Photodegradation of Multilayer Films Based on PET Copolymers

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ABSTRACT: An investigation was conducted on the effects of photodegradation of multilayer films based on PET copolymers. The films were composed by different layers with PET, PET/PEN, and PET/PEI copolymers with a total thickness of 23 μm. The films produced by coextrusion followed by a biaxial orientation in an industrial equipment were exposed to the ultraviolet radiation in the laboratory for periods of up to 600 h. The samples were investigated by FTIR-ATR, UV/visible spectroscopy, fluorescence spectroscopy, size exclusion chromatography, mechanical properties, and scanning electron microscopy. The results showed that the photooxidation is concentrated at the surface layers and that coextruded films were more sensitive to the UV radiation effects. The deterioration in mechanical properties with exposure and the fracture behavior were shown to be consistent with the amount of degradation that occurred in the films. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 51–57, 2007

Key words: polyesters; coextrusion; photochemistry; degradation

INTRODUCTION

The widespread use of polymer films and sheets in applications such as packing, food containers, covering materials for panels, and other consumer goods have stimulated the investigations to obtain materials with best performance and lowest cost. Poly(ethylene terephthalate) (PET) is one of the main polymers used as films, but in certain applications a multilayer material produced by coextrusion may be required to fulfill specific requirements. This may occur when properties such as permeability, clarity, welding, mechanical strength, or durability are not obtained with the base polymer. The production of multilayer films by the coextrusion technique is used to deal with this problem, when the proper combination of components is chosen.

The study of the photodegradation and photostabilization of PET has been done by different groups,[1–13] and some conclusions about the kinetic and mechanisms of the photooxidative process have been obtained. Other polyesters such as poly(ethylene naphthalate) (PEN), polycarbonate, and poly(buthylene terephthalate) have also been investigated.[14–21]

However, to our knowledge, no attention was given to the study of the photodegradation of multilayers films based on PET. Like ordinary films, this type of material may be exposed to the ultraviolet radiation during outdoor use and hence be subject to problems such as loss of transparency, yellowing, and reduction in mechanical properties. Depending on the type of layer combination, the exposed surface and the whole film may be more resistance or more vulnerable to photooxidation when compared to the PET films. In some cases, a coextruded film with the presence of photostabilizers only at the external layer may be produced, reducing the total amount of additive necessary.

In a previous work, an investigation was done on the surface photodegradation of PET films containing ultraviolet absorbers.[5] The use of a combination of techniques showed that the differences in the extent of chemical degradation at the bulk when compared to the surface may be significant, affecting the formation of degradation products and the mechanical properties of the film. The present work is a further development of the previous study and focuses on coextruded PET films. The main objective is to compare the characteristics of photodegradation of multilayer with ordinary (monolayer) PET films, both of them prepared without a photostabilizer. Films produced by biaxial extrusion in an industrial equipment were exposed in a weathering chamber for various periods and then analyzed by FTIR-ATR, UV/visible, fluorescence spectroscopy, size exclusion chromatography (SEC), and mechanical prop-

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erties. Scanning electron microscopy (SEM) analyses were done to show the consequences to the fracture behavior.

EXPERIMENTAL

PET was used in the form of bioriented films, produced by extrusion in the industrial production line of Terphane (Recife, Brazil). Two types of films were prepared, (i) PET homopolymer and (ii) PET copolymer. Hereinafter they are labeled as PET and co-PET, respectively. Both films have a thickness of 23 µm and, according to the manufacturer, they contain 0.06% SiO_2, used as an antiblocking agent. The PET copolymer was actually coextruded films of the type A/B/A/C, where A: poly(ethylene naphthalate)-co-poly(ethylene terephthalate) (PEN/PET) copolyester, with 89% of PET and 11% of PEN and a thickness of 1.35 µm; B: poly(ethylene terephthalate) (PET) homopolymer, 17.3 µm thickness; and C: poly(ethylene isophthlate)-co-poly(ethylene terephthalate) (PEI/PET) copolyester, with 18% of PEI and 82% of PET and a thickness of 3 µm.

