Analysis of photooxidation of polymer materials by photoacoustic Fourier transform infra-red spectroscopy

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Photoacoustic (PAS) *FT*i.r. spectra of photooxidized polypropylene samples have been recorded and the samples have also been analysed using transmission micro-*FT*i.r. analysis of cross-sectioned layers. The oxidation profiles monitored were shown to arise from oxygen diffusion limitation and also from the heterogeneous absorption of light by the TiO_2-pigmented samples. The intensity of the carbonyl absorbance measured by PAS-*FT*i.r. has been determined and it is shown that the front layer degradation monitored by both techniques (PAS-*FT*i.r. and micro-*FT*i.r.) has identical values. This rapid and non-destructive technique may thus be applied to quantitatively measure the surface degradation of aged polymers.

(Keywords: photoacoustic; photooxidation; infra-red spectroscopy)

INTRODUCTION

It is now widely recognized that a reliable prediction of the long-term durability of polymeric materials exposed to natural ageing can be obtained by extrapolation of the lifetime determined from artificial accelerated weathering in the laboratory[1]. The approach currently developed requires an understanding of the oxidation process and the characterization of the oxidation kinetics in well defined conditions. These attempts to monitor polymer oxidation are often complicated by the fact that the exposed samples are unhomogeneously oxidized. At the macroscopic level the heterogeneities can result from oxygen-diffusion limited effects[2,3]. If the rate of oxygen consumption exceeds the rate of oxygen permeation, oxidation occurs in the surface layers whereas the core remains practically unoxidized[4,5]. The importance of this effect depends on several parameters: intrinsic parameters linked to material geometry (e.g. sample thickness), coupled with the oxygen consumption rate, which depends on the reactivity of the polymer, the presence of additives and the oxygen permeability of the material; external parameters are the conditions of accelerated ageing and the oxygen pressure during ageing[6]. The combination of these parameters leads to the definition of an optimal thickness below which no limitation of the oxidation rate by oxygen diffusion occurs.

In the case of artificial photoageing, the acceleration must only be due to higher light intensities (limited to the range of monophotonic excitation) and higher temperatures (limited by the unvariance of the activation energy)[1]. Depending on the different parameters defined above, the optimal thickness of a transparent sample (for which light absorption occurs, at least initially, homogeneously through the whole sample) can range from a few micrometres to a few hundred micrometres for exposures carried out in a 'medium-acceleration' photoageing unit.

Detailed information on the oxidation of polymer films can be obtained from i.r. spectroscopic analysis of the irradiated samples. This technique also permits measurement of the effects of heterogeneous oxidation. Two simple methods are generally used: the intensity of an oxidation band can be monitored as a function of the sample thickness[7], or for microtomed slices as a function of the cross-sectional position[8,9]. However, it has to be pointed out that the first technique does not allow an oxygen-diffusion effect to be distinguished from a limitation of the degradation by u.v. absorption either by an initial chromophor or by u.v.-absorbing photoproducts. The second method is not so easily applied to the analysis of thin films and is usually reserved for monitoring heterogeneous oxidation of thick films (a few millimetres in thickness). Moreover the brittleness of the exposed outer layers makes it difficult to collect the microtome shavings. Consequently the samples often consist of a powder which must be mixed with KBr and pressed into small pellets. The data collected from the analysis of the first layers near the surface are often less accurate in such conditions.

Another approach that is very sensitive to surface oxidation is attenuated total reflection (a.t.r.). spectroscopy. This method can be applied to both thick and thin films. By varying the reflecting elements and the angle of incidence, one may monitor the depth dependence of oxidation products in the range of 0.1 μm to a few micrometres[10,11]. However, this technique requires intimate contact between the polymer sample and the reflecting crystal. This is not always possible with degraded materials since the outer surface roughens and often becomes brittle and deformed. Poor quantitative

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data are collected most of the time. Roughened surfaces also result in reduced spectral quality. Moreover with thin films the surface of the sample is often not large enough to fit the reflecting crystal.

