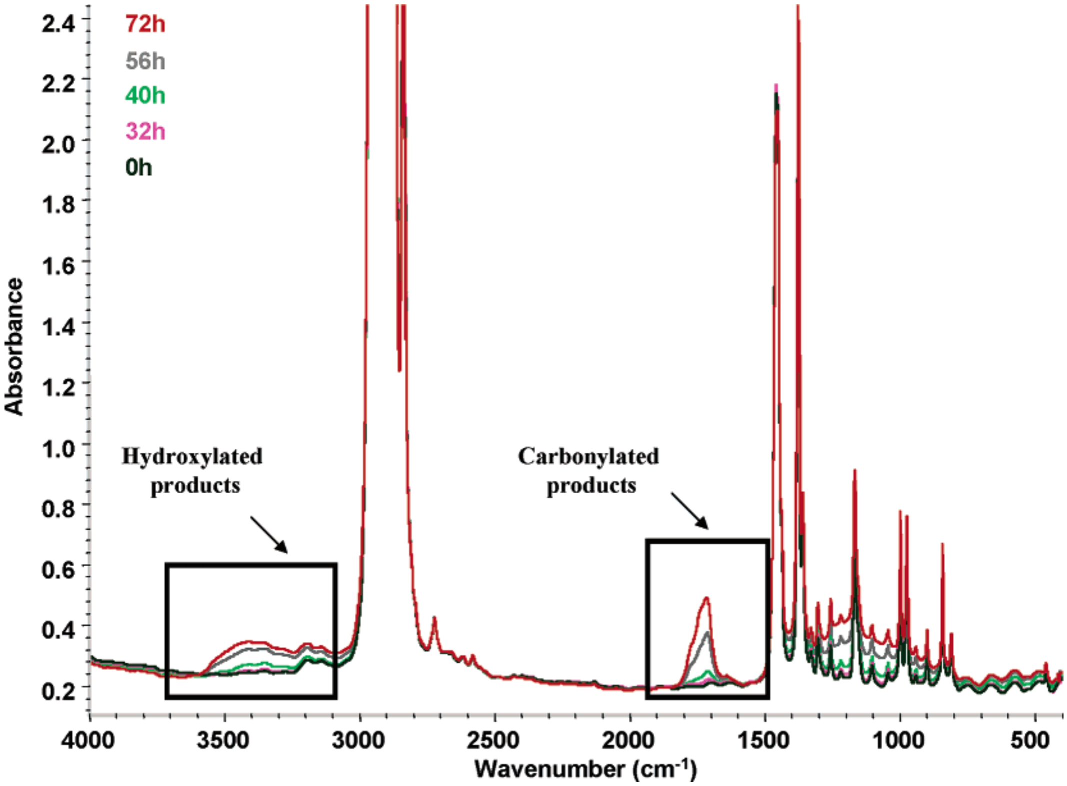

Figure 1. FTIR spectra of a PP nanocomposite film photooxidized at $\lambda > 300$ nm, 60 °C.

