

Use of Photoacoustic Spectroscopy in Studying the Natural Weathering of Polyethylene Films

ALI ANANI, AMAL MOBASHER, and FIRAS A. RASOUL,* *Kuwait Institute of Scientific Research, P.O. Box 24885, Safat, Kuwait*

Synopsis

Photoacoustic spectroscopy was used to assess the degradation of polyethylene under local natural weathering conditions. The results obtained are in good agreement with those obtained using infrared spectroscopy and from mechanical testing. Photoacoustic spectroscopy supports the accepted mechanism of polyethylene degradation.

INTRODUCTION

The use of photoacoustic spectroscopy (PAS) in studying the weathering of polymers is growing.^{1,2} In this work we report the use of PAS in studying the natural degradation of polyethylene (PE) under local conditions. Kuwait's weather is representative of the Arabian Gulf climate.³ The harsh weather is characterized by high UV radiation, high humidity, and repeated thermal cycling during the day. PAS was found convenient to monitor the weathering of PE. The results were compared with those obtained using IR spectroscopy and mechanical testing.

The use of PAS to study the degradation of PE offers several advantages in the UV, visible, and near IR regions over conventional techniques.^{4,5} Some of these advantages are:

- (a) Sample preparation is unnecessary.
- (b) It is usually faster, more sensitive to sample constituent changes, and yields more reproducible results than most techniques.
- (c) It is nondestructive.
- (d) It provides an optical depth profile of the absorption spectra, a unique analytical procedure.
- (e) It can provide accurate information on the thermal properties of the samples.
- (f) It is immune to light scattering or light reflection.
- (g) Completely opaque samples can be investigated without difficulty.

EXPERIMENTAL

An exposure site was chosen so that samples were exposed to an aggressive combination of high temperature, humidity, and solar radiation. The exposure racks were installed to face the equator and were located in an open area near the sea so that no shadow could fall on any of the samples during the day. The

* To whom all correspondence should be addressed.

racks were equipped with polytetrafluorethylene (PTFE) clips⁶ capable of holding samples of any convenient size. The angle of exposure was 45°. ⁷ This angle was selected because it is known that, in a tropical desert climate, cloudless skies permit the relatively low winter sun to favor 45° exposure, so that samples will be exposed to the sun.²

Samples were mounted on wooden racks (painted white) 75 cm above the earth's surface (according to ASTM D-1435, 82) to eliminate any differences resulting from UV radiation and absorption of infrared energy from the soil onto the exposed samples.^{4,8} Photoacoustic spectra were recorded on a Princeton Model 6001^{4,5} Spectrophotometer. A 1000-W xenon lamp was used as a source of excitation. A pyroelectric detector compensated for any variation in lamp intensity that might occur during the spectrum gathering.

The spectral range of this equipment is from 200 to 2600 nm at any modulated frequency between 10 Hz and 2 kHz at a scanning rate of 200 nm/min. The sample cell was made of high quality quartz and accepted samples in liquid or solid form. The exit slit of the light scanning monochromator was 2 mm, at which the resolution of the spectrometer was 8 nm. Carbon black was used as a reference against which all the spectra were normalized.

Air rather than helium proved to be sufficient as a coupling between the sample and the microphone because a strong signal was obtained from our samples. The equipment was completely controlled and operated by a microprocessor. IR spectra were recorded by a Beckman Spectrophotometer (Model IR 4260) using the reflectance technique. An Instron (Model 1195) was used to measure the mechanical properties of the exposed and nonexposed polymeric materials, according to ASTM D 882-75B, 1981 for tensile properties of thin plastic sheeting.

Polyethylene was supplied by the Packaging and Plastic Industries Company (Kuwait). Except for the pigment, the ingredients were the same for all films. In all samples, pigments used were chrome-based and were added in equal concentrations. Film thickness was 0.2 mm.

