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Photolysis and photooxidation of poly(butylene terephthalate)–fibre glass systems

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The photooxidation and photolysis of poly(butylene terephthalate)–fibre glass (PBT–FG) were studied, and a comparison with the photochemical behaviour of PBT was made. It was found that the same photoproducts were formed in PBT and PBT–FG, and that fibre glass had no influence on the different routes involved in the mechanisms of photolysis and photooxidation. The determination of the photoproduct concentration profiles in PBT–FG and PBT showed that photooxidation and photolysis were limited to a depth of 50 μm in the irradiated surface. Moreover, it was found that the ratio between the rates of formation of the photoproducts in PBT–FG and PBT was equal to the ratio between the contents of PBT in PBT–FG and pure PBT.

(Keywords: photolysis; photooxidation; PBT–FG)

INTRODUCTION

The photochemical behaviour of aromatic polyesters has been the subject of several studies. The attention of researchers has been mainly focused on poly(ethylene terephthalate)[1–6] and, more recently, poly(butylene terephthalate) (PBT)[7–9]. Mechanisms accounting for photolysis and photooxidation of PBT have been proposed[7] and recently confirmed on the basis of identification of the different photoproducts that are formed on irradiation at short ($\lambda = 254$ nm) and long ($\lambda > 300$ nm) wavelengths. Photooxidation has been shown to be a pure photolytical change in which oxygen is not involved in the photoinduced oxidation pathway.

The present paper reports on the photochemical behaviour of PBT–fibre glass (FG). The influence of FG on the photochemical behaviour of polymers in general and aromatic polyesters in particular has not been described in the scientific literature. Two main questions that deal with the role of FG in the photochemical reaction of PBT have to be answered.

1. At the molecular level, it is expected that there be an influence of the FG on the chemical reaction of PBT on irradiation? In other words, can the interactions of the FG with the polymer matrix modify the nature of the photoproducts or the reaction stoichiometries?
2. Since FG is incorporated at a relatively large percentage, the profiles of light absorption by the system and permeability to oxygen of the reinforced material are expected to be different. Will these modifications of the characteristics of the system influence the behaviour of the polymer at the macroscopic level?

We report here a comparative study of the photochemical behaviours of PBT–FG and PBT. Several aspects are studied that concern the nature of the photoproducts and the reaction stoichiometries, as well as the influence of FG on the kinetics of photochemical reaction and the oxidation profiles in the polymer.

Results obtained in conditions of natural outdoor weathering are also reported and compared to those obtained in artificially accelerated photoageing conditions.

EXPERIMENTAL

The PBT samples with and without FG were obtained from Rhône–Poulenc (France). The PBT–FG sample contained 30% FG. Both samples were obtained in the form of plaques, and thin films were sliced with a Reichert and Jung microtome (2050 Supercut). Different thicknesses were chosen from 10 μm to 170 μm in order to study the influence of film thickness on the photochemical behaviour of the polymer. The different films were purified by extraction in ethanol for 70 h at room temperature and dried in a vacuum line.

Irradiations were carried out in a SEPAP 12-24 unit at a temperature of 60°C. This unit allowed irradiation at 'long' wavelengths ($\lambda \geqslant 300$ nm) with a controlled temperature of the samples (60°C). These photoageing units have been described elsewhere[10,11].

U.v.–visible spectra of the polymer films were recorded with a Perkin–Elmer UV 554 equipped with

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an integrating sphere. I.r. spectra were recorded with a Nicolet 20 SX Fourier transform i.r. (*FT*i.r.) spectrometer (dry air purged bench, summations of 64 scans, nominal resolution 2 cm^{-1}).

Photoproducts were identified by coupling the i.r. analysis to chemical derivatization reactions using reactive gases on the photooxidized or photolysed samples. These treatments included reactions with SF_4 and NH_3 to identify carboxylic acids[12,13].

Photoproduct profiles were recorded using the micro *FT*i.r. spectroscopic method described elsewhere[14]. This method is based on a cross-sectional analysis of films microtomed in a plane parallel to the irradiation axis. The irradiated samples were embedded in a commercial epoxy resin (Araldite) for the microtoming operations.

Natural outdoor weathering of the samples was carried out at Clermont-Ferrand on the roof of the CNEPs building (45° south) from January until July 1991.