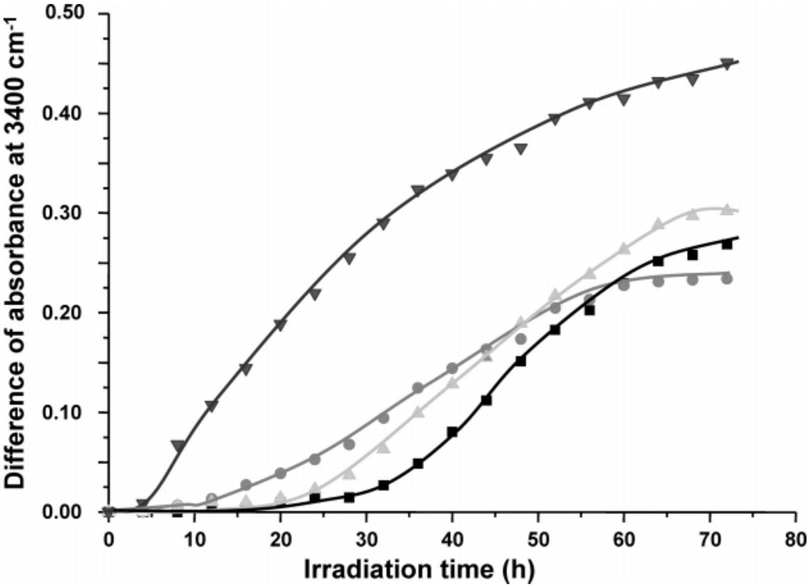

Figure 2. Evolution of absorbance at 3400 cm^{-1} as a function of irradiation time for nanocomposite films photooxidized at $\lambda > 300$ nm, 60 °C: (–■–) PP + AO (0.1%); (–●–) PP + MMT + AO (0.1%); (–▲–) PP + PpgMA + AO (0.1%); (–▼–) PP + PpgMA + MMT + AO (0.1%).

oxidation by the diffusion of oxygen occurs in the experimental conditions used here.[10]

The kinetic curves of photooxidation of PP and the blend PP/PPgMA have been previously plotted and compared with those obtained in the presence of montmorillonite.[3] The most relevant analysis on this set of curves is based on the comparison between the times necessary before the oxidation starts. During this induction period where no oxidation of the polymer is detected, it is generally admitted that the remaining processing antioxidant plays its stabilizing role, which makes it disappear, because phenolic antioxidants are consumed as sacrificial additives.[11] The comparison of the oxidation rates of the four types of samples described above (Figure 2) shows that the presence of the compatibilizer PPgMA has only a weak effect on the induction time, whereas the length of this induction period is dramatically reduced in the presence of MMt.

In both the cases of PP and PP/PPgMA, the oxidation starts after approximately 20 h of irradiation. A slight shift is

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observed for PP/MMt with an induction time around 12 h. The induction period decreases to 4 h in the case of the PP/PPgMA/MMt nanocomposites. The dramatic influence of the organoclay on the induction period suggests an interaction between the phenolic groups of the antioxidant and the montmorillonite.

At the opposite end, no important modification of the oxidation rates at the permanent regime that follows the induction period was noted. However, if one takes into account the whole curves, the results given in Figure 2 indicate that the samples with MMt are largely more sensitive to oxidative degradation.

It has already been reported that phenols adsorb on clays,[12,13] which could in turn reduce their stabilizing activity as antioxidants in polymeric media. It has also been noticed that PP nanocomposites degrade much more rapidly than pure PP, as shown by the absence of an induction period, but nothing was mentioned about the activity of antioxidants.[4] This effect is similar to those formerly reported in a study of the photooxidative degradation of polyethylene/montmorillonite nanocomposites. However, no interpretation was given to the observed phenomena.[5]

Extraction of the Antioxidants. To directly evaluate the impact of the antioxidant, we have tried to eliminate the processing antioxidant by Soxhlet extraction with hexane and ethyl acetate as solvents. This allows comparison of the oxidation rates of the different samples without additive.

After 24 h extraction in hexane, the IR spectra of the films (Figure 3) show a decrease of the CO absorption band of the ester function of the antioxidant.

