

Photocatalytic Degradation of Some Polyolefin-TiO₂ Composites Evaluated by Molecular Spectroscopy

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The photochemical degradation of polyolefin-TiO₂ composite films was investigated and described in relationship with the concentration of photocatalyst and after different exposure times. UV-Vis-NIR and IR spectra reveal the presence of various degradation products, which are in direct connection with the photodecomposition mechanism. Various ratios between the absorbance of some typical IR characteristic bands can lead to the evaluation of photocomposition of polyethylene and polypropylene composite films containing TiO₂ nanoparticles. The results show that the photocatalytic degradation of composites is significantly faster than the simple photolytic decomposition of pure polypropylene and polyethylene and could be used as a solution for the destruction of this type of wastes.

Keywords: photo-catalysis, composites, polypropylene, crystallinity, molecular spectroscopy

The photochemical degradation of polyolefins has been widely investigated and largely described in literature [1]. Initially, the reason was mainly due to the extensive efforts that have been made in order to stabilize polymers to light and weathering and to control photodestruction in industrial and domestic applications [1]. Nowadays, plastic waste disposal has been recognized as a major worldwide environmental issue and different types of methods have been proposed for polymer recycling. Thermal and catalytically degradation of polymer wastes were proposed and they represented appropriate methods to transform them into fuel oils. However, the main problem, which remains unsolved, is to harvest polymer wastes from the environment.

The method investigated takes this issue into account, the chemical stability and non-biodegradability of such wastes together with the necessity to maintain properties of this type of materials during a reasonable period. Thus, when such materials will become wastes some degradation processes will continue in the environmental conditions and to some extent lead to the polymer degradation [2,3].

Anatase has proved to be an efficient photocatalyst for the photodegradation of organic polymeric films due to the species generated by light, that lead to some types of radicals, which initiate the degradation of the polymer chains, as was proved by the detection of functional groups formed during photodegradation [4].

Polyethylene and polypropylene-TiO₂ nanocomposite films were exposed to light irradiation under simulated conditions of solar light in a Xenotest apparatus and the effect of ageing was evaluated by UV-Vis-NIR and FT-IR spectroscopy. Influence of ageing on structural modifications in relationship with mechanisms of photodegradation were investigated, and some parameters which described well the process were calculated.

Experimental part

Titanium dioxide - Aeroxide P25 was purchased from Evonik and was used as it was received. Low density polyethylene 150E (PE) was obtained from Dow Chemical and polypropylene Moplen HP 500N (PP) was obtained from Basell Polyolefins.

Composites were prepared by direct melt-mixing PP or PE with TiO₂ (P25) in a Brabender twin screw extruder at 140-170°C. The films were prepared by compression molding in an electrically heated press at 50 kN and 140-170°C.

Photodegradation experiments were conducted in a Xenotest 150S+ (Atlas) according to ISO-150-B02 (Irradiance=42 w/m²; Test chamber temperature =35°C; Relative humidity=40%).

FTIR spectra were recorded on a Jasco FTIR 6300 spectrometer equipped with a Golden Gate ATR (diamond crystal) from Specac, in the range 400-4000cm⁻¹ (30 scans at a resolution of 4 cm⁻¹). Diffuse reflectance UV-Vis-NIR were recorded on a Jasco V-570 spectrometer equipped with a ILN 451 integrating sphere (150 mm), in the range 200-1800 nm.

Results and discussions

Polypropylene photodegradation

To assess the effect of light exposure, doped and non-doped PP films with nanometric Degussa titanium dioxide (P25) were studied by infrared spectroscopy after exposure to artificial light. The concentration of titanium dioxide in PP films was 1 and 2% to determine whether the photocatalytic degradation process of PP is influenced by doubling the photocatalyst concentration. As can be seen from the study of ATR-FTIR spectra of blank PP specimens, no visible structural changes are observed during Xenon lamp exposure for 192 h. By comparing the FTIR spectra, the preservation of all structural characteristics of PP throughout the exposure is observed, including the position, intensity and ratio of the spectral band intensities.