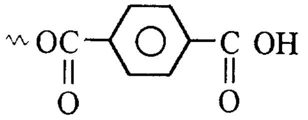
RESULTS AND DISCUSSION

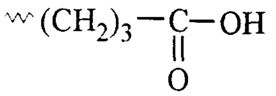
Photooxidation at long wavelengths ($\lambda \geq 300$ nm) in the SEPAP 12-24 unit

Important changes in the i.r. absorption spectra of PBT–FG films exposed to irradiation at $\lambda \geq 300$ nm in air were observed as follows.

1. A broad band appeared in the hydroxy region with two maxima at 3485 cm^{-1} and 3260 cm^{-1}. The latter was steadily displaced towards 3230 cm^{-1} as the irradiation time was increased. These absorption maxima have been observed previously in the case of PBT photooxidation and attributed to the formation of alcohols and acids[7]. An absorption maximum was also observed as a shoulder at 3512 cm^{-1} and attributed to absorption by alcohols.
2. The initial strong band between 1800 cm^{-1} and 1600 cm^{-1} arising from the C=O stretching vibration of the ester function was enlarged at both extremities. The difference spectra between the photooxidized samples and the original samples showed absorption maxima at 1695 cm^{-1} and 1740 cm^{-1} and a shoulder at 1770 cm^{-1}. Two weak bands were also detected at 1610 cm^{-1} and 1575 cm^{-1}. Chemical treatment of the photooxidized samples with SF_4 led to the disappearance of the bands at 1695 cm^{-1} and 1740 cm^{-1} and the development of an intense absorption band at 1815 cm^{-1} and a weak band at 1841 cm^{-1}. This behaviour confirms the presence of an aromatic acid (**I**): the absorption maxima at 1695 cm^{-1} and 1740 cm^{-1} correspond to the dimer and the monomer, and the band at 1815 cm^{-1} corresponds to the aromatic acid fluoride formed by reaction with SF_4.

The formation of an aliphatic acid (**II**) can be deduced from the observation of the maximum at 1841 cm^{-1}, which corresponds to the aliphatic acryl fluoride. However, the absorption band corresponding to the C=O vibration of the aliphatic acid in the dimeric form was not monitored, as a consequence of the absorption of the PBT ester groups. All the different observed maxima correspond to carboxylated oxidation photoproducts observed in photooxidized PBT[7] and recently identified[9]; for instance in the region 1230–1150 cm^{-1} a slight increase in absorption was observed, with a maximum at 1180 cm^{-1} previously attributed to formates[15].


(I)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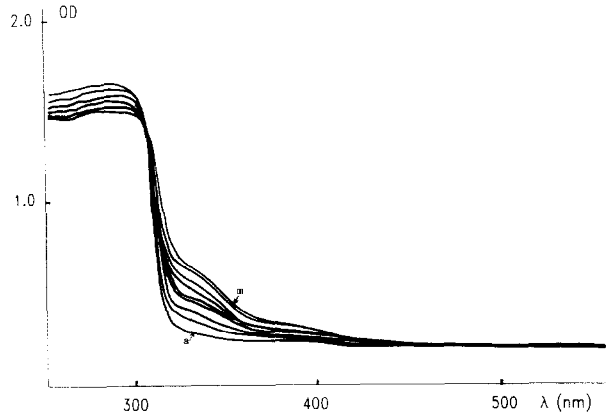
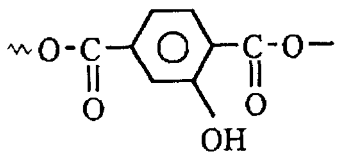
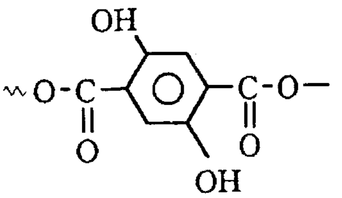


Figure 1 Changes in the u.v.-visible spectrum of a PBT–FG film (thickness 50 μm) irradiated in the SEPAP 12-24 unit in the presence of air from (a) 0 h to (m) 299 h


(III)


(IV)

It appears then, that according to i.r. spectroscopy the same products were formed in PBT–FG and PBT by photooxidation.

Similar conclusions were obtained from analysis of the u.v.–visible spectra of the PBT–FG films after irradiation. After irradiation in air, these samples showed an increase in absorption in the range 300–450 nm (*Figure 1*). The main feature is a large absorption band with a maximum around 340 nm. The shape of this band is the same for PBT and PBT–FG. Part of this absorption has been attributed to the formation of mono- and dihydroxy-substituted aromatic photoproducts (**III**) and (**IV**), which can be detected by their absorption in the range[7] 440–450 nm.