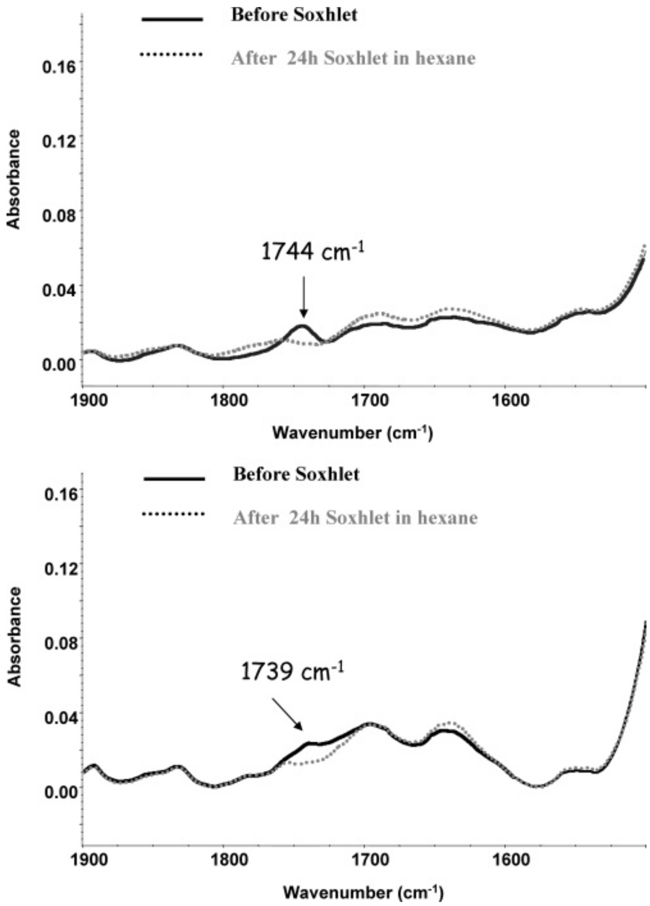

Figure 3. FTIR spectra of films before and after Soxhlet extraction in hexane: (a, top) a PP film; (b, bottom) a PP/MMt film.

The frequency of the absorption maximum can be determined by subtraction between the spectra. The results show that it depends on the composition of the samples. The absorption maximum is 1744 cm^{-1} in the case of PP, whereas a shift of 5 cm^{-1} units is observed for the samples with MMt (1739 cm^{-1} in the case of PP/MMt films). The same shift is observed for films of PP/PPgMA without or with MMt. This gives primary evidence of the interactions between the ester group of the antioxidant and montmorillonite. Similar effects have been already observed and reported in previous studies.[14] In the presence of pigment, the interactions between HALS and pigment lead to a shift of the IR absorption band of the ester group in the HALS molecule from 1736 to 1730 cm^{-1}. However, the important point is that such interactions are not likely to modify the efficiency of the antioxidant as it is the phenol group of the molecule that is the active function against degradation.

The kinetic curves of oxidation of the samples after Soxhlet extraction are plotted on Figure 4.

This figure shows the variations of the absorbance at 3400 cm^{-1} vs irradiation time for the four different formulations. The shapes of the curves given in Figure 4 indicate that after the extraction of the antioxidant, the induction periods are drastically shortened for the PP, PP/PPgMA, and PP/MMt samples. One can attribute the remaining induction period to the fact that a complete extraction of the antioxidant is difficult to obtain or at least depends on the composition of the sample. For example, the presence of MMt or PPgMA can modify the permeability (diffusion and solubility) of the polymer to the solvent and as a consequence modify the extent at which the additive can be extracted. In the case of the PP/PPgMA/MMt sample, one observes no modification of the kinetic curve for samples with or without antioxidant. This result suggests that the antioxidant has no stabilizing effect on PP in the case of PP/PPgMA/MMt. Moreover it is interesting to note that the curve obtained for extracted PP tends toward that of PP/PPgMA/MMt, which confirms the inefficiency of the antioxidant in the presence of dispersed clay.

Influence of Stabilizer Concentration. A second way to study the influence of the antioxidant is to compare the effect of various concentrations of the additive. This has been done by increasing the concentration of the antioxidant from 0.1 to 0.6%. The kinetic curves of oxidation of the corresponding samples are given in Figure 5.