RESULTS AND DISCUSSION

The natural weathering study was carried out on locally processed low-density polyethylene films, which were pink, yellow, green, blue, black, and transparent (liner and agricultural grade). Polymer deterioration usually starts at the surface and then penetrates into the bulk. This behavior is manifested by cracking, crazing, discoloration, and changes in the texture of the films.⁹

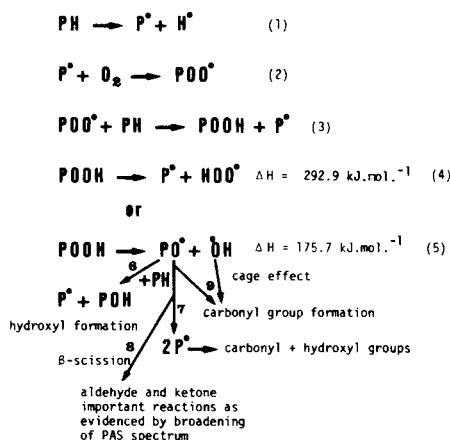
Visual Observation

It was observed that discoloration was followed by the development of cracks in yellow and pink films. Only slight color changes were observed in green, blue, and black films, although cracks and brittleness did develop during the summer (May–October). Complete discoloration of pink and yellow films occurred after only 60–70 days of exposure whereas during the winter (November–April) discoloration occurred after 100 days of exposure. In addition, the brittleness of these films was severe after 60 days of summer exposure (concurrent with discoloration) in contrast to winter exposure, in which no brittleness or cracking

was observed even though the films were completely discolored. These findings are in agreement with the work reported by Minac et al.,¹⁰ in which yellow films showed the least resistance to weathering. PAS for the visible region also conform with these observations.

IR and PAS Spectra

No samples of polyethylene films except pink and blue showed carbonyl group absorption before exposure. After 35 days of natural weathering, IR spectra of all polyethylene films except black showed¹⁰ the formation of carbonyl group absorptions at 1715 cm⁻¹. The intensity of the carbonyl absorption peak is greater in the yellow and pink films and less in the transparent films. A dramatic increase of the carbonyl group was observed after further exposure to solar radiation. During this exposure period, all polyethylene films also showed the formation of hydroxyl and hydroperoxide absorptions in the region of 3500–3600 cm⁻¹:



Scheme 1. Mechanism of polyethylene degradation.

Evaluations were made over the entire year. It is worth comparing the IR absorption changes of each polyethylene film exposed to solar radiation during the first and second periods, i.e., summer and winter, respectively. Figure 1 shows plots of IR absorption values of PE agriculture and, after normalization, during both exposure periods using the procedure of Carlson and Wiles.¹¹

The increase in the carbonyl absorption at 1715 cm⁻¹ was dramatic during the summer exposure period but was much less so during winter. This can be seen very clearly for polyethylene agriculture (Fig. 1). Similarly, the increase in absorption at 3500–3600 cm⁻¹ is larger during the summer than during the winter. These increases imply that the rate of formation of the carbonyl, hydroxyl, and hydroperoxide groups were much greater during the summer exposure period than during the winter and that this was directly related to the rate of polyethylene degradation (see Scheme 1). The presence of traces of carbonyl groups in the pink and yellow polyethylene at the start of the natural weathering might have accelerated their degradation upon exposure.⁹

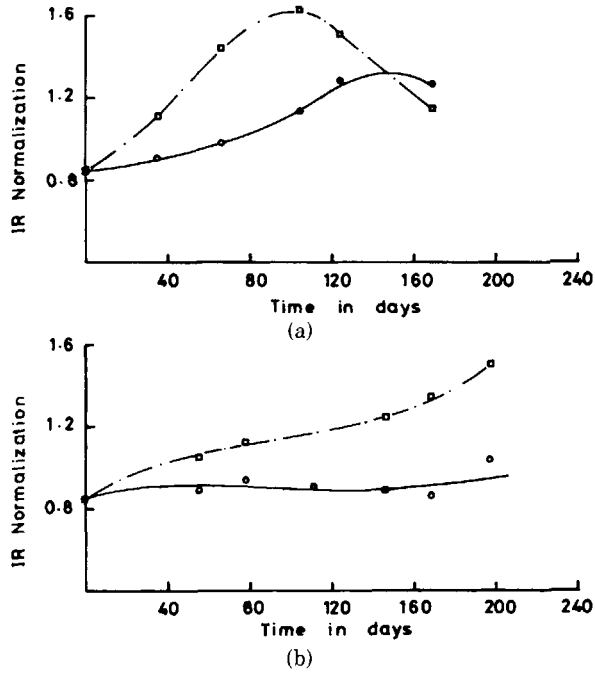


Fig. 1. Increase in the IR absorption at 1715 cm^{-1} (□) and 3415 cm^{-1} (○) for the polyethylene agriculture exposed to natural weathering during the summer (a) and winter (b) months.