Fibre glass appears, then, to have no influence on the nature of the oxidation photoproducts from PBT. In order to check if the FG had an influence on the reaction stoichiometries, the relationships between the variations in i.r. absorption at several wavenumbers were plotted for PBT and PBT–FG. For example, *Figure 2* shows the plot of $\Delta D(3512\,cm^{-1})$ vs. $\Delta D(3260\,cm^{-1})$. These absorption maxima correspond respectively to the O–H vibrations of alcohols and acids. It is seen in *Figure 2* that the results are independent of the presence of FG. This result was confirmed by several other similar plots.

From a kinetic point of view, the oxidation rates of PBT–FG and PBT can be compared by plotting the variations in absorption at $3260\,cm^{-1}$ and $1695\,cm^{-1}$ as a function of irradiation time (*Figures 3* and *4*). *Figures 3* and *4* show that the oxidation curves have the same shape and that the oxidation rate of PBT–FG is always 70% that of PBT. The same observation was made when oxidation rates were measured from the increase in u.v.–visible absorption at 340 nm. This point will be discussed later.

The spatial distribution of oxidation photoproducts was monitored for both PBT–FG and PBT materials irradiated in the form of thick plaques (a few millimetres thick). The i.r. spectra were recorded every 11 μm from the irradiated surface towards the core of the sample. *Figures 5* and *6* present the plots of absorption at $3512\,cm^{-1}$ as a function of depth for PBT and PBT–FG, respectively. The results demonstrate that oxidation occurred only in the first 50 μm of the surfaces of PBT and PBT–FG materials. Moreover, the absorption measured in the case of PBT–FG was always lower than that measured in the case of PBT.

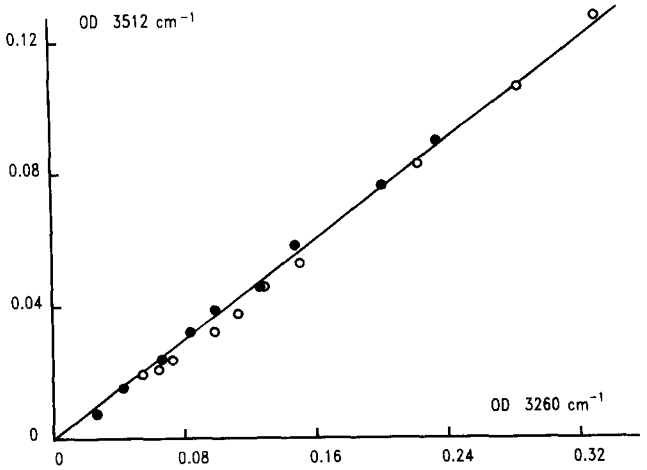


Figure 2 Absorption at $3512\,cm^{-1}$ vs. absorption at $3260\,cm^{-1}$ for PBT–FG (●) and PBT (○) samples (thickness 48 μm)

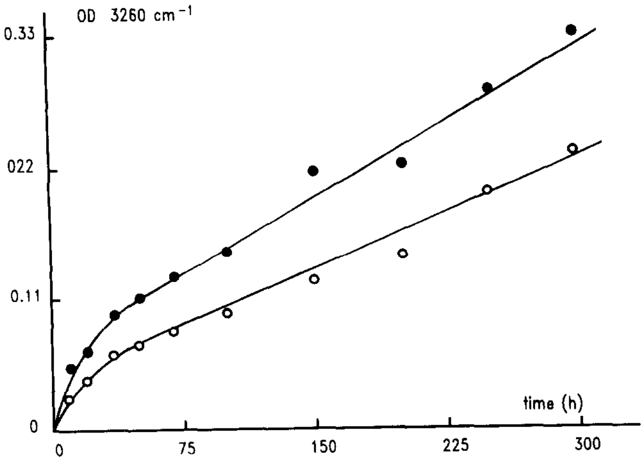


Figure 3 Absorption at $3260\,cm^{-1}$ vs. irradiation time (SEPAP 12-24 unit, O_2) for PBT–FG (●) and PBT (○) samples (thickness 48 μm)