The side of the film facing the ultraviolet source was the PEN/PET (layer A). The samples exposure was conducted in a Comexin weathering chamber using Q-Panel UVA fluorescent lamps. These lamps are 1.2 m long and produce ultraviolet light that matches reasonably well with sunlight, with a cut-off at 290 nm.[22] The weathering cycle was defined as follows: 4 h under UV light at 60°C and 4 h in the dark under condensed water at 50°C. The films were placed in the chamber with aluminum frames with a distance lamp to film set at 7 cm. At this distance, the irradiation intensity reaching the sample surface is about 3.2 W/m^2. Under these conditions the specimens are submitted to a combination of photo-, thermal, and hydrolytic degradation, offering very harsh conditions to the sample deterioration. In the results shown below the exposure time is reported as number of hours under ultraviolet radiation and not the total time.

After selected exposure times, the films were analyzed by spectroscopy, SEC, and mechanical testing. Infrared spectroscopy scans were obtained with a Nicolet Avatar 360 FTIR equipment in a range of 400–4000 cm^{-1}, with a resolution of 2 cm^{-1}. The spectra were collected after 21 scans and the carboxyl end-groups index (CEGI) was determined as the ratio of the peak at 3290 cm^{-1} and the reference peak (taken at 2970 cm^{-1}).[1] Experiments were done both in transmission and in reflection. The film was thin enough to allow suitable measurements through the thickness direction, giving the extent of degradation in the whole section. To quantify the degradation at surface layer, the attenuated total reflection (ATR) device was used, and the experiments were done with a KRS-5 crystal
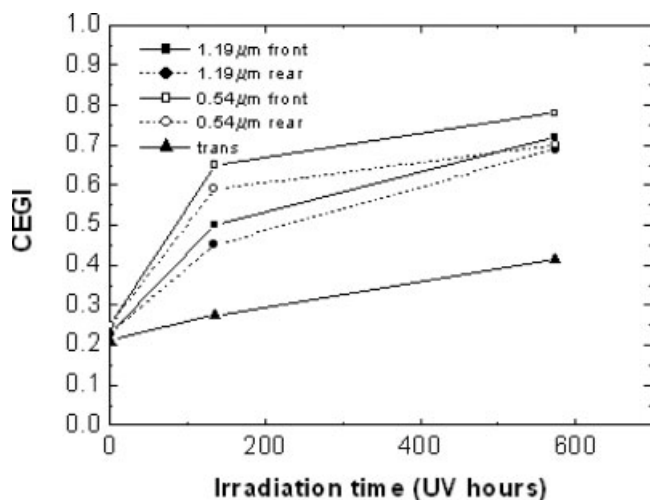
using two incident angles, 45° and 60°. The depth of measurement under these conditions was 0.54 and 1.19 µm, respectively.[23] This procedure was conducted at both the exposed and unexposed surfaces and showed to be a valuable tool to investigate the photodegradation of films.[5]

The absorption characteristic in the UV–visible range was evaluated with a Perkin–Elmer Lambda 6 spectrometer with a resolution of 2 nm and a scan speed of 300 nm/min. The optical density was taken as the absorption at 400 nm. Fluorescence emission spectra were obtained at room temperature in a Spex-Fluorolog-2 model FL-111 fluorometer. Excitation at 340 nm was chosen with the purpose of monitoring the fluorescence of mono-hydroxylated species (fluorescence emission at 460 nm), known to be generated during the photodegradative process of PET.[4,9,24] SEC analyses were conducted in Shimadzu equipment (model Class LC10) with a series of Progel columns at 22°C and with a UV–visible detector set at λ = 254 nm. The solvent flow rate was 1 mL/min and the equipment was calibrated with narrow molecular weight polystyrene.