With regard to nanometric titanium dioxide doped samples, it can be argued that the photocatalytic degradation process begins to be detectable in the FTIR spectrum by the appearance of the characteristic carbonyl band situated at 1716 cm⁻¹, mainly after 72 h of irradiation. The 1716 cm⁻¹ band is broad and includes the stretching vibrations of the carbonyl groups in ketones, lactones (1776 cm⁻¹) and esters formed during photocatalytic decomposition, as seen in figure 1.

The appearance of the 1640 cm⁻¹ band is associated with the bending vibration of the water molecules and can

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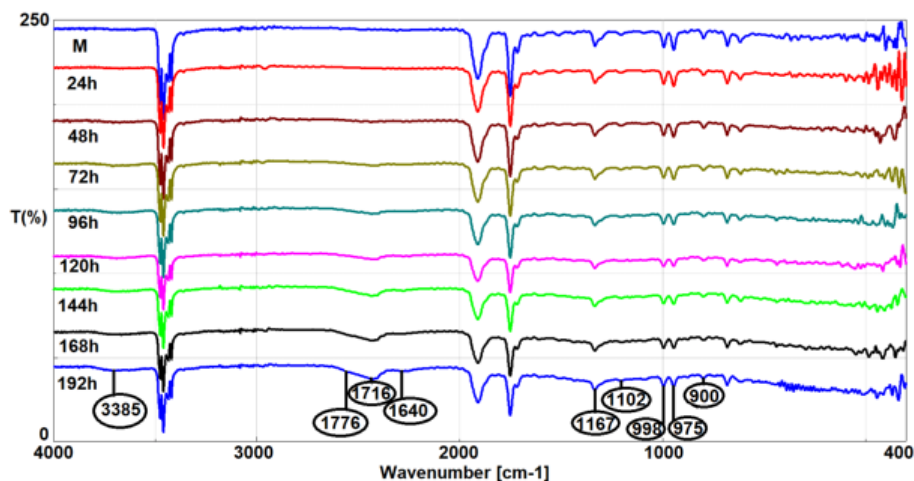


Fig. 1. ATR-FTIR spectra of PP-TiO₂ during irradiation

be correlated with the increase of the hydrophilic character of the polymer, as the degradation advances. As photodegradation progresses, there is a decrease of the characteristic band for deformation vibration of the methyl geminal groups (manifested as a doublet). Also, the band at 1102 cm⁻¹ decreases in intensity, as the degradation advances, after it was previously converted into a doublet. This band can be attributed to the stretching vibration of C-O bonds from alcohols and C-O-C from cyclic ethers. Such species may appear and disappear during the course of the photocatalytic oxidation process of polypropylene.

If we analyze the influence of the photocatalyst quantity on the degree of polypropylene photocatalytic decomposition, it is observed that in the FTIR spectrum there are no major structural changes after doubling the titanium dioxide quantity for the same exposure time (192h), under Xenon lamp illumination.

As the photodegradation assisted by titanium dioxide advances, in the spectrum appear characteristic bands of the species generated during the process. Thus, at 3385 cm⁻¹ there is a broad band due to the hydroxyl groups associated by hydrogen bonds. The photodegradation mechanism proposed and sustained by other authors [5,6] involves the formation in the first stage of hydroperoxides that decompose with the formation of aldehydes or ketones, acids, lactones or esters, as shown in figure 2. Support for the formation of different species with carbonyl groups and for the reaction mechanism is the broad carbonyl band with several peaks and shoulders and variation of the intensity and position of the carbonyl band during the photodegradation.

Another characteristic of the FTIR spectra is given by the intensity variation of the bands at 975 and 998 cm⁻¹, which is directly correlated with the degree of crystallinity of polypropylene and is influenced by its polymorphism. Thus, taking into account the fact that successive determinations are made on the same polypropylene sample with the same thermal history, a correlation can be made between the intensity ratios of the bands

mentioned above and the variation of crystallinity. This is important because it can explain changes in the properties of samples exposed to light, especially during the first 72 h, when there are no significant structural changes in the IR spectra. It is observed that from the beginning there is a change in the intensity ratio of the two bands, the variance of crystallinity being calculated with the relation:

$$\Delta \text{crystallinity (\%)} = \left[\left(\frac{I_{998}}{I_{975}} \right)_{\text{exposed}} - \left(\frac{I_{998}}{I_{975}} \right)_{\text{initial}} \right] \times 100$$

The recorded FTIR spectra shows the intensity variation of the two bands during photodegradation, as can also be seen in figure 3.