In the case of PP samples, the increase of the concentration of the processing antioxidant from 0.1 to 0.6% results in an increase of the induction period from 20 to 28 h. For the samples with montmorillonite, increasing the concentration of additive from 0.1 to 0.6% results in an increase of the induction time from 12 up to 22 h. These results show that modifying the concentration of the antioxidant results in a

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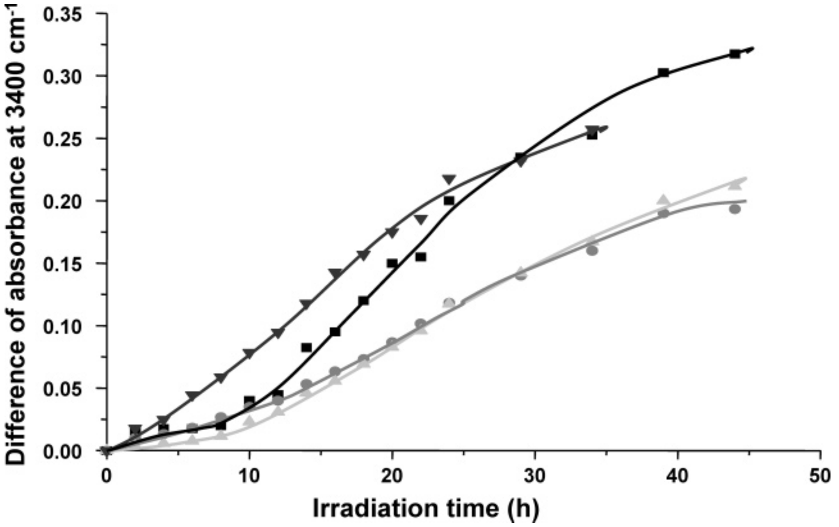

Figure 4. Evolution of absorbance at 3400 cm^{-1} as a function of irradiation time for nanocomposite films after 32 h Soxhlet extraction in hexane: (−■−) PP; (−●−) PP + MMT; (−▲−) PP + PPgMA; (−▼−) PP + PpgMA + MMT.

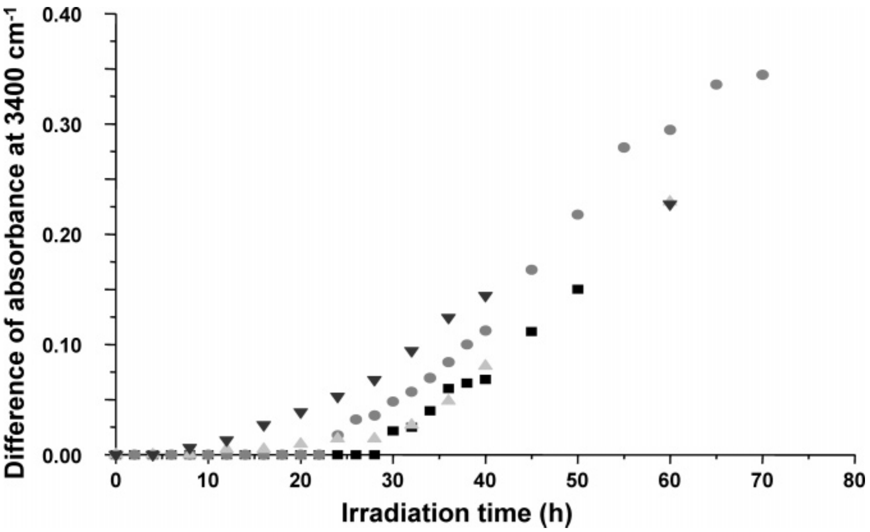

Figure 5. Evolution of absorbance at 3400 cm^{-1} as a function of irradiation time for PP and PP/MMt films with different concentration of phenolic antioxidant (AO): (■) PP + AO (0.6%); (●) PP + MMT + AO (0.6%); (▲) PP + AO (0.1%); (▼) PP + MMT + AO (0.1%).

variation of the induction period. However, one can observe here again that, for the samples containing MMt, the presence of montmorillonite has a negative effect on the efficiency of the stabilization. This negative effect is observed even in the case of high concentrations of antioxidant.