For mechanical properties measurements, samples 2 cm wide and 10 cm long were tested in a Testometric Micro 350 machine operating with a crosshead speed of 10 mm/min at 23°C. The values of tensile strength and maximum elongation reported here represent averages of at least six samples. After tensile testing, the fracture surfaces of the specimens were inspected with a Phillips XL30 Scanning Electron Microscope operating at 15–20 kV. The samples were sputtered with a gold layer to avoid charging problems.
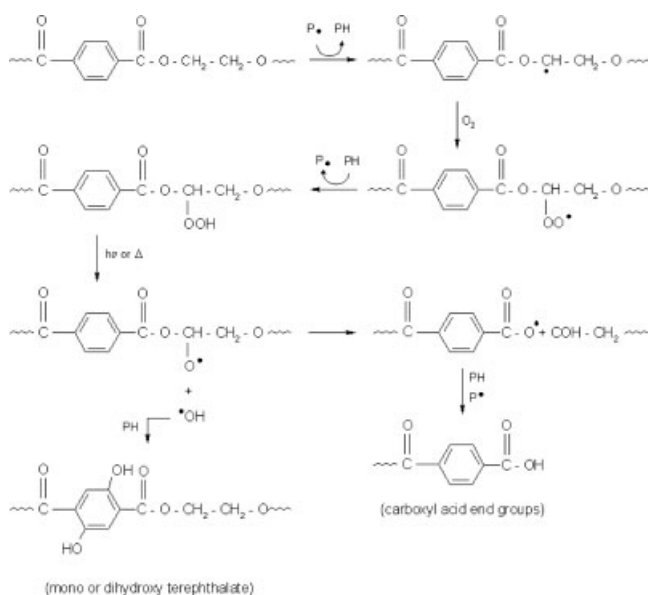
Scheme 1 Photooxidative reactions undergone by PET during UV exposure leading to carboxyl end-groups and aromatic hydroxylated species.[5]
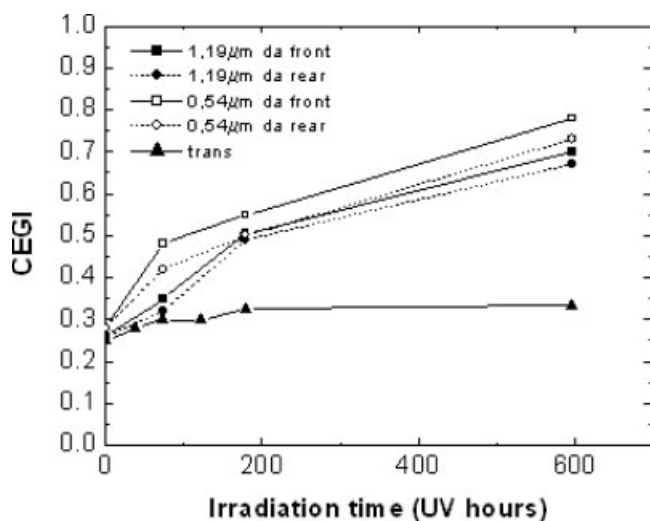
Figure 1 The effect of exposure time in the CEGI of the co-PET films.

Scheme 2 Photooxidative reactions undergone by PEN during UV exposure leading to naphthanoic acid end groups.[14]
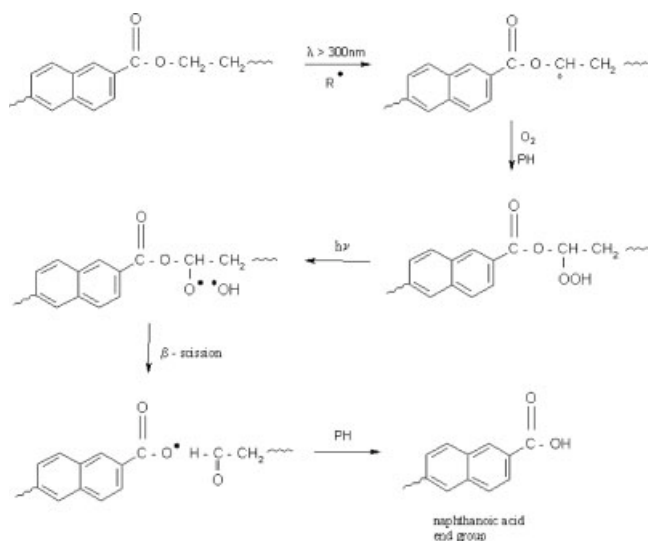
RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy

A number of authors reported that carboxyl end-groups are formed during PET photodegradation and the CEGI is a useful parameter to quantify this polymer degradation.[1,2,25,26] This index is based on the increase of absorption at 3290 cm^{-1}, attributed to OH stretching vibrations at carboxylic acid functional groups.[2] According to Scheme 1, carboxyl end-groups are formed during the photooxidation of PET as a consequence of the reaction with the esther groups and hence the CEGI can be used to follow the extent of chemical degradation. Figures 1 and 2 show the evolution of the CEGI with the irradiation time for co-PET and PET films, respectively, in experiments performed in transmission and in reflection. With both types of films, the

