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Environmental degradation of isotactic polypropylene plates as studied by positron annihilation lifetime spectroscopy

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Abstract

Outdoor degradation of isotactic polypropylene (PPI) plates was studied by means of positron annihilation lifetime spectroscopy (PALS), absorption infrared spectroscopy, differential scanning calorimetry (DSC) and density measurements. Infrared spectra reveal the presence of oxygenated species into the exposed polymer induced by external agents. Results from thermal and density analysis suggest an increase of crystallinity of the sample with exposure time. Positron data strengthen such a conclusion, showing a reduction of the amorphous zones as monitored by the corresponding decrease of positronium (Ps) formation. Furthermore, an estimation of the average sizes of the free volume holes and of the defects in the crystalline regions was obtained.

Keywords: Differential scanning calorimetry; Infrared spectroscopy; Polymer degradation

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1. Introduction

In previous works [1,2] the outdoor degradation of isotactic polypropylene (PPI) films, 26, 50 μm thick, was studied. It was shown that a continuous reduction of mechanical strength takes place; furthermore, the formation of oxidized products containing carbonyl groups begins after about 700 h. This duration may be considered as induction time, which precedes the actual degradation of PPI films. After 2500 h of exposure time the film becomes extremely brittle with negligible strength. The outdoor useful life of PPI bar is considerably higher than the film life of the studied materials. This suggests that the degradation mechanism in PPI bar changes with the sample thickness probably due to the fact that the bulk of the material reacts gradually with external agents while the film is wholly involved in weathering processes, since the beginning of the exposure.

This paper shows the results obtained by studying the relationship between the modified structure of PPI plates 2 mm thick outdoor exposed at different exposure times and its free volume and thermal properties mainly by positron annihilation lifetime spectroscopy (PALS) and differential scanning calorimetry (DSC). PALS is a relatively simple technique which can probe the properties of the free volume holes in a non-destructive way [3]. It is based on the fact that some of the positrons injected into the material under investigation are trapped in regions with reduced electron density where they may form a bound positron–electron system, positronium (Ps). According to the different spin orientation of the two particles we distinguish the Ps ground state into *para*-Ps (*p*-Ps) and *ortho*-Ps (*o*-Ps). *p*-Ps is scarcely influenced by the environment, whilst *o*-Ps interacts with the surrounding electrons belonging to the cavity where *o*-Ps is trapped ('pickoff' process [4]). It results in a correlation between *o*-Ps lifetime and sizes of the cavity, which can be cast in a quantitative form by suitably modelling the trapping site [5–7].

2. Experimental

Experiments were carried out on plates prepared by compression molding at 190 °C for 2 min with a 20 bar pressure PPI (Moplen T 30 S supplied from Monteshell

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s.p.a.). The polymer had a melt index 3′3 g/10′, and average M_w 441000 D.

The melting and crystallization enthalpy as determined by DSC analysis were, respectively, 80.2 and 92.1 J/g. The PPI plates were not stabilized to light; infrared spectrum of pristine material did not exhibit meaningful peaks attributable to vinyl or oxygenated groups. The plate was mounted on wooden frames inclined at 45° to the horizon and was exposed facing south-west on a terrace (38°11′20″ north, 15°33′30″ east) about 20 m above the ground. The exposure tests started in March 2000 at Messina (Italy). The weathering process was followed by infrared spectroscopy (FTIR), thermal analysis (DSC), density measurement and PALS. All the measurements were carried out at the end of the exposure tests, in order to have the same aging in all the samples, including the pristine one.

Absorption infrared spectra were recorded on a Nicolet Nexus FTIR spectrometer. Thin films of exposed PPI suitable for the infrared analysis were obtained by compression of a small piece of PPI plate under two stainless steel plates at room temperature.

DSC curves were obtained on a DSC-2 Perkin–Elmer instrument using aluminum pans under nitrogen. Indium was used as the standard for calibrating the temperature axis and the enthalpy output.