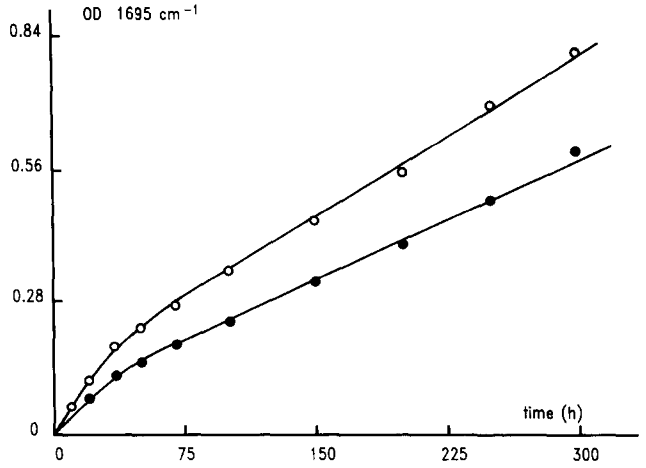


Figure 4 Absorption at $1695\,cm^{-1}$ vs. irradiation time (SEPAP 12-24 unit, O_2) for PBT–FG (●) and PBT (○) samples (thickness 48 μm)

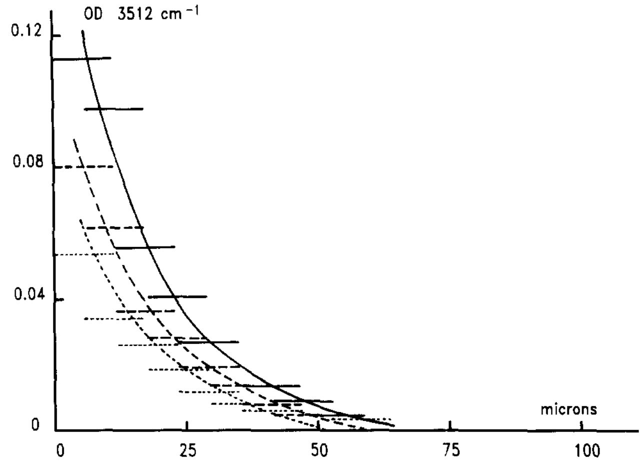


Figure 5 Oxidation profile measured from the variations in absorption at $3512\,cm^{-1}$ as a function of the depth for a PBT–FG plaque (thickness 3 mm) irradiated for various times in the SEPAP unit: (· · · ·) 100 h; (-----) 200 h; (——) 300 h

The results so far show the following features.

1. The same products are formed in photooxidized PBT and PBT–FG and the relative concentrations of these photoproducts are identical. Fibre glass presents a neutral effect, so the different pathways of the photooxidation mechanism proposed for PBT[7,9] can be applied to describe the photooxidation of PBT–FG.
2. The oxidation is limited to the superficial layers, i.e. the first 50 μm near the irradiated surface, for both PBT and PBT–FG. In the case of PBT, this limitation to the extent of oxidation has been shown to result from limitations on the penetration of light. Photolysis experiments described below show that in the case of PBT–FG it is also the absorption of light

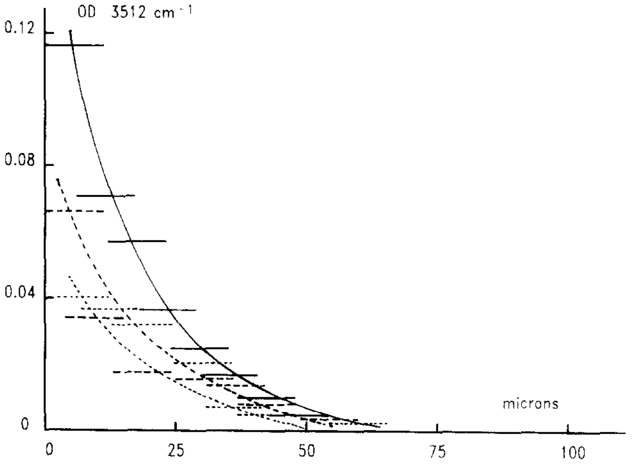


Figure 6 Oxidation profile measured from the variations in absorption at 3512 cm^{-1} as a function of the depth for a PBT plaque (thickness 3 mm) irradiated for various times in the SEPAP unit: (· · · ·) 100 h; (-----) 200 h; (——) 300 h