chemical degradation was higher at the exposed surface in comparison to the unexposed face and it was higher closer to the film surface (depth of 0.54 µm) when compared to deeper layers (1.19 µm) and to the bulk (transmission). Two factors may account for this type of behavior: (i) the dependence of chemical degradation with the oxygen concentration. The deeper the position within the film, lesser oxygen is present and hence the photooxidative degradation becomes slower. This aspect is more accentuated for co-PET films, because the PEN is about five times less permeable to oxygen than PET.[14] (ii) These polymers have a strong absorption of UV light at wavelengths shorter than 315 nm (Figs. 5 and 6). As a consequence, much less radiation reaches the film in deeper positions.
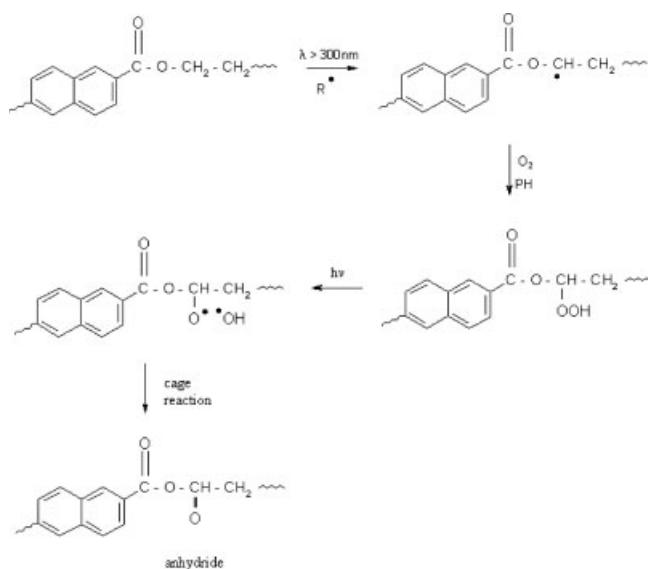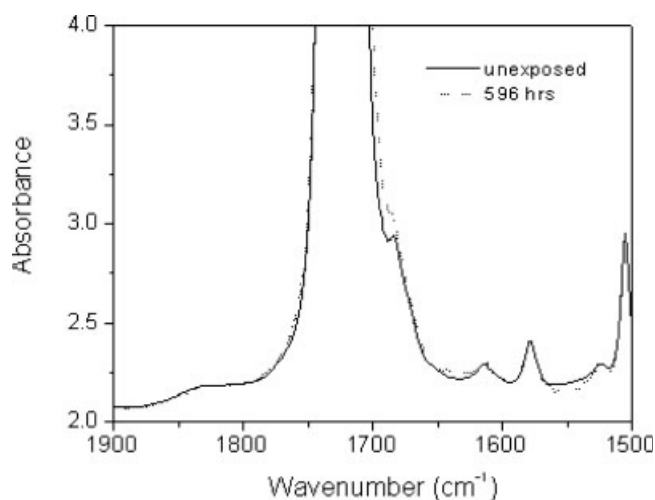

Scheme 3 Photooxidative reactions undergone by PEN during UV exposure leading to anhydride species.[14]
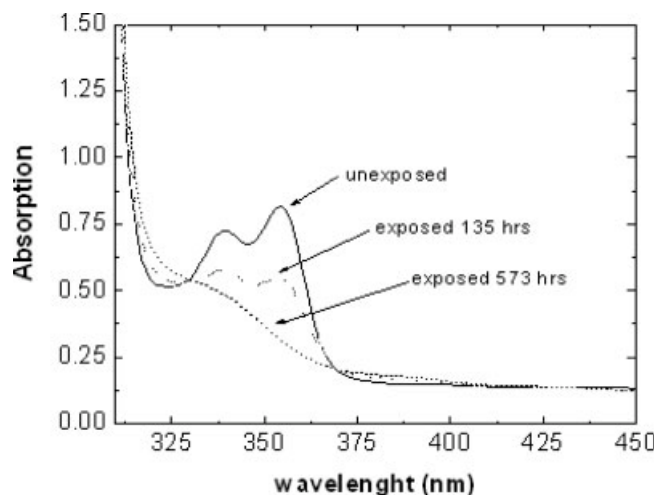