Density measurements of the pristine and weathered samples were obtained using the Sartorius kit: YDK01-OD with a sensibility of 10^{-4} g.

Concerning the positron measurements, the positron source consisted of a droplet of ^{22}Na from a carrier-free neutral solution (activity: 0.3 MBq), dried onto two identical Kapton foils (thickness 1.08 mg cm^{-2}), which were afterwards glued together. Care was taken to confine the glue at the edge of the foils, thus preventing the glue from reaching the region interested to annihilation. The source was inserted in the specimen in the usual 'sandwich' configuration. Positron spectra were collected through a conventional fast–fast coincidence set-up, having a resolution of about 230 ps. Measurements were carried out at room temperature. Each spectrum contained about 3×10^6 counts; three spectra for each sample were collected. Deconvolutions were carried out through the computer code *LT* [8] with a suitable correction for the positrons annihilated in the Kapton.

3. Results

The outdoor degradation process of PPI mainly induces the formation of oxygenated species in the sample [1,2]. This process seems to proceed preferentially in the amorphous phase of the PPI with a consequent increase of the crystallinity percentage [9]. These new oxygenated species can be revealed in infrared spectra by detection of their characteristic C=O stretching vibration bands in the spectral region near 1700 cm^{-1}.

The infrared spectra of PPI plates exposed for 0, 2520, 4896 and 11640 h are shown in Fig. 1. In all spectra we can observe the characteristic bands pattern of crystalline PPI [10,11].

The spectra of pristine (Fig. 1(a)) and 2520 h (Fig. 1(b)) PPI plates do not exhibit signals attributable to carbonyl stretching vibrations in the region near 1700 cm^{-1}. The spectrum of 4896 h sample (Fig. 1(c)) clearly shows a broad absorption band centered at 1740 cm^{-1} certainly attributable to the presence of new carbonyl groups inside the polymer. In the spectrum of 11640 h (Fig. 1(d)) the carbonyl vibrations bands reach an appreciable absorption intensity.

Infrared spectra of these thick samples suggest the existence of an induction time (> 2520 h) that precedes the degradation; at higher time the infrared absorption bands of oxygenated species become detectable and increase their intensity with the exposure time.

Fig. 2 shows DSC curves for a few samples at different exposure times. The peak temperature appears decreasing with exposure time. Indeed, photooxidation which takes place in the outdoor exposed samples induces formation of oxygenated products as it results from the infrared spectra. The obtained mixture is characterized by a different peak temperature in comparison to the value measured in the pristine sample. The higher the content of oxygenated products, the lower the peak. Fig. 3 shows the behavior of melting enthalpy versus exposure time: the collected data indicate that the enthalpy increases with the exposure time. This result suggests a crystallinity increase of the weathered samples in comparison to the pristine one; consequently, an increase of the density ρ is expected. The values of the samples density collected in Table 1 agree with this hypothesis. The increase both of density and melting enthalpy may be attributed to increasing of crystallinity and probably in part to the formation of oxygenated derivatives of the exposed polypropylene.

The increase of crystallinity and density should be correlated to a decrease of the free volume which is available in the amorphous regions. Experimental estimation of the free volume has been obtained through the positron spectroscopy. Positron spectra were deconvoluted

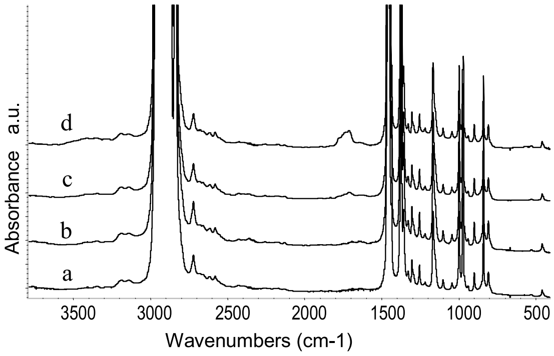

Fig. 1. Infrared spectra of PPI after: (a) 0 h; (b) 2520 h; (c) 4896 h; (d) 11640 h of exposure time.