Based on these observations, we can explain the variation in the transmittance of PP films exposed to Xenon light before the first structural changes become visible in the IR spectrum. Probably breakdown of macromolecular chains induces an increase in crystal thickness, as has been observed by other authors [7,8].

Analyzing the DR-UV-VIS-NIR spectra of the blank PP films exposed under the same conditions, the following considerations can be made: a) In the visible range, as the exposure time increases, it was observed that there was an increase in sample reflectance of more than 5% at 410 nm, due to surface phenomena reported by other authors [5], in terms of cracking and exfoliation, increased roughness and loss of gloss due to superficial degradation; b) in the NIR domain the increase in the number of methyl groups onto the surface is confirmed as a result of the degradation by the increase of the characteristic band at 1705 nm compared to the 1725 nm (characteristic of the methylene groups) as shown in figure 4.

It was also observed that while titanium dioxide concentration increased and the advancement of photodecomposition at the surface of films, there is a marked decrease of the methyl and methylene groups, confirmed by the decrease of the corresponding bands from 1195 and 1211 nm, respectively. Also, the bands corresponding to the methylene groups at 1389 and 1436

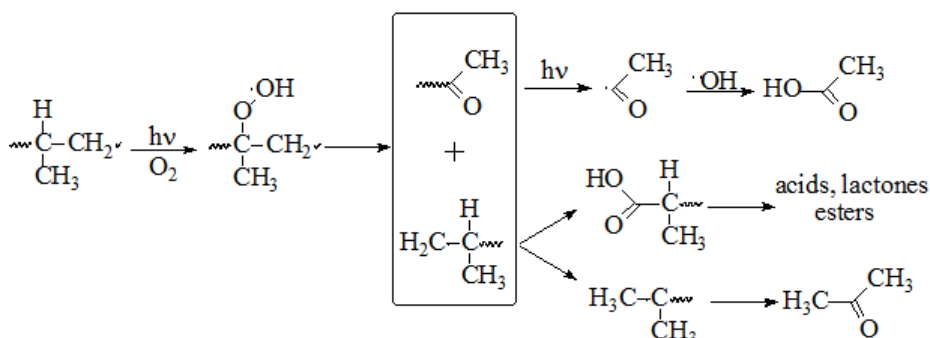


Fig. 2. Mechanism of polypropylene photocatalytic degradation

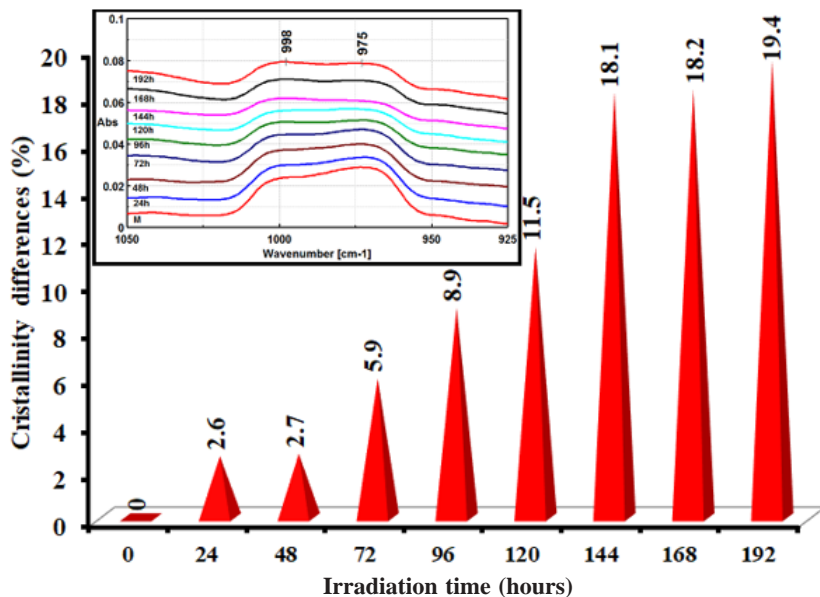


Fig. 3. Variation of PP crystallinity during irradiation (inset-FTIR characteristic bands)