Figure 2 The effect of exposure time in the CEGI index of PET films.
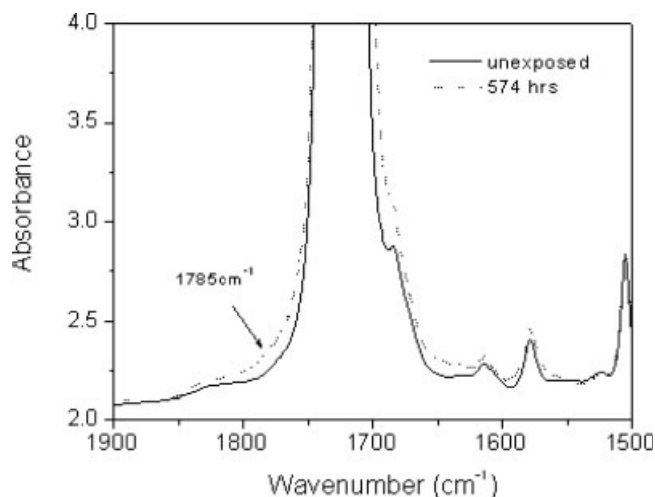
Figure 3 FTIR spectra of co-PET films in the region 1500–1900 cm^{-1}.

The use of the CEGI to quantify the chemical degradation of co-PET films was based on the fact that carboxyl end-groups can also be formed during the photooxidative process of PEN, as shown in Scheme 2. During the UV exposure of PEN anhydride groups are also formed (Scheme 3) with absorption in the infrared spectrum at 1785 cm^{-1}.[14] Figure 3 shows the increase of this absorption for co-PET films exposed to UV radiation, whereas for PET this is not observed (Fig. 4). The quantification of anhydride groups of PEN using FTIR, however, is rather difficult to carry out, since this absorption is overlapped by others from the undegraded molecules. Although this might be seen as an underestimation of PEN degradation in the co-PET films, the content of PEN is relatively small at the surface layer. Actually, the data obtained by FTIR were consistent to those obtained by SEC measurements (see later section).
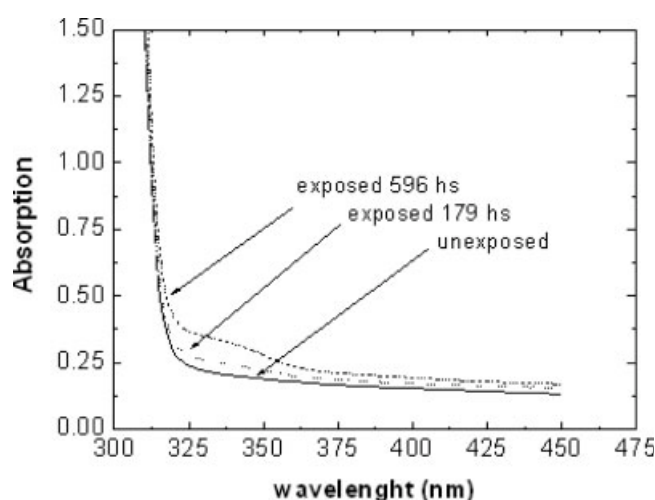

Figure 5 Absorption curves for nonexposed and exposure co-PET films obtained by UV–visible spectroscopy.

UV–visible spectroscopy

The spectra obtained from UV–visible spectroscopy of co-PET and PET films for different exposure times are given in Figures 5 and 6, respectively. The PET films shows a high absorption at wavelengths shorter than 325 nm (Fig. 5), whereas the unexposed co-PET film had two peaks, centered at $\sim$ 339 and $\sim$ 354 nm (Fig. 6), and this is the contribution of the PEN repeat unity.[14] After light exposure, the peak at 355 nm undergoes a marked decrease with photooxidation. The absorbance at 339 nm also decreases with UV exposure but to a lesser extent since this is partially compensated by the increase of absorbance below 330 nm. On the other hand, a slight increase in absorption intensity in the range of 370 and 400 nm is clearly noted. Figure 6 shows more clearly the increase in absorption of PET films for a wide range of wavelength ($\sim$ 310–360 nm).

Figure 4 FTIR spectra of PET films in the region 1500–1900 cm^{-1}.

Figure 6 Absorption curves for nonexposed and exposure PET films obtained by UV–visible spectroscopy.

This increase in absorption can be attributed to the presence of aromatic hydroxylated species (Scheme 1), produced during the photooxidation of PET.[4,9,27] Even though these types of structures in PET/PEN and PET/PEI were not identified in the literature of polymer degradation, it is likely that similar aromatic structures could also be generated during the photodegradative process of the co-PET films. We will refer to this appearance later on in this article when dealing with fluorescence data. The increase in optical density at longer wavelengths may cause a change in the product color, like yellowing.[28] Actually, this is one of the main concerns in certain applications where film clarity is an important requirement.

