Surface characterization of photodegraded poly(ethylene terephthalate). The effect of ultraviolet absorbers

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Abstract

The surface characterization of photodegraded poly(ethylene terephthalate) was investigated. Films obtained by bi-axial extrusion were exposed in a laboratory weathering chamber for periods of up to 1100 h of irradiation. Samples prepared with and without an ultraviolet (UV) absorber were tested by infrared, UV–visible and fluorescence spectroscopy. The results indicated that the unstabilized films are very susceptible to the degradation effects causing a large deterioration, especially in surface layers. The presence of an ultraviolet light absorber effectively reduced the formation of carboxyl end-groups at the surface as well as in the bulk of the films. In the case of samples with UV absorber the fluorescence data showed a barrier imposed by this additive in the formation of the monohydroxy-terephthalate. Scanning electron microscopy of fracture surfaces showed that film ductility is highly reduced after exposure.

Keywords: PET; Weathering; Photodegradation

1. Introduction

The degradation and stabilization of some types of polymers, like polyethylene and polypropylene, have been extensively investigated throughout the years and the degradation mechanisms, as well as their controlling factors are reasonably well established [1–9]. On the other hand, only a few articles on the photodegradation and photosubilation of polyethylene terephthalate (PET) were published [10–16]. They emphasized the mechanisms of chemical degradation, exposure procedures and mechanical properties.

It is well known that during PET photolysis the main degradation event is chain scission, leading to a decrease in molar mass, evolution of volatile products (like CO and CO2) and generation of carboxyl end-groups. The carboxyl end-groups, usually taken as an indication of chemical degradation, are observed mainly at the sample surface and can be detected by Fourier transform infrared (FTIR) spectroscopy using the attenuated total reflectance accessory (FTIR-ATR). Blais et al. [11] used ATR to study the chemical degradation of PET films without UV stabilizers. They reported that carboxyl end-groups are formed at the surface layers after a short period of irradiation, whereas they take longer to be produced in the bulk. Other researchers [17] also detected a higher extent of degradation within the surface layers of PET films in comparison to the bulk. Not many discussions were done to describe the reasons for a depth-profile degradation in thin films containing ultraviolet stabilizers and this remains a matter that requires further investigation.

Attempts to develop PET films more resistant to UV radiation have been carried out, with different UV stabilizers used in practical applications. However, the details of the photodegradation and photostabilization processes are not fully understood. This is reflected in the small number of publications involving photostabilization of PET [18–21]. In addition, no work has been done to demonstrate the influence of stabilizers at the surface layers. This type of investigation is very important because the surface appearance and mechanical properties of films and thick products are rather dependent on the depth-profile of chemical degradation [22]. Cracks initiated at degraded
surface layer propagate into the sample interior causing failure, sometimes in a fragile fashion. This type of discussion is usually done with thick products [8,9,23,24], in which the differences between surface and bulk are much more evident.

This work investigate the characteristics of surface degradation of PET films prepared with and without a photostabilizer. Films produced by biaxial extrusion were exposed in a weathering chamber for various intervals and then analyzed by FTIR-ATR, fluorescence spectroscopy and size exclusion chromatography. Details of the depth-profile of chemical degradation were discussed based on results obtained with various methods. The consequences to the fracture behaviour are shown by scanning electron microscopy analyses.

2. Experimental

PET was used in the form of bi-oriented films, produced by extrusion in the industrial production line of Terphane (Recife, Brazil) using a grade with an intrinsic viscosity of 0.7 dl/g. According to the manufacturer, all films contained 0.06% SiO₂, used as an antiblocking agent. Two types of films were prepared, (i) unstabilized PET and (ii) with a UV absorber. Hereinafter they are labeled as uPET and PET-UV, respectively. The thickness of these films and the additive contents are given in Table 1. The UV absorber was a hydroxyphenyl triazine type produced by Ciba Specialty Chemicals with the trade name Tinuvin 1577 and it was used in a master batch with PET as a vehicle. The chemical structure of Tinuvin 1577 is shown in Fig. 1.

The 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 [25]. 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 dark cycle was used to simulate for a complete day (24 h), enabling oxygen penetration into the film bulk, without being immediately consumed. It does not contribute to the formation of new carboxyl end groups through hydrolysis since these reactions need high temperatures (>100 °C) [26–28]. Under these conditions the specimens were submitted to a very harsh conditions to the sample deterioration. The films were placed in the chamber with aluminum frames with the distance of the lamp to film set at 7 cm. At this distance the irradiation intensity reaching the sample surface was approximately 3.2 Wm⁻². The reported exposure time denotes the time under UV radiation and not the total time in the chamber.