Influence of Stabilizers. The results given above show clearly that MMt hinders antioxidants in stabilizing polypropylene, which results in a dramatic decrease of the photochemical stability of the polymer. To characterize the influence of the organomontmorillonite on the efficiency of different kinds of stabilizers, we have studied samples containing a redox antioxidant (HALS) in the same conditions of aging. The HALS used here was chosen because it has a tertiary methylated amine group (Chart 2), which is supposed to have less interaction with acidic species and also less hydrogen interaction with the clay platelets compared to the nonmethylated amine group.[15] The rates of photooxidation of this series of samples are reported in Figure 6 and compared with those of the samples with the phenolic antioxidant.

On the basis of the results given in Figure 6, two types of comments can be made. First, it has to be recalled that, in the case of the HALS light stabilizer, the damages caused by irradiation are shifted back to more than 500 h for a PP film. In the presence of MMt, the induction time falls down to 170 h, and in the case of the PP/PPgMA/MMt nanocomposite, the appearance of oxidation photoproducts can even be detected after only 100 h of irradiation. These results give evidence that interactions between the organomontmorillonite and the light stabilizer drastically reduce its efficiency in the presence of the nanoclay. A study of the stabilization of polypropylene by HALS in the presence of talc has pointed out the problems related to the interactions of stabilizers with pigments and fillers.[14] Antagonistic effects reported between HALS and talc[16] have also been observed in the case of

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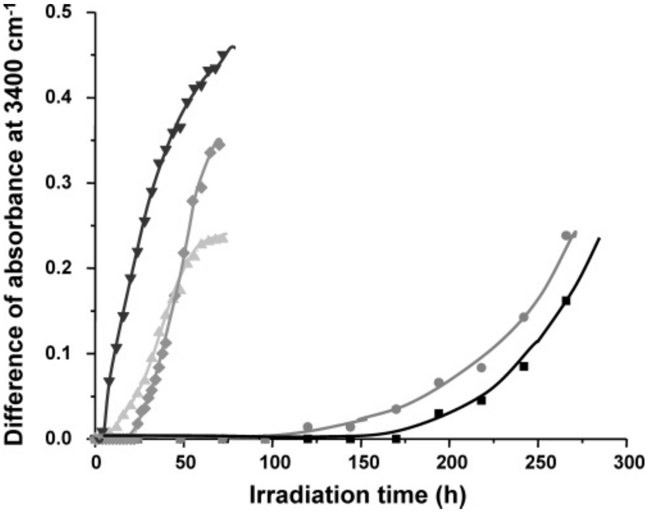

Figure 6. Evolution of absorbance at 3400 cm^{-1} as a function of irradiation time for nanocomposite films with or without a redox antioxidant (HALS): (−■−) PP + AO (0.6%) + HALS (0.6%) + MMT; (−●−) PP + AO (0.6%) + HALS (0.6%) + PpgMA + MMT; (−▲−) PP + AO (0.1%) + MMT; (−▼−) PP + AO (0.1%) + PpgMA + MMT; (−◆−) PP + AO (0.6%) + MMT.

transition metals.[17] The efficiency of conventional HALS can be reduced by their adsorption on other additives or fillers.

All the results reported in this article about the photooxidation of polypropylene/montmorillonite nanocomposites show that the mechanism of oxidation of the polymeric matrix is not modified by the clay. However, the influence of the organoclay on the durability of the nanocomposite material finds expression in the efficiency of stabilizers. With the two kinds of stabilizers tested that are, conventionally, a processing one with a phenolic function and a long-term stabilizer which is a redox antioxidant (hindered amine light stabilizer), the main conclusion is that the presence of organomontmorillonite decreases the efficiency of the stabilizer.

One possible explanation for this antagonism between the clay and the additives is that adsorption or intercalation phenomena of the antioxidant with the silicate layered phase occurs. However this intercalation would lead to a swelling of the clay. Complementary results based on X-ray diffraction pattern were obtained that compared the organomontmorillonite and a mixture of MMt and the phenolic antioxidant or the redox one. These results indicate quite clearly that the interlayer spacing is unchanged in both cases, which suggests that no swelling occurs with both stabilizers.