It therefore appeared that these standard techniques were not totally adapted to the analysis of aged materials, specially when thin films were concerned*. For this reason, since 1986 we have developed a different technique to monitor heterogeneous oxidation in thin films (e.g. 100–300 μm)[4]. The method, based on micro-*FT*i.r. spectroscopy, consists in analysing the photooxidized sample in a plane perpendicular to the axis of irradiation. For this purpose, the irradiated film is first embedded in a resin and then sliced with a microtome in a plane corresponding to the irradiation axis. The thin slices (typically 50–80 μm) are then analysed by transmission i.r. spectroscopy through an i.r. microscope. A small area is isolated by an image-masking aperture and the oxidation profile is monitored by moving the analysed area from the front layers to the back layers.

This method has been successfully applied to the characterization of many different polymer systems[5,6,12,13]. However, the accuracy of the data collected for the outer surface layers is questionable since that surface could be partly damaged by the microtome. For this reason, we have applied a non-destructive analysis of the surface based on photoacoustic *FT*i.r. spectroscopy (PAS-*FT*i.r.). The key advantage of PAS-*FT*i.r. is that it requires virtually no sample preparation and is relatively independent of the surface morphology of the sample. The theory and advantages of PAS-*FT*i.r. have been reviewed by many authors (see for example refs 14–16).

In the following study, photoacoustic detection is used to obtain quantitative data on artificially aged polymer films with minimal preparation. The data obtained by PAS-*FT*i.r. are compared to those obtained by the micro-*FT*i.r. spectrophotometric method.

EXPERIMENTAL

The material used was a heterophasic polypropylene supplied by Himont. The polymer contained only processing antioxidants as additives. Pigmented samples coated with 0.5% TiO_2 in the rutile form were also studied.

Plates with a thickness of 6 mm were obtained by injection moulding (melt temperature 200°C). Films with a thickness of 50 μm were prepared by heat pressing at 190°C for 2 min followed by quench cooling in water.

The polymer samples were irradiated in a SEPAP 12.24 unit at a temperature of 60°C. This medium-accelerated photoageing device has been described in several papers (see for example refs 17 and 18). It allows irradiation at wavelengths above 300 nm. Previous data showed 240 h in the SEPAP unit to be equivalent to about 1 year of outdoor exposure in Clermont-Ferrand, France, for the unstabilized sample.

The back of the samples was masked during irradiation in order to protect it from photooxidation.

The i.r. spectra (transmission mode) of the thin films were recorded by using a Nicolet 800 *FT*i.r. spectrometer (nominal resolution 4 cm^{-1}, 32 scan summations).

The analysis by micro-*FT*i.r. spectroscopy was carried out following a procedure described previously[4]. The embedding resin was a commercial epoxy resin. The i.r. spectra were recorded on a Nicolet 800 coupled to a Nic-Plan microscope (nominal resolution 8 cm^{-1}, 128 scan summations).

A photoacoustic attachment (MTEC 200) was used with the Nicolet 800. A spectrometer velocity of 0.16 cm s^{-1} was selected for all measurements. Background spectra were recorded with carbon black. Spectrometer and detector amplifier gains were adjusted to 1 and 8, respectively, for all the polymer samples measured, and 1 and 2 for the background spectra. The spectra were recorded at a spectral resolution of 8 cm^{-1} and measurement runs corresponded to 128 scan summations. The samples analysed were obtained from the thick plates in the form of discs with a diameter of 1 cm.

RESULTS AND DISCUSSION

Photoacoustic spectroscopy.

Theoretical predictions for thermally thick and optically transparent samples show that the magnitude of the photoacoustic signal generated from the surface of the sample depends on the modulation frequency of the incident light. The frequency dependence of the photoacoustic signal varies as $\omega^{-3/2}$.