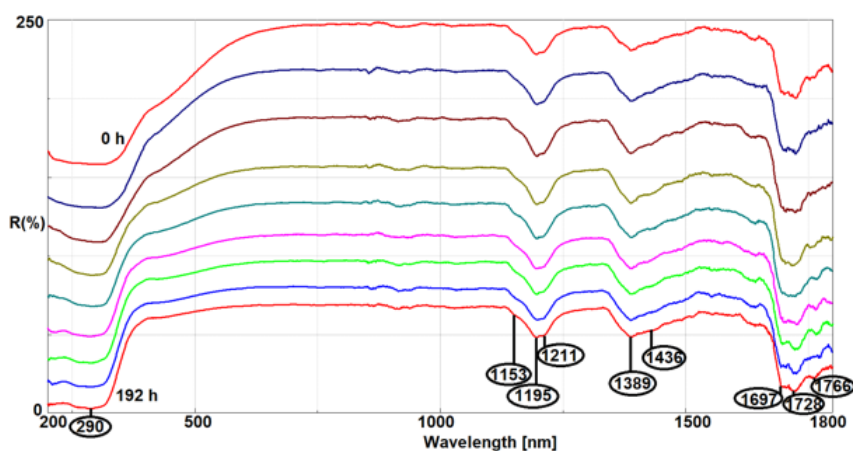


Fig. 4. The DR-UV-Vis-NIR spectra of PP-TiO₂ during irradiation

nm decrease, while the ratio of the 1697 nm (corresponding to the methyl group) and 1728 and 1766 nm respectively (corresponding to the methylene groups) changes in favor of the former, which attest the surface formation of species with methyl groups, during photodegradation. In the spectrum we can also see the intensification of the band at 1153 nm corresponding to the formation of the CO groups on the surface, with the increase of the catalyst amount. In the visible range, there can be observed an increase in diffuse reflectance, an attenuation of the shoulder at 414 nm, and the appearance of a band centered at 290 nm due to the presence of carbonyl compounds on the surface, as seen in figure 4.

Polyethylene photodegradation

Regarding PE films, both blank and composites exhibit characteristic absorption bands (2920, 2850, 1460 and 719 cm⁻¹) corresponding to the stretching and deformation vibrations of the methylene groups, showing that the polymer matrix is not affected by the incorporation of titanium dioxide nanoparticles, as seen from figure 5.

The photocatalyst amount did not determine major structural changes in the FTIR spectra for the same exposure time (192h), under Xenon light irradiation. From the ATR-FTIR spectra of blank PE samples, during the exposure to artificial light of the Xenon lamp for 192 h, minimal structural changes were observed, starting with

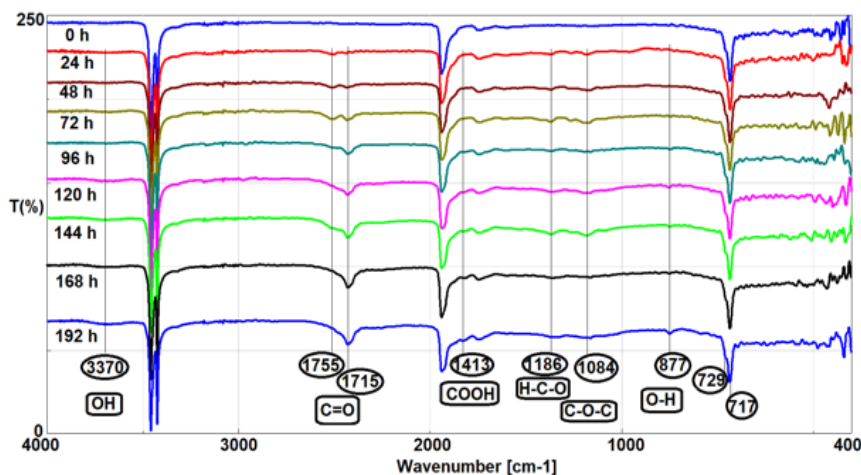


Fig. 5. ATR-FTIR spectra of PE-TiO₂ during irradiation

96 hours of exposure, with the appearance of a very small carbonyl band at 1719 cm⁻¹. Comparing the FTIR spectra show the preservation of all structural characteristics of PE during the exposure to Xenon light.