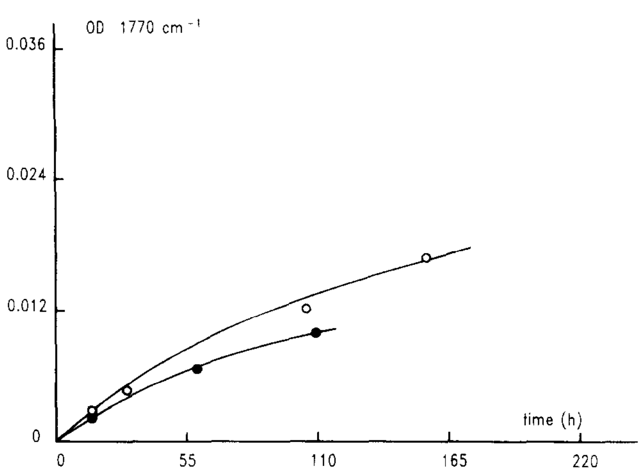


Figure 7 Absorption at 1770 cm^{-1} vs. irradiation time (SEPAP 12-24 unit, vacuum) for PBT–FG (●) and PBT (○) samples (thickness 48 μm)

responsible for the heterogeneous oxidation of PBT, despite the fact that PBT–FG contains only 70% PBT. The explanation for this comes from the similarity between the u.v.–visible absorption spectra of PBT and PBT–FG.

3. PBT–FG presents the same oxidative behaviour as PBT. The only consequence of the presence of FG is a limitation of the oxidation rate to 70% that of PBT.

Photolysis at long wavelengths ($\lambda \geq 300$ nm) in the SEPAP 12-24 unit

Irradiation of PBT–FG samples in the absence of oxygen, led to the following changes in the i.r. spectra.

1. The broad band observed under conditions of photooxidation also appeared in the region 3700–3100 cm^{-1}. Two maxima were observed at 3260 cm^{-1} and 3470 cm^{-1}, corresponding respectively to acids and alcohols.
2. In the carbonyl region, the widening of the initial ester band occurred mainly around 1700 cm^{-1}. The only absorption maxima in the difference spectra appeared at 1610 cm^{-1}, 1695 cm^{-1} and 1770 cm^{-1}. These maxima, observed for PBT, correspond respectively to *meta*-substituted rings[7,8], aromatic acids[7,8], and γ-lactones[8].
3. In the region of the C–O stretch of the ester group, modifications similar to those reported above for photooxidation were seen, i.e. an increase in absorption between 1230 cm^{-1} and 1150 cm^{-1} without a definite maximum, except for a weak band at 1180 cm^{-1} (formates).

These results are very similar to those reported previously for PBT[7]. Moreover, it was observed that the different photoproducts obtained reached the same relative concentrations.

The changes in the u.v.–visible spectra of PBF–FG and PBT under conditions of photolysis were also very similar: an increase in absorption occurred without any defined maximum over almost all the 300–450 nm zone.

Concerning the kinetic aspects of the photolysis, very similar results to the case of photooxidation were obtained. *Figure 7* shows the changes in absorption at 1770 cm^{-1} with time for PBT–FG and PBT samples. The rate of photolysis measured for PBT–FG is approximately 70% the rate measured in the case of PBT.

The determination of the spatial distribution of the photolysis products in PBT–FG gave the following results.

1. In a study of the influence of the thickness of the photolysed films on the rate of photolysis, it was observed that the rate reached a plateau for a thickness above 50 μm.
2. The determination of the concentration profiles of the photolysis products by micro *FT*i.r. spectroscopy showed that the photolysis products were formed only in the first 50 μm of the irradiated surface.

Analogous conclusions to those reported above for photooxidation can now be drawn.

1. The photolyses of PBT–FG and PBT involve the same pathways and lead to the same photoproducts. Fibre glass takes no part in these processes.
2. The reactions are limited to the first few layers of the polymers, representing approximately 50 μm. Fibre glass also limits the penetration of light in PBT–FG. As a consequence, the rate of photolysis in the case of PBT–FG is always 70% that measured in the case of PBT.

Natural weathering of PBT and PBT–FG

PBT–FG and PBT samples were exposed in the form of films to outdoor weathering in Clermont–Ferrand (France) for a few months.

The changes in the i.r. spectra of PBT–FG and PBT were very similar. In the hydroxy region, a broad band with maxima at 3485 cm^{-1} and 3260 cm^{-1} was observed. In the carbonyl zone, the difference spectra showed absorption maxima at 1695 cm^{-1} and 1740 cm^{-1} and a shoulder at 1785 cm^{-1}. Similar absorption bands were reported earlier in this paper for the case of photooxidation carried out under conditions of artificially accelerated ageing in the SEPAP 12-24 unit.