According to the theory, the thermal diffusion length, μ, is related to modulation frequency, ω, through the following equation:

$$\mu = (k/\rho C \pi \omega)^{1/2}$$

where k is the thermal conductivity, ρ is the density, C is the specific heat, ω is the modulation frequency ($\omega = 4\pi V \bar{\nu}$) with V the mirror velocity (cm s^{-1}) and $\bar{\nu}$ the wavenumber (cm^{-1}).

For the polypropylene samples analysed, values of thermal conductivity $K = 0.135$ W m^{-1} K^{-1}, density $\rho = 0.902$ g cm^{-3} and specific heat $C = 1.926$ J g^{-1} K^{-1} were used[19]. Using these values, the thermal diffusion lengths μ calculated at both 1715 and 1161 cm^{-1} were respectively 11 and 13 μm.

Figure 1 shows the PAS-*FT*i.r. spectrum of the unpigmented sample before irradiation. This i.r. spectrum

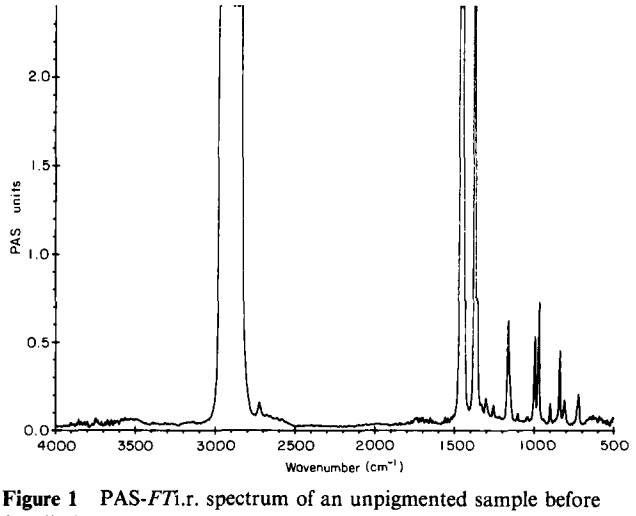

Figure 1 PAS-*FT*i.r. spectrum of an unpigmented sample before irradiation

* The use of thin films in conditions of accelerated artificial ageing permits the avoidance of diffusion-limited processes, and consequently the outdoor behaviour of the polymer material can be reproduced. In addition the use of thin films may be recommended to facilitate the spectrophotometric analysis by transmission techniques, and to improve the sensitivity oxidation detection (no unreactive zone superposes on the oxidized layers and dilutes the effects of ageing)

is given in PAS units. For further comparisons with transmission spectroscopy, the PAS-*FT*i.r. spectra had to be calibrated in absorbance units. This was done by measuring the thickness dependence of the absorbance of several samples with thicknesses varying from 6 to 60 μm. *Figure 2* shows the evolution of absorbance measured at 966 cm^{-1} as a function of thickness. The absorbance at 966 cm^{-1} for a sample 13 μm thick is calculated to be 0.08 from this figure. This value gives a calibration of the PAS spectrum at least for that wavenumber. It is determined that 1 PAS unit at 966 cm^{-1} corresponds to 0.135 absorbance units. Since the thermal diffusion length at 1715 cm^{-1} is 11 μm, it is deduced that 1 PAS unit would correspond to 0.119 absorbance units at 1715 cm^{-1}.

Figure 3 shows the PAS-*FT*i.r. spectrum of the unpigmented sample irradiated for 147 h in the SEPAP unit. It was first checked that the thermal diffusion length was not modified by the ageing since the PAS intensity of the intrinsic bands remained unchanged. Considering the calibration described above, it was possible to determine the absorbance of the carbonyl band at 1715 cm^{-1}. A value of 0.13 was calculated from the obtained data.