Fluorescence spectroscopy

The data obtained by fluorescence spectroscopy are related to the production of fluorescent species when excited at 340 nm, which are generated from reactions dependent on UV radiation and oxygen.[5] Similarly to FTIR-ATR, the analyses were carried out at both faces. Figures 7 and 8 display the emission spectra of co-PET and PET films, respectively, before and after exposure. Because of the naphthalene emission property, the spectrum of the unexposed co-PET film showed the presence of stronger emissions when compared to one obtained with the PET film. However, the emission intensities of unexposed co-PET films are different at the two faces. This is a consequence of the difference in composition: layer A (UV side) is a PET/PEN copolymer and layer C (the side not facing the UV source) is a PET/PEI copolymer. After light exposure, these emissions, for co-PET and PET films, had their intensities reduced, probably due to the oxidation of the monomeric unit. As a consequence, co-PET films showed a drastic reduction in fluorescent emission. The aromatic-hydroxylated species are formed by the scission
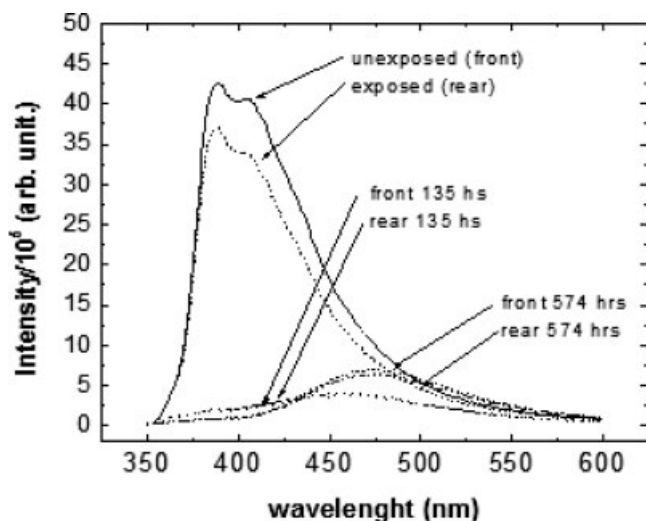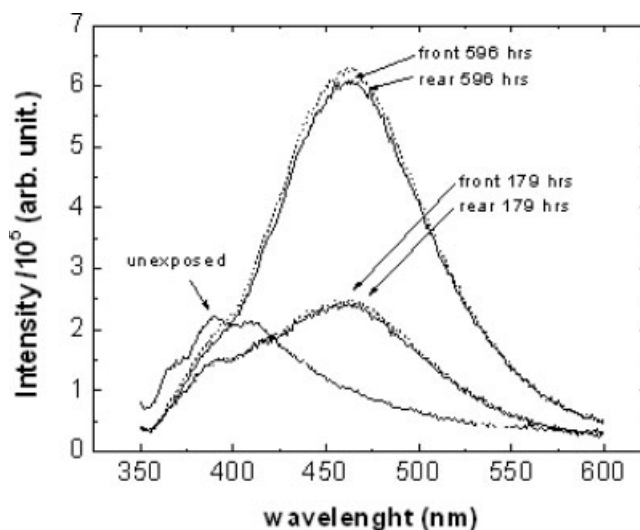

**Figure 8** Fluorescence emission spectra of PET films.

of hydroxyl radical on aromatic ring, as seen in Scheme 1. Since PET, PEN, and PEI have different aromatic structures, the aromatic-hydroxylated species could also differ. As a consequence, the emission of these species is centered at different wavelengths. Excitation at 340 nm resulted in a broad peak centered at 460 nm for PET (Fig. 8) and at 475 nm for co-PET films (Fig. 7), due to the presence of aromatic-hydroxylated species generated during of the photodegradation process.[5] These results are consistent with the assumption made from the UV/VIS data that the increase in absorption at 330–340 nm was due to aromatic hydroxylated species. The aromatic-hydroxylated species formed during degradation of PET, PET/PEN, and PET/PEI copolymers are probably different and thus the fluorescent spectrum of these films is different. This emission (centered at 475 nm) appeared at short exposure times and increased steadily with prolonged exposure. Moreover, this peak is also seen at the nonexposed face, which implies that these species are also formed with longer wavelengths, since the UV absorption of PET is very strong at wavelengths below 310 nm (Fig. 4).