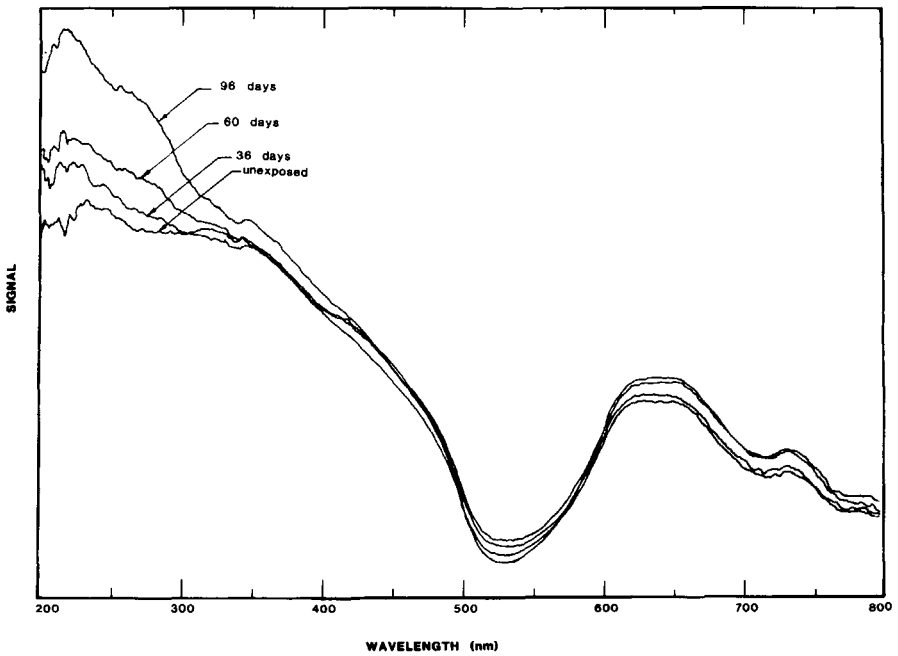


Fig. 2. Photoacoustic spectra of polyethylene green exposed to natural weathering during the summer period.

Results of PAS

Results obtained in the visible and ultraviolet region (200–800 nm) for green and yellow polyethylene are shown in Figures 2 and 3. Figure 2 shows the disappearance of the PAS band in the visible region. It can be seen from Figure 3 that PE yellow exposed to natural weathering during summer shows a disappearance of peak in the wavelength region of 350–550 nm, which results in discoloration, as was observed visually; this change in color was noted from the PAS. More interesting is the increased broadening of the $n-\pi^*$ absorption of the carbonyl group as the polymer degrades (maximum absorption range = 250–320 nm; Fig. 2).⁸ This is in agreement with Kamal and Saxon,¹² who suggested that broadening in the near UV spectrum after short exposure intervals outdoors could be used to predict the resistance of polymers to discoloration. PAS offers a direct method of measuring such resistance.

The broadening of carbonyl absorption results from β -scission of the polymer skeleton.¹² The PAS spectrum (Fig. 2) is broadened as a result of such degradation, indicating that β -scission, which has a tremendous bearing on the mechanical property of changes of a polymer, is more important than crosslinking (step 8 of Scheme 1).

It has generally been agreed that chain scission leads to a loss in tensile strength in contrast to network structure development through crosslinking, in which tensile strength normally increases.⁶ Therefore, it was thought desirable to study the mechanical properties of naturally weathered PE yellow (see Fig. 4). It can be concluded from this figure that tensile strength decreases with increasing time of exposure, as was expected from the broadening of the PAS spectrum, thus