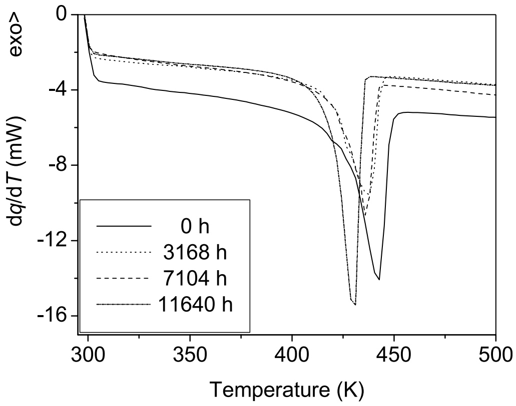

Fig. 2. DSC curves showing the peak temperature for differently exposed PPI samples.

Table 1
Density ρ in pristine and weathered PPI. Crystallinity χ (calculated from the melting enthalpy) is also shown

Exposure time (h)	ρ (g cm^{-3})	χ (%)
0	0.906 ± 0.002	39 ± 2
3168	0.907 ± 0.002	42 ± 2
7104	0.911 ± 0.002	49 ± 2
11640	0.916 ± 0.002	55 ± 2

into four components; the results are displayed in Table 2. The shortest component can be attributed to decays from *p*-Ps. The second component can be ascribed to decays of the positrons not forming bound states, but annihilated in bulky PPI, in the free volume as well as in defects of the crystalline regions. The longest components are attributed to decays from *o*-Ps trapped in the crystalline defects (the third one) and in the free volume holes (the last one). Although it is generally assumed that Ps is formed in the amorphous regions of the polymers, a contribution to the *o*-Ps component also from defects present in the crystalline zones should be considered [12]. Dimensions of free volume holes are distributed around average values, and a corresponding distribution of *o*-Ps lifetimes is expected. However, the statistics of our spectra did not allow us to obtain reliable distribution widths. Therefore, we will limit ourselves to discuss the results in terms of average lifetimes. According to Table 2 the *o*-Ps lifetimes τ_3 and τ_4 do not depend on the exposure time, which means that the crystalline defects and the free volume holes do not display significant size variations with the weathering of PPI, at least in the range of exposure time investigated by us. We can estimate the size of the cavities hosting *o*-Ps by modeling the holes as spheres and using the Tao–Eldrup equation [5,6]. From the average values of τ_3 and τ_4 we get $d_3 = 3.4 \pm 0.2$ Å and $d_4 = 6.6 \pm 0.2$ Å for the average diameters of crystalline defects and of free volume nano-holes, respectively. These values should be considered only rough approximations of the real sizes, since cavities are irregularly shaped.

Concerning *o*-Ps intensities, I_3 is independent, within the errors, of the weathering process, while I_4 decreases with the exposure time. This is coherent with the previous discussion: indeed, the increase of crystallinity is accompanied by a corresponding decrease of the amorphous volume and Ps formation in these regions is reduced.

The behavior of I_4 is correlated to the crystallinity χ of our samples, which can be calculated by comparing the melting enthalpy values (Fig. 3) to that of an ideal PPI 100% crystalline (206.9 J/g [13]). The results are shown in the last column of Table 1. If we plot I_4 versus χ we get a satisfactory linear fit (Fig. 4), with a correlation coefficient > 0.99. The interpolating straight line, $i = 33.5 - 0.34\chi$, predicts that intensity goes to zero for a 100% crystalline polymer, which strengthens our interpretation on I_4.