When nanometric titanium dioxide doped samples were analyzed, it can be argued that the photocatalytic degradation process begins to be detectable in the FTIR spectra by the appearance of the characteristic carbonyl band located at 1715 cm⁻¹, from the beginning, so as seen in figure 5. The band is broad and includes the stretching vibrations of carbonyl groups in lactones, esters, keto acids and monomeric acids (1755 cm⁻¹) that are formed during photocatalytic decomposition. Together with this band also appears the one located at 1413 cm⁻¹ due to the coupling of the deformation vibration of the hydroxyl groups with the carbonyl stretch. Also, the appearance of the broad band at 3370 cm⁻¹, is associated with the stretching vibration of the hydroxyl group, that can be correlated with the increasing of the surface hydrophilic character, as the exposure progresses.

Moreover, in the spectra there are bands located at 1186 and 1084 cm⁻¹, as well as at 877 cm⁻¹. These bands can be attributed to the stretching vibration of C-O bonds from alcohols and C-O-C from cyclic ethers, but the last band can be also attributed to peroxide species.

The photodegradation mechanism proposed and sustained by other authors [9-12] involves the formation in the first stage of the superoxide anion and of the hydroxyl radicals, by the action of electrons and voids (generated by photocatalyst under the action of UV radiation) on the oxygen and water molecules at the surface of the polymer. These reactive species attack the polymer chain to form radicals which in the presence of oxygen form

hydroperoxides that decompose with the formation of aldehydes or ketones, acids, lactones or esters [13], as shown in figure 6.

Another characteristic of the FTIR spectra is given by the variation in the intensity of the bands at 729 and 717 cm⁻¹, corresponding to the methylene rocking vibrations, which can be directly correlated with the degree of polyethylene crystallinity. The 717 cm⁻¹ band is associated with the amorphous component, while the 729 cm⁻¹ band is correlated with the crystallinity of the sample [14]. As it was expected, the samples of PE are highly amorphous and the ratio of absorbance (A₇₂₉/A₇₁₇) lead to a variation ranging from 0.325 in the case of the initial PE-TiO₂ composite up to 0.405 for the same sample irradiated for 192 h.

The DR-UV-VIS-NIR spectra of the PE composite films exposed under the same conditions show the appearance of a shoulder at 274 nm, corresponding to the surface formation of the carbonyl compounds. Also, in the spectrum a shoulder appears at 1160 nm indicating the formation of carbonyl groups and a band at 1410 nm, which increases in intensity as the exposure advances and is due to the formation of OH groups, as seen in figure 7. However, it was quite clear that for this type of composite films, this method proves to be of minor importance for the study of photodegradation.

Lastly, we must mention the most important index used in order to quantify the degree of photodegradation of polyolefin composites, namely the carbonyl index (CI) [15,16]. This index is calculated from the ratio between the absorbance of carbonyl groups (generated during photodegradation) stretching vibrations and the absorbance of methylene scissoring (characteristic to polyolefin materials):