Size exclusion chromatography

During photodegradation PET, PEN, and PEI molecules undergo both chain scission reactions and the formation

Figure 7 Fluorescence emission spectra of co-PET films.

TABLE I
SEC Data of co-PET and PET Films Before and After Laboratory Exposure

| PET			Co-PET		
Irradiation time (h)	M_n	M_w	Irradiation time (h)	M_n	M_w
0	19.000	43.000	0	22.000	47.000
179	13.000	34.000	135	14.000	39.000
596	12.500	28.000	574	9.500	26.000
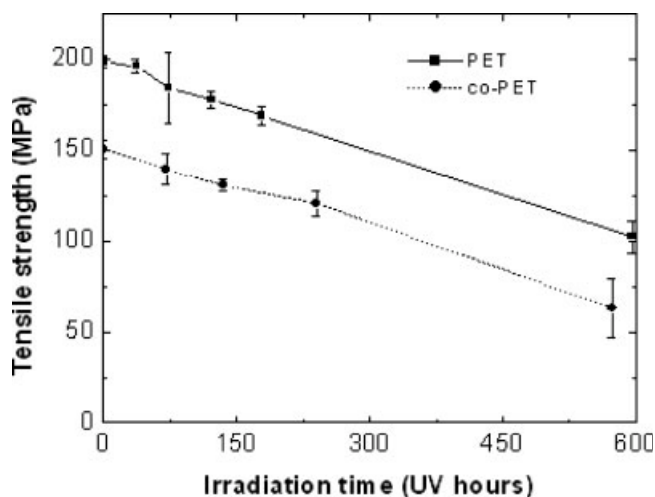
Figure 9 Tensile strength after different periods of exposure.

of carboxyl end-groups. The data obtained by SEC for the co-PET and PET films for selected exposure times are given in Table I. The weight average molecular weight (M_w) of coextruded films before exposure is $\sim 47,000$ but after 574 h exposure a reduction to $\sim 26,000$ is observed, representing a decrease of almost 45%. PET films had a decrease in M_w of about 35% for approximately the same exposure period. This is consistent with the higher extent of degradation measured by the CEGI in transmission (Fig. 1) for the co-PET films.

## Mechanical properties and fractography

The mechanical properties investigated were tensile strength and maximum elongation. The Young's modulus normally is much less affected by photodegrada-
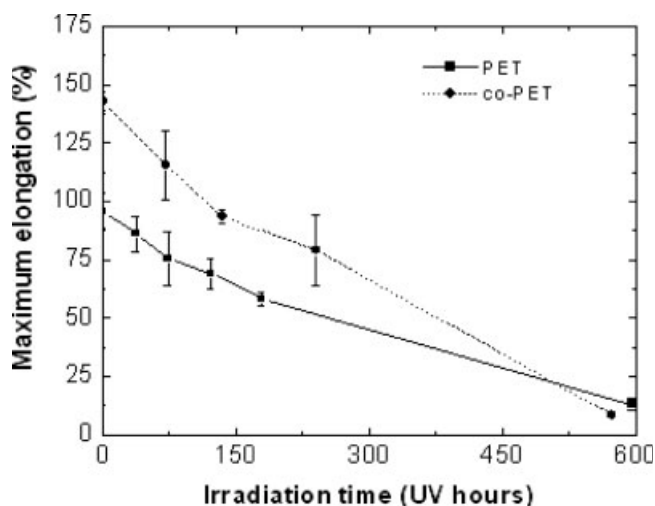
Figure 10 The effect of exposure time on maximum elongation.

tion[29] and hence was not reported here. The tensile properties of both films showed a significant and similar decrease with exposure time (Fig. 9), a typical behavior of a polymer that undergoes chain scission reactions during weathering. This is a direct consequence of molecular mass reduction, as seen in Table I. The reduction in maximum elongation was more significant in co-PET when compared to PET films (Fig. 10), as a more direct consequence of a higher drop in molecular weight of co-PET films. It is well known that for ductile polymers such as PET the maximum elongation is a property more sensitive to the degradation effects than the tensile strength. These results are in agreement to CEGI and molecular weight data.