After various exposure times the films were analyzed by infrared spectroscopy using a Nicolet Avatar 360 FTIR equipment in the range of 400–4000 cm⁻¹, with a resolution of 2 cm⁻¹. Surface spectra were measured using an ATR attachment. The depth of penetration of the infrared beam into the sample is dependent upon the choice of the reflecting crystal and the angle of incidence of the beam. The reflection crystal was KRS-5 at nominal angles of incidence 45 and 60°, leading to penetration depth of 1.19 and 0.54 μm, respectively. FTIR analyses were also conducted in transmission, giving an indication of the total change throughout the film cross section (bulk properties). The index of carboxyl end-groups was determined as ratio of the peak at 3290 cm⁻¹ (assigned to the O–H vibration of the –COOH group) and the reference peak 2970 cm⁻¹ [11]. For a given reflection element and substrate, the experimentally observed intensity of an ATR absorption band depends on the sample area, the contact degree of the sample with element, and the effective thickness. Consequently, it is difficult to make an absolute quantitative comparison of ATR intensities of a given IR absorption (for example the peak at 3290 cm⁻¹) for differently exposed films. This problem can be overcome by using a poly(ethylene terephthalate) band as an internal standard. Ideally this band should not be affected by change in long- and short-range order, or by extensive photo-oxidative reactions. The changes in the optical density of the carboxyl end groups (–COOH) absorption band at 3290 cm⁻¹ were periodically determined throughout the irradiation period by ATR and transmission spectroscopy [29]. The values are expressed as normalized by using the peak at 2970 cm⁻¹ (C–H vibration) in order to overcome variation in optical densities which result from differences in contact between the

<table>
<thead>
<tr>
<th>Film type</th>
<th>Thickness</th>
<th>Additives</th>
<th>Crystallinity (%)</th>
</tr>
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<tbody>
<tr>
<td>uPET</td>
<td>23</td>
<td>–</td>
<td>28.5 ± 2.0</td>
</tr>
<tr>
<td>PET-UV</td>
<td>23</td>
<td>0.1% of Tinuvin 1577</td>
<td>31.9 ± 0.8</td>
</tr>
</tbody>
</table>

a Based on extrusion feeding.

b Obtained by SC.
polymer film and the ATR crystal when ATR measurements were made.

UV-visible spectroscopy experiments were done with a Perkin–Elmer Lambda 6 spectrometer with a resolution of 2 nm and a scan speed of 300 nm/min. 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 [14,30,31].

Scanning electron microscopy of the fracture surface (after tensile testing) was done in a Phillips XL 30 microscope at 15–20 kV after being sputtered with a gold layer. The tensile properties of these samples were presented elsewhere [18].

3. Results and discussion

3.1. Fourier transform infrared spectroscopy—FTIR

A number of authors have reported that carboxyl end-groups are formed during PET photodegradation and that carboxyl index (CI) is a useful parameter to quantify the extent of PET degradation [11,12,15,32]. It is also well known that carboxyl end-groups act as catalyst to promote further degradation [33], thus enhancing the importance this parameter.

Fig. 2 shows CI values obtained for uPET submitted on the weathering chamber at different exposure times. The experiments were done in three different situations: (i) at the exposed surface (i.e. side of the film facing the ultraviolet source), using two incident angles and measuring at depths of 0.54 and 1.19 μm as described before; (ii) at the unexposed face (i.e. side of the film not facing the ultraviolet source), using the same incident angles; (iii) in transmission, giving the extent of chemical degradation at the whole film. The ATR experiments (shown as results at surface layers) were able to detect the differences of carboxyl index at depths of 0.54 and 1.19 μm, proving to be a valuable tool to investigate photodegradation of films. For both the exposed and the unexposed surfaces the extent of chemical degradation 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). This is the result of the dependence of chemical degradation to the oxygen concentration. The deeper is the position within the film, lesser oxygen is present and hence the photo-oxidative degradation becomes slower.

Fig. 2 also shows that the difference between CI values at the exposed and non-exposed faces of the film, although detectable, is not very significant. This is somewhat surprising, since PET possesses in its main chain a chromophore group that absorbs the UV radiation strongly at λ = 310 nm, resulting in a much lower intensity of radiation arriving at the other face (see in Fig. 3 a UV–visible spectroscopy for this effect). However, the mechanism of carboxyl end-groups generation, according to Day and Wiles [14], is independent of the wavelength of the incident radiation. Hence, if PET absorbs strongly the radiation up to 310 nm (as shown in Fig. 3), larger wavelengths do get across the film reaching the other face, making the generation of carboxyl end-groups at the non-exposed face feasible. Also, worth noting is that the values of CI at surface layers, even at the rear side, are higher than those obtaining in transmission, indicating that other chemical reactions leading to carboxyl groups take place at the film surfaces.