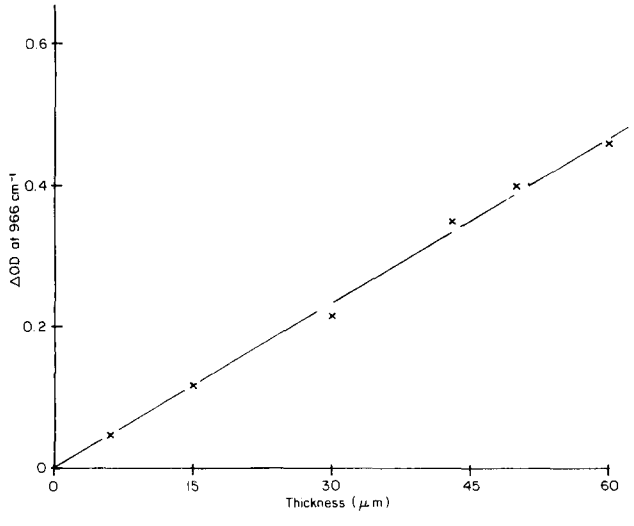

Figure 2 Variations of absorbance at 966 cm^{-1} measured by transmission *FT*i.r. spectroscopy as a function of film thickness

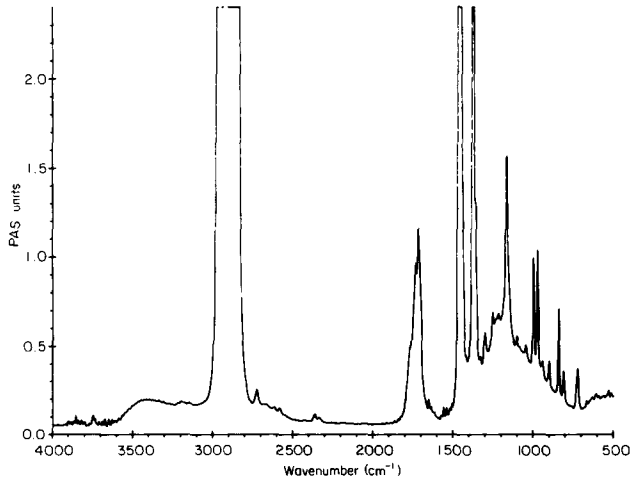

Figure 3 PAS-*FT*i.r. spectrum of an unpigmented sample irradiated for 147 h in the SEPAP unit

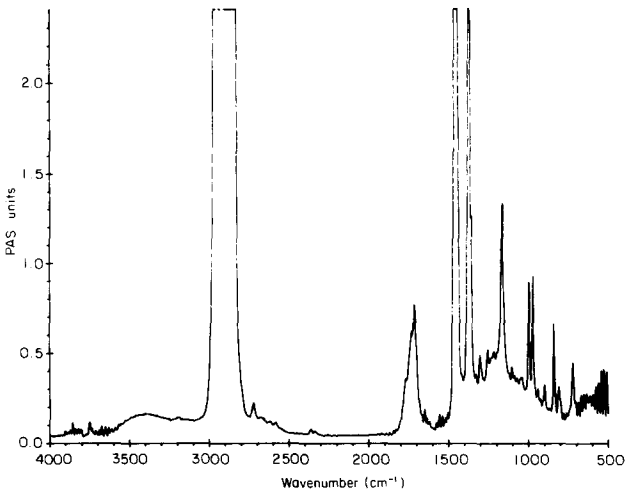

Figure 4 PAS-*FT*i.r. spectrum of a pigmented sample irradiated for 147 h in the SEPAP unit