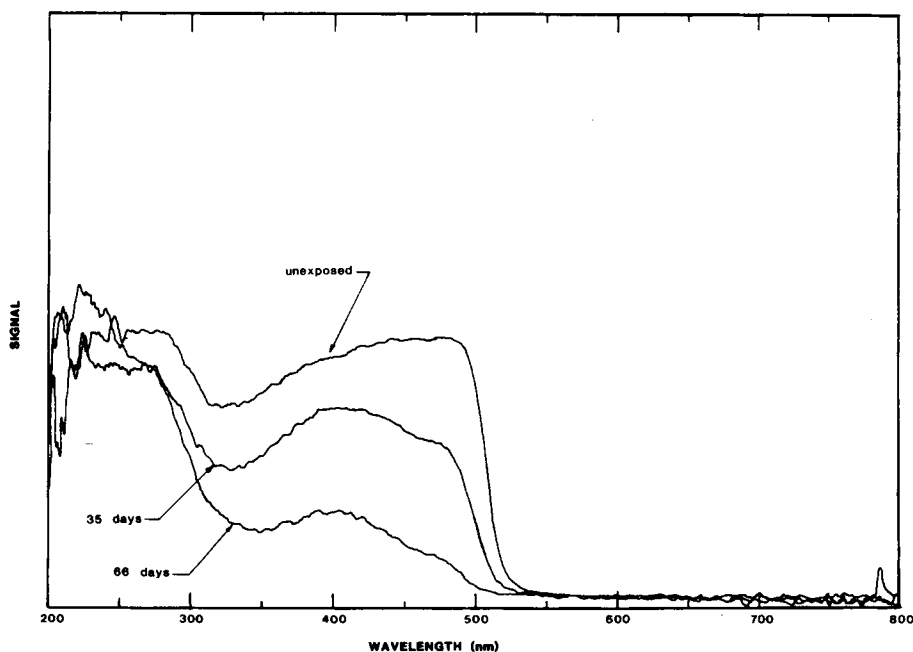


Fig. 3. Photoacoustic spectra of polyethylene yellow exposed to natural weathering during the summer period.

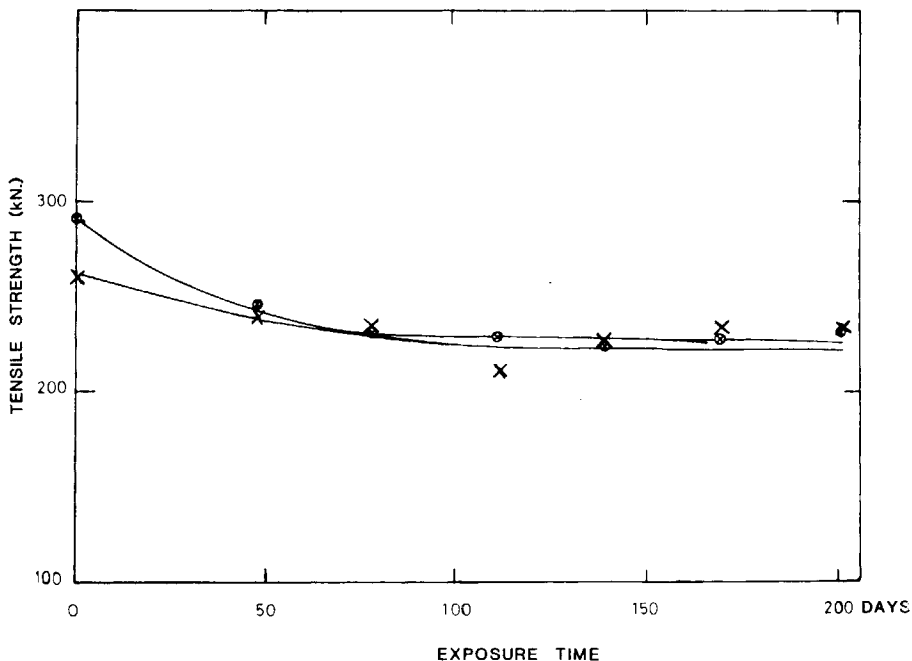


Fig. 4. Decrease in tensile strength of polyethylene yellow (⊙) and polyethylene agriculture (X) exposed to natural weathering during the winter period.

giving further support to the generally accepted mechanism depicted in Scheme 1.

The β -scission (step 8 of Scheme 1), which contributed significantly to degradation as shown by the broadening of the PAS spectra, leads subsequently to the formation of the C=O group rather than to the OH group, in agreement with IR findings (Fig. 1).

CONCLUSIONS

PAS results give further support to the generally accepted mechanism of PE degradation and are in agreement with previous conclusions arrived at by using IR spectroscopy and mechanical testing methodology.

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