Figure 8 shows the oxidation kinetics of PBT–FG and PBT measured by the increase in absorption at 3260 cm^{-1} as a function of irradiation time. It can be seen from this figure that the rate of oxidation of PBT–FG is 70% that of PBT. The curves reported in *Figure 8*

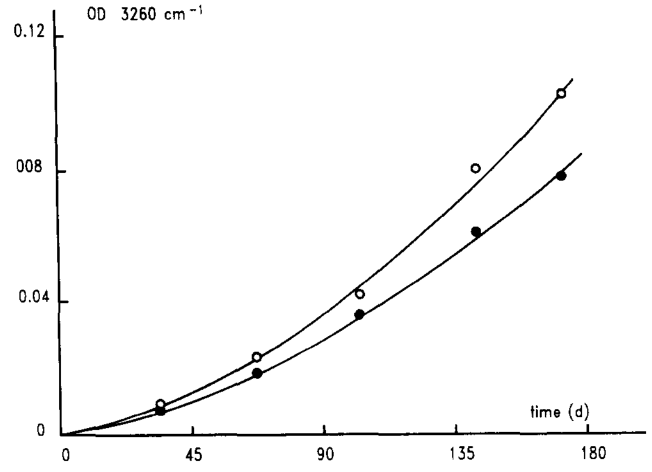


Figure 8 Absorption at 3260 cm^{-1} vs. irradiation time (natural exposure, Clermont–Ferand, January to July 1991) for PBT–FG (●) and PBT (○) samples (thickness 50 μm)

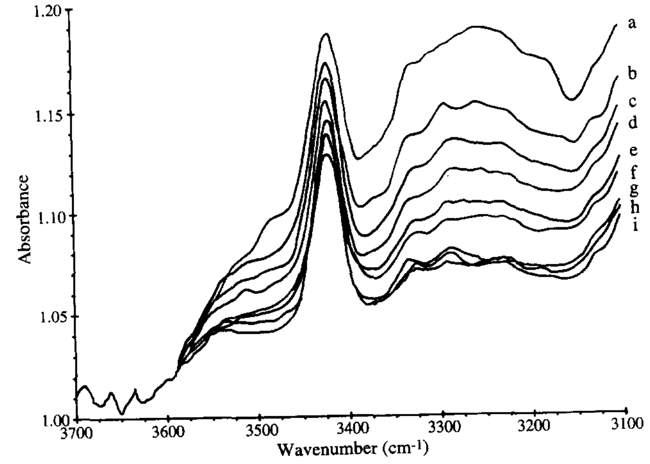


Figure 9 Changes in the i.r. spectrum of PBT–FG exposed to natural weathering conditions for 92 days as a function of the depth at which the measurement was made: (a) 0–11 μm; (b) 6–17 μm; (c) 12–23 μm; (d) 18–29 μm; (e) 30–41 μm; (f) 42–53 μm; (g) 60–71 μm; (h) 66–77 μm; (i) middle of the plaque

can be compared to the curves reported in *Figure 3*. In accelerated photoageing, the curves presented two different phases: up to approximately 75 h a significant increase in rate was observed, and in the second phase photooxidation proceeded with a linear and lower rate. In natural ageing the oxidation rate continuously increased during irradiation. This different behaviour can be attributed to the fact that outdoor irradiation was performed from January to July, which means that the variation in the oxidation rate was the result of an increase in both the mean temperature and the intensity of incident light.

Oxidation profiles of samples aged in natural conditions were also determined. *Figure 9* shows the changes in the i.r. spectrum of a PBT-FG plaque (3 mm thick) in the zone 3700–3100 cm^{-1} as a function of depth of measurement. It is clear from this figure that oxidation is limited to the first 50 μm. The same behaviour was seen in the case of PBT.

This general behaviour of PBT–FG and PBT in natural weathering conditions was not unexpected, since it has been shown in this paper that the oxidation was limited only by the absorption of light and not by oxygen diffusion.

These results verify that the artificially accelerated photoageing experiments reported herein are representative of natural photoageing because (1) the same photoproducts are formed in artificial and natural ageing, (2) the oxidation is limited to the superficial layers as a consequence of the attenuation of the absorption of light through the first 50 μm of PBT or PBT–FG for both forms of exposure and (3) the oxidation rate of PBT–FG is 70% that of PBT in both conditions of natural and artificial ageing.

An acceleration factor could be determined from the available results but it would be largely overestimated since the natural exposure was started in January and ended before summer began. However, recent experiments carried out in the laboratory over a longer period of exposure indicated an acceleration factor of 14 from the ratio of the oxidation rates of PBT determined for irradiation in the SEPAP 12-24 at 60°C and natural exposure in Clermont–Ferrand.

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