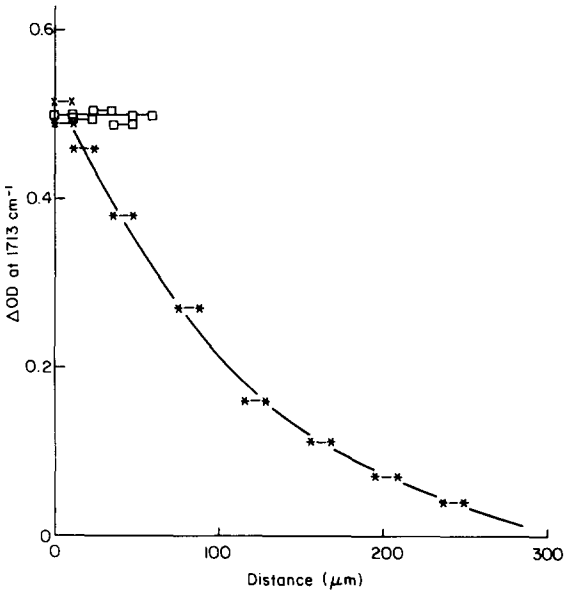

Figure 5 Oxidation profiles measured at 1713 cm^{-1} for an unpigmented sample (analysed thickness 50 μm): *, micro-*FT*i.r. spectroscopy profiling on a thick sample (6 mm); □, micro-*FT*i.r. spectroscopy profiling on a thin sample (50 μm); ×, PAS-*FT*i.r. absorbance corrected to fit a 50 μm thickness

Similar experiments were carried out for the pigmented samples. *Figure 4* shows the PAS-*FT*i.r. spectrum of the sample irradiated for 147 h. From the calibration, the carbonyl band intensity at 1715 cm^{-1} was calculated. A value of 0.08 was found, corresponding to a thickness of 13 μm.

*Micro-*FT*i.r. spectrophotometry*

The oxidation profiles through the thick plates of pigmented and unpigmented samples were monitored following the procedure briefly described in the Experimental section. The thickness of the microtomed layers was 50 μm and these layers were analysed every 10 μm. *Figures 5* and *6* show the results obtained with the unpigmented and pigmented polymer, respectively. Both figures show pronounced profiles, but with different shapes. In the case of the unpigmented samples, the oxidation extends up to 300 μm and the shape of the profile is obviously only attributed to a diffusion-limited process. The oxidation of the pigmented sample occurs

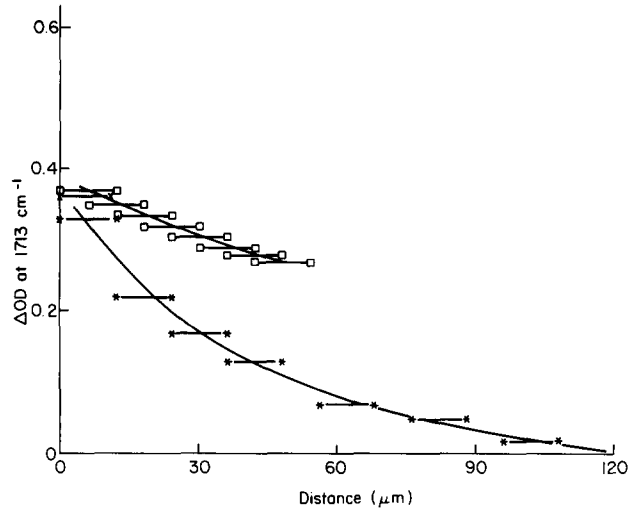

Figure 6 Oxidation profiles measured at 1713 cm^{-1} for a pigmented sample (analysed thickness 50 μm): *, micro-*FT*i.r. spectroscopy profiling on a thick sample (6 mm); □, micro-*FT*i.r. spectroscopy profiling on a thin sample (50 μm); ×, PAS-*FT*i.r. absorbance corrected to fit a 50 μm thickness