Fig. 4 shows CI data determined by FTIR (transmission and ATR) spectra of samples containing the UV absorber (PET-UV) submitted to ultraviolet radiation. The results indicate that the degradation is more intense near the film surface, paralleling the data found with the films not containing the UV absorber. Again, a large difference of CI between the exposed and non-exposed faces is not observed. In this case, however, the degradation was relatively the less in both faces.

Day and Wiles [14] argued that the generation of carboxyl end-groups does not involve reaction with oxygen. They proposed a Norrish type II pathway (Scheme 1).
through a six-member ring transition state, as the reaction responsible for its formation. This fact, however, does not explain the difference between the surface and the bulk of the film, since sufficient UV radiation would be available in those two sections.

From the data here obtained, a reaction mechanism can be proposed to account for our main findings (Scheme 2). In this Scheme the radicals $R_z$ can be generated by Norrish type I reactions [14] or generated in this reaction cycle.

In the case of PET-UV samples the difference between exposed and non-exposed faces may be simply due to the presence of the absorber, with an absorption band centered at 340 nm, acting as a filter (see Fig. 3). Therefore, this range of UV light, which is the most likely to promote photochemistry, does not reach the other face, diminishing the amount of carboxyl end-groups formed.

A practical importance of the depth-profile of degradation of PET films is reflected in the mechanical properties and fracture behaviour. Even though the whole film is not extensively degraded (as seen by the FTIR transmission analyses of Figs. 2 and 4), a large deterioration in tensile properties was observed during exposure [18]. In the unstabilized PET the tensile strength and maximum elongation showed a decrease of 50 and 80%, respectively, after 596 h exposure. This represents a serious handicap in the outdoors applications of PET films. It is very likely that the degraded surface layer causes crack nucleation that propagates into the relatively, intact underlying material leading to a catastrophic failure. Images obtained by scanning electron microscopy show that before exposure (Fig. 5(a)) the fracture was ductile, as seen by a large proportion of drawn material. After exposure (Fig. 5(b)) the fracture surface had much less topography variations, which is typical of a fragile failure. This confirms the effect of the degraded layer in causing the whole film to failure under service.

3.2. 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 (Scheme 2).

Similarly to FTIR-ATR, the analyses have been carried out at both faces, exposed and non-exposed. Fig. 6 displays the emission spectra of uPET samples before and after exposure in the weathering chamber. The non-exposed sample showed the presence of a ground state dimer, with emission at 390 and 410 nm, and an excimer, with emission at 370 nm [30,34]. After light exposure, these emissions had their intensities reduced, probably due to a loss of interaction between chromophores caused by chain scission. Excitation at 340 nm revealed the fluorescence of mono- or dihydroxyated species, as a peak centered at 460 nm, which are known to be generated during the photodegradative process of PET [14,30,31].

This emission appears at very short exposure times (Fig. 6(a)) and increases steadily with prolonged exposure (Fig. 6(b)). Moreover, this peak is also seen in the non-exposed face, which implies that these species are formed with
longer wavelengths, since the UV absorption of PET is very strong at wavelengths below 310 nm (Fig. 3).

Fig. 7 shows emission spectra of PET-UV samples at different exposure times. The emissions at 370 and 390 nm, from the excimer and the ground state dimer, respectively, were not seen here. This must be due to the presence of the UV absorber additive, which filters ultraviolet radiation with wavelength below 340 nm (see Fig. 3). However, the emission from the monohydroxy-terephthalate species is easily observed at the exposed face as a band at 460 nm, with intensities somewhat lower than those for the unstabilized films. For the non-exposed face the increase in the irradiation time did not result in an increase in fluorescent properties. This is an indication that the photochemical reactions responsible for the formation of this species are promoted by radiation above 310 nm, a threshold imposed by PET molecular structure. In view of the fact that the UV absorber is active in a range with an upper limit of 360 nm (Fig. 3), one may speculate that monohydroxy-terephthalate groups are produced from radiation ranging between these two limits (310 and 360 nm), once they were observed at the non-exposed face of PET-UV samples at a very lower intensity. It is possible that this lower intensity band, which exists in non-exposed and unstabilized sample, is not observed due to band overlapping from the ground state dimer and excimer bands (high intensity, see Fig. 6(a)).

4. Conclusion

Photodegradation of PET films takes place essentially at the sample surface due to its strong ultraviolet absorption characteristics and oxygen starvation at deeper layers. At the non-exposed face the degradation occurs in high levels as well, indicating that PET absorption at wavelengths higher than 310 nm can also induce degradation processes. The presence of an ultraviolet light absorber effectively reduced the formation of carboxyl end-groups at the surface as well as in the bulk of the films. In the case of the samples with UV absorber the fluorescence data showed a barrier imposed by this additive in the formation of the monohydroxy-terephthalate, especially at the non-exposed surface. Moreover, it was apparent that the wavelength
range between 310 and 360 nm is responsible for its production.

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