Therefore, weathering of PPI seems to influence the available free volume in the sense that the more ordered disposal of the molecules decreases the volume of the amorphous regions without involving a shrinking of the free volume holes. On the other hand, pressure-densified amorphous polymer glasses exhibit decreased free volume hole sizes [14]. This suggests that the amorphous regions of

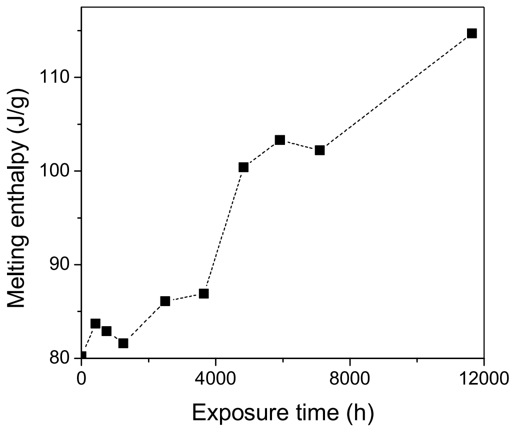

Fig. 3. Melting enthalpy of PPI samples versus the exposure time.

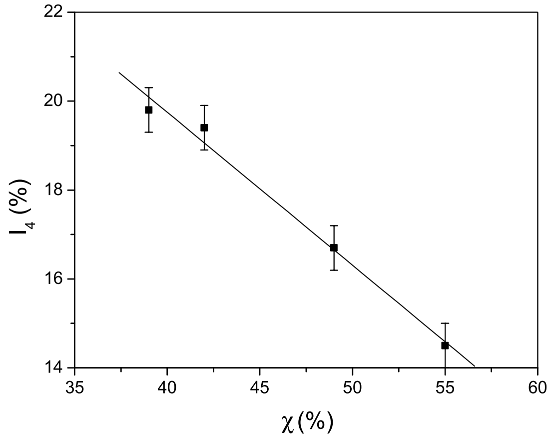

Fig. 4. *o*-Ps intensity I_4 in PPI samples as a function of crystallinity χ.

Table 2
Positron annihilation lifetime spectra in PPI versus the exposure time

Exposure time (h)	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)
0	0.12 ± 0.01	10 ± 1	0.34 ± 0.01	59 ± 2	1.1 ± 0.1	10.6 ± 0.7	2.47 ± 0.03	19.8 ± 0.5
3168	0.13 ± 0.01	10 ± 1	0.35 ± 0.01	59 ± 2	1.0 ± 0.1	11.2 ± 0.7	2.49 ± 0.03	19.4 ± 0.5
7104	0.13 ± 0.01	9.5 ± 0.9	0.36 ± 0.01	63 ± 2	1.0 ± 0.1	10.6 ± 0.7	2.44 ± 0.03	16.7 ± 0.5
11640	0.11 ± 0.01	8.1 ± 0.8	0.36 ± 0.01	67 ± 2	1.0 ± 0.1	10.4 ± 0.7	2.45 ± 0.03	14.5 ± 0.5

our samples do not undergo densification during the outdoor degradation.

It is known that PALS results in polymers can be influenced by radiation damage induced by the positron source. Such effects can be considerable at low temperatures [15,16]. In our measurements we did not observe systematic variations of the longest component's intensities in the various subsequent runs concerning a given weathering process. Therefore, we do not consider radiation effects from the positron source of primary importance in order to interpret our measurements, according to the data shown in Ref. [17], obtained through a positron source whose activity was comparable to ours.

4. Conclusions

In this study we investigated the effect of outdoor degradation of PPI through infrared, calorimetric, density and PALS measurements. The results from the various techniques are in agreement each other. The outdoor degradation process takes place after about 2520 h of exposure with the formation of oxygenated species. The increase of density with weathering is well correlated to the increase of melting enthalpy, which can be interpreted as an increased crystallinity in the exposed samples. PALS data allow for a microscopic interpretation of such conclusion, since the decrease of the amorphous regions manifests itself through a decreased Ps formation, but the characteristic sizes of free volume holes do not display significant variations during weathering.

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