If one considers the polarity of the phenol or amine functions of the stabilizers, and the facts that the polymeric matrix is hydrophobic whereas the clay has still an hydrophilic affinity (even though the presence of organic cations), the stabilizers might be inhomogeneously distributed in the nanocomposite material.[18] This could favor the adsorption of the stabilizers on the clay. However, our experimental results show that the additives can be easily removed by solvent extraction, which indicates that the interactions with the nanocomposite are not so strong.

Another explanation is the following. The organomontmorillonite used is a natural montmorillonite which contains iron. Chemical analysis of the clay confirms the presence of a low amount of iron.[3] It is recalled that iron and, in more general terms, metals are likely to induce the photochemical degradation of polymers. Iron at low concentration has a prooxidant effect, which is due to the metal ion of iron that can initiate the oxidation of the polymer by the well-known redox reactions with hydroperoxides.[19]

The kinetic aspects of the oxidation of filled polymers have been summarized.[20] Special attention was given to the interactions between fillers and stabilizers. It was concluded that the transition metal ions, such as Fe, display a strong catalytic effect by redox catalysis of hydroperoxide decomposition, which is probably the most usual mechanism of filler accelerating effect on polymer oxidation. A characteristic of such catalytic effect is that it does not influence the steady-state oxidation rate but it shortens the induction time. In our case, such a catalytic effect with iron could explain the influence of MMt on the photooxidation of nanocomposite materials. The influence of silica conventional fillers on polypropylene oxidation has been reported in the literature.[21] The silicas tested varied in terms of pore volume and surface area as well as metal ion content. The effect of the different silicas on the photooxidation rate of polypropylene was compared to the surface properties and the metal ion contents. It was shown that rather than correlating with surface area or porosity, the order in activity parallels the total metal ion content of each silica. During polymer oxidation, metal ions serve principally as catalysts for the accelerated decomposition of hydroperoxides.[22] This result could also be in favor of the hypothesis of the important role played by iron in the case of these natural layered silicate nanofillers.

Results dealing with the fire properties of nanocomposites[23,24] indicate that the presence of iron makes a very large difference between natural clay and iron-free clays. In the presence of iron, stronger modifications of peak heat release rate and the onset temperature of the degradation are noticed.

The influence of iron impurities on the activity of additives could be studied by using synthetic fillers free of iron. A recent investigation carried out in our laboratory deals with elastomer−clay nanocomposites made with synthetic montmorillonite-like clay prepared by hydrothermal synthesis. The results that were obtained show here again antagonism between the nanofiller and the antioxidant.[25] This indicates that the sole impact of iron is not likely to explain the influence of natural clay on the oxidation of stabilized polymers.

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The third point that has to be taken into account is the degradation of the alkylammonium cations. In a previous paper,[3] we have shown that the photooxidation of modified montmorillonite revealed an oxidation of the organic part of the exchanged clay. Such a reaction produces more radical species and constitutes a supplementary way that is likely to initiate the degradation of the polymer matrix. Another degradation pathway caused by the organoclay could result from the decomposition of alkylammonium during processing. It has been shown[26] that organoclays decompose during processing at high temperature by a Hofmann elimination mechanism to produce several byproducts. The α-olefins formed in this reaction are sensiitve toward photooxidation and could participate in the initiation of the polymer degradation.

Conclusion

At this stage of the research on the long-term durability of nanocomposites in photooxidative conditions of aging, it is difficult to establish a hierarchy between the three plausible hypotheses that have been proposed to explain the loss of stability of stabilized nanocomposites. The lower efficiency of the stabilizers could result from the degradation of the alkylammonium cations, which are a sensitive site in terms of radical initiation. It could result from the presence of structural iron that has photocatalytic activity. It could also result from the adsorption of additives onto the clay, which partially inhibits their stabilizing activity.

The next step of our investigations on the photochemical properties of nanocomposites will be to examine the photodegradation of other polymers with inorganic montmorillonite such as Na-MMt or with synthetic clay which is free of iron cations.

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