Images obtained by SEM of the fracture surfaces (after tensile testing) showed that before exposure [Figs. 11(a) and 12(a)] the fracture was mainly ductile for both films, as seen by a large proportion of drawn material. After exposure [Figs. 11(b) and 12(b)] the fracture surface had much less topography variations, which is typical of a fragile failure. This is consistent
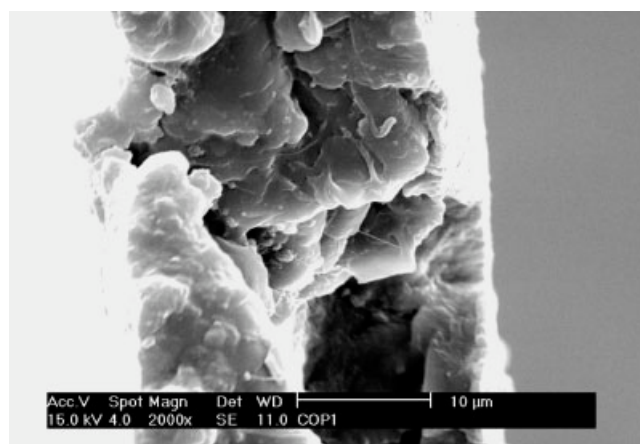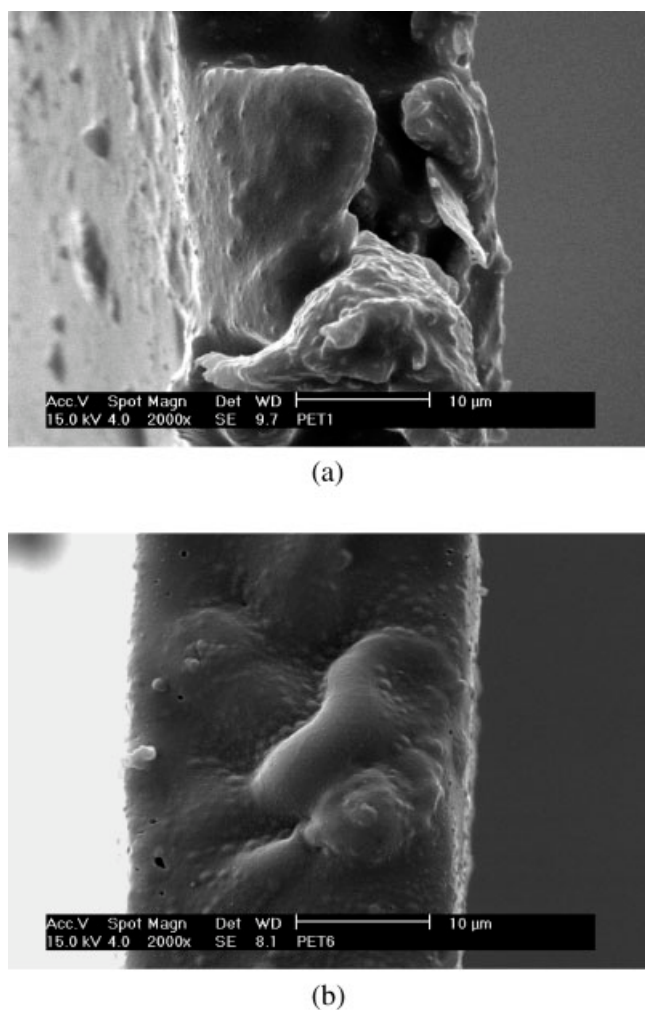

(a)

(b)

Figure 11 SEM of the fracture surfaces of co-PET films: (a) unexposed; (b) exposed for ~ 600 h.

Figure 12 Fracture surfaces of PET films: (a) unexposed; (b) exposed for ∼ 600 h.

with the tensile properties of these samples. Since most degradation occurred at the film surface (Figs. 1 and 2), these results also confirm that the degraded surface layer gives the highest contribution to the failure of polymer products under service.

CONCLUSIONS

Using ATR-FTIR technique it was possible to detect the extent of chemical degradation at a depth of as low as 0.54 µm from the exposed and nonexposed surfaces, revealing a large difference in degradation effects between the film surface and the bulk. With the combination of techniques such as FTIR, UV–visible, and fluorescence spectroscopy, it was shown that during photooxidation different chemical groups are formed in

PET, PET/PEN, and PET/PEI layers. Measurements of degradation by SEC and FTIR showed that the coextruded films were more sensitive to the ultraviolet causing a higher reduction in mechanical properties.

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