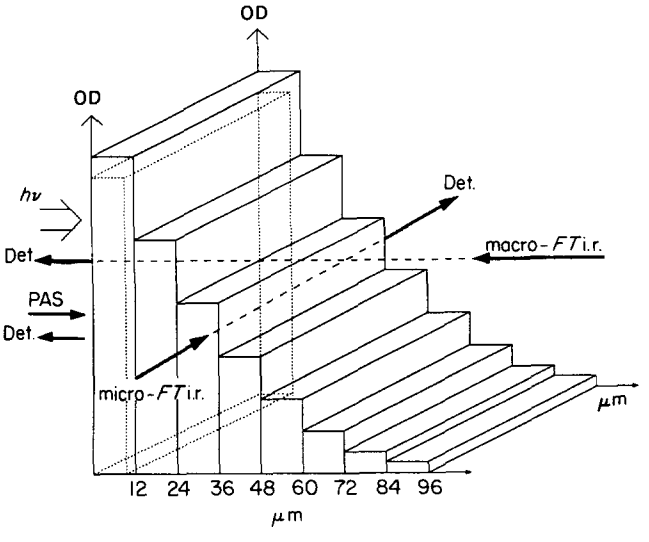

Figure 7 Comparison of the different methods of analysis of a photooxidized sample: PAS-*FT*i.r. spectroscopy, transmission micro-*FT*i.r. spectroscopy and transmission macro-*FT*i.r. spectroscopy

only in the first 100 μm near the front surface. This result means that, besides the diffusion-limited process, the reaction is also controlled by a limited penetration of light in the sample due to TiO_2; the shape of the profile results from the combination of both effects. Lastly, it is observed on these figures that the unpigmented sample is less oxidized than the pigmented one, which confirms previous findings on the protective role of TiO_2 coating in polypropylene photooxidation[20].

Oxidation profiles were also monitored for thin films (50 μm) of pigmented and unpigmented samples exposed for the same time (147 h) in the SEPAP unit. The results obtained are plotted in *Figures 5* and *6*. In the case of the unpigmented film no profile was observed. In contrast to the thick plate, the thin film was homogeneously oxidized. This difference is attributed to the fact that oxygen diffusing from the back surface of the thick sample cannot reach the bulk. This observation is in good accordance with the classical theoretical oxygen concentration models giving the steady-state oxygen concentration for a material exposed to oxygen on both sides[2,21].

A weak profile was observed with the pigmented thin films. Since it has been shown above that no diffusion-limited process occurred for this thickness (50 μm), this profile may be attributed to u.v. light absorption by the polymer matrix, eventually corrected by a weak photocatalytic effect due to TiO_2, even coated by a passivating agent. The profile is less pronounced for the thin film than for the thick plate, which corroborates the former observations on unpigmented samples. Moreover, it should be noted that the absorbance value of the carbonyl in the front layers was identical for both the thin and thick samples.

Macro-FT*i.r. spectroscopy*

The thin films (50 μm) irradiated in the SEPAP unit were analysed by transmission spectroscopy before being embedded and sliced for further microscopic investigations reported above. The absorbance value recorded for the unpigmented sample (0.5) was obviously the same as the value monitored for the film by micro-*FT*i.r. spectroscopy. With the pigmented sample, a value of 0.3 was determined. This value fitted quite well with the mean value calculated by integration of the profile measured for the pigmented thin film.

CONCLUSION

In *Figures 5* and *6*, the absorbances determined from the PAS spectra and corresponding to a thickness of 11 μm have been reported, corrected to fit a thickness of 50 μm. The values obtained were 0.37 and 0.52 for the pigmented and unpigmented samples, respectively. These values are in good agreement with the values determined by techniques based on transmission spectroscopy; micro-*FT*i.r. spectroscopy gave values of 0.35 and 0.50 for the pigmented and unpigmented samples, respectively.

Figure 7 summarizes the different approaches reported in this paper for monitoring the oxidation of polymer samples submitted to photooxidative ageing.

The results obtained with PAS-*FT*i.r. spectroscopy show that this technique can be successfully applied to the quantitative measurement of polymer surface ageing. Moreover, considering possibilities of varying the mirror velocity of the interferometer, depth profiling can be carried out. Some encouraging results have been obtained which will be reported in a future publication.

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