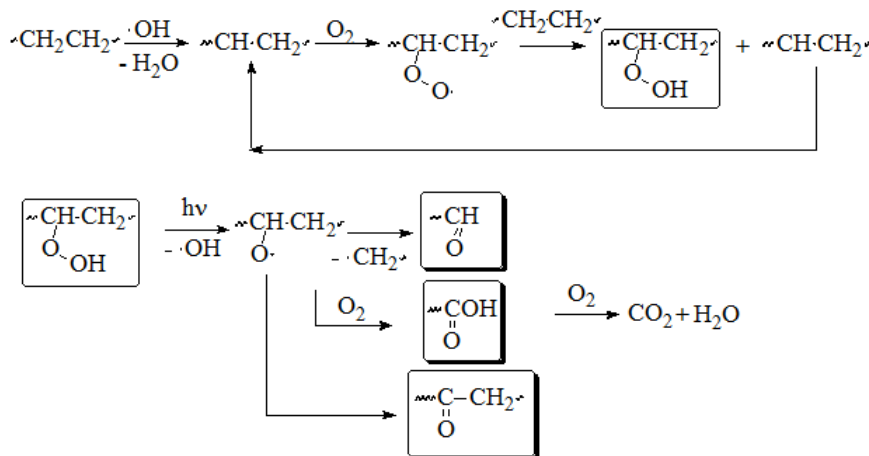


Fig. 6. Mechanism of PE photocatalytic degradation

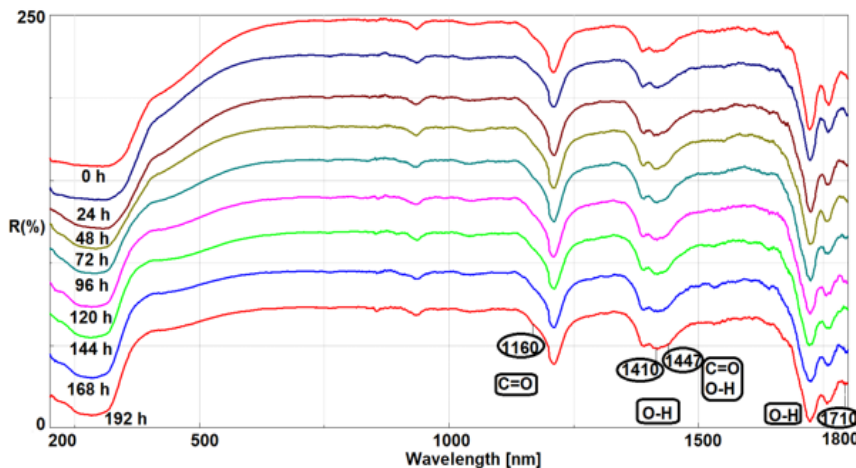


Fig. 7. The DR-UV-Vis-NIR spectra of PE-TiO₂ during irradiation

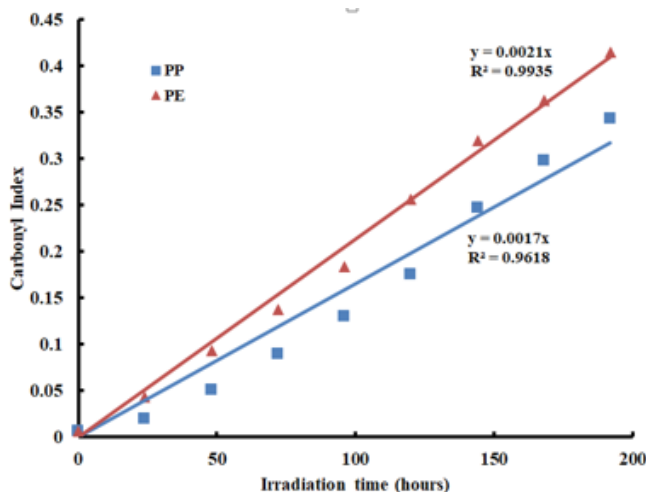


Fig. 8. Carbonyl index of polyolefin-TiO₂ composites during photodecomposition

$$CI(PP) = \frac{A_{1719}}{A_{1456}} \quad CI(PE) = \frac{A_{1715}}{A_{1470}}$$

In all the cases, CI increases during exposure to light due to the photo-oxidative processes, as can be observed from the figure 8.

The evolution of the CI of all samples follow the photocatalytic decomposition of PE and PP and rises linearly as a function of irradiation time. As can be observed from the figure 8, the linear fit is very accurate in the case of PE (squared correlation coefficient $R^2=0.9935$), while for PP ($R^2=0.9618$) the correlation is weaker probably as a result of carbonyl broad absorption bands (due to the formation of acids, ketones, lactones, esters, peracids).

Conclusions

Films of PP and PE composites containing 1% by weight TiO₂-P25 photocatalyst were seriously degraded under exposure to artificial Xenon light. Degradation generate mostly carbonyl species belonging to carboxylic acids, ketones, esters, peracids, and lactones.

The photodegradation can be followed by molecular spectroscopy, especially using FTIR spectra. From structural changes it can be proposed mechanisms for photodegradation. Ratio between the absorbance of different bands can be used for the evaluation of the photocatalytic decomposition and destruction of the polymeric chain, and also for the estimation of crystallinity differences.

The most important parameters which described very well the photocatalytic decomposition of polyolefins are the carbonyl index and the differences of crystallinity.

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