Outdoor Ageing
of an Ethylene–Propylene Copolymer:
A Positron Annihilation Study

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An investigation on the environmental degradation of an ethylene–propylene copolymer was carried out through positron annihilation lifetime spectroscopy, density and differential scanning calorimetry measurements. Polymer sheets were exposed to sunlight up to 11000 hours. Density and melting enthalpy increase with ageing, while *ortho*-positronium intensity decreases; *ortho*-positronium lifetime does not show significant variations up to 4400 hours. At higher exposures it starts to decrease. Outdoor ageing produces an increased crystallinity of the copolymer; also a degradation occurs with formation of carbonyl groups. The corresponding Ps inhibition is the main reason for the decrease in *ortho*-positronium intensity, the other one being the reduced amount of the amorphous phase available. The lifetime decrease observed at the highest exposures can be interpreted in terms of a shrinking of the nanoholes trapping positronium.

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1. Introduction

Copolymers and blends may offer improved physical and mechanical properties with respect to the starting polymers [1]. In the case of polyethylene (PE)

and polypropylene (PP) blends, a heterogeneous material with interesting performances [2] is produced, consisting of a mixture of ethylene–propylene copolymers with different ethylene/propylene ratios used as compatibilizers in the blend, since it is known that PE and PP are practically immiscible. In the present paper we studied the outdoor ageing of a commercial PE–PP copolymer; to this purpose we used different techniques: thermal analysis, density measurements and positron annihilation lifetime spectroscopy (PALS), in order to get information on the modifications induced by weathering.

2. Experimental

Experiments were performed on Adflex C202G as received from Montell (Ferrara, Italy). Sheets of 2 mm thickness were obtained by compression moulding polymer granules for two minutes at 190°C with a 20 bar pressure. Unstressed sheets were mounted on plexiglass frames tilted at 45° with respect to the horizontal plane and were exposed facing south-west on a terrace at about 20 m above ground at Messina, Italy (38° 11′ 20″ north; 15° 33′ 30″ east). Samples underwent exposure times up to 11000 hours. Analyses were carried out on samples withdrawn after different times of exposure. All the samples were analysed after the end of the whole exposition experiment in order to compare samples with the same "intrinsic" temporal ageing.

Differential scanning calorimetry (DSC) thermal measurements were performed with a Mettler-Toledo 822 instrument, indium and zinc calibrated. Samples of about 15 mg were heated from 193 to 493 K at a scanning rate of 10 K/min, in nitrogen atmosphere.

Density measurements of the pristine and weathered samples were obtained through a Sartorius balance (model ME215P: readability 10^{-5} g, repeatability 1.5×10^{-5} g), equipped with a kit for the measurement of the density.

Concerning the positron measurements, the positron source (activity: 0.3 MBq) was inserted between two specimens of the same sample in the usual "sandwich" configuration. The thickness of each specimen was sufficient to stop all the injected positrons. Positron spectra were collected through a conventional fast-fast coincidence setup equipped with plastic (NE111) scintillators, having a resolution of about 230 ps. Each spectrum contained about 3×10^6 counts; three spectra for each weathered sample were collected. For 3 samples (pristine, 5928 and 11000 hours weathered) a lifetime study versus temperature was also undertaken, in order to investigate the thermal behaviour of nanoholes for different exposure times. In this case samples were inserted inside a liquid nitrogen cryostat (DN 1714 Oxford Instruments) which ensured stability of the temperature within 1 K. Measurements were carried out with a positron spectrometer equipped with big BaF_2 scintillators to increase efficiency; resolution was about 320 ps. Each spectrum contained about 2×10^6 counts. All the deconvolutions were carried out through the LT program [3].

3. Results and discussion

Thermal analysis was carried out on 3 samples: the pristine one and two samples exposed to 5928 and 11000 hours, respectively. The results are summarized in Table I. In all cases a glass transition is visible at around 235 K; melting temperature decreases when the exposure time increases. Melting enthalpy $\Delta H_{\rm m}$ increases with exposure time, which suggests an increased crystallinity in the exposed samples. Since it is known from X-ray diffraction (XRD) that the crystalline fraction $\chi = 0.47$ for the pristine sample [2], the values of χ for the other samples are calculated from $\Delta H_{\rm m}$ and are shown in Table I.

TABLE I

Glass transition temperature $T_{\rm g}$, melting temperature $T_{\rm m}$, melting enthalpy $\Delta H_{\rm m}$ and percentage crystallinity χ for three different samples.

Exposure time [h]	$T_{\rm g}$ [K]	$T_{\rm m}$ [K]	$\Delta H_{\rm m}$ [J/g]	χ [%]
0	237	414.4	29.7	47^a
5928	233	409.4	33.6	53
11000	236	408.1	35.4	56

^{a}from Ref. [2]

Density results are shown in Table II. An increase with the exposure time is noted, which is expressed through a linear relationship (correlation coefficient: 0.996). This result can be interpreted in terms of an increased percentage of crystallinity, in agreement with the conclusions from thermal analysis. The corresponding decrease in the amorphous regions involves possible changes of the free volume, which can be investigated by means of the positron spectroscopy.

TABLE II

Density of pristine and weathered ADFLEX versus the exposure time.

Exposure time [h]	0	1008	3912	4416	5928	11000
Density [g cm^{-3}]	0.873 (3)	0.877 (3)	0.882 (3)	0.883 (3)	0.887 (3)	0.896 (3)

Positron spectra were deconvoluted into three components by requiring a lifetime distribution for the longest one; the results are displayed in Table III and in Fig. 1. Only the longest component, due to annihilations from *ortho*-positronium (*o*-Ps) trapped in the free volume holes, will be considered. *o*-Ps intensity I_3 decreases with the exposure time, while *o*-Ps lifetime τ_3 does not change significantly up to 4400 hours; only at the highest exposure times τ_3 decreases. Furthermore, the dependence of τ_3 on temperature (Fig. 1) is similar for all the samples. Width

TABLE III

o-Ps parameters versus the exposure times.

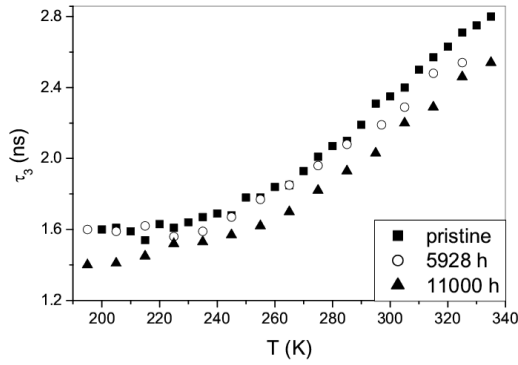| Exposure time [h]	τ_3 [ns]	I_3 [%]	σ [ns]
0	2.31	32.6	0.75
1008	2.31	28.6	0.76
3912	2.29	25.8	0.70
4416	2.30	24.3	0.64
5928	2.17	23.4	0.68
11000	2.08	20.7	0.69

Fig. 1.   *o*-Ps lifetimes versus the temperature in samples with different exposure times.

of the lifetime distribution σ_3 is largely independent of the exposure time (Table III). σ_3 increases with temperature in a similar way in the three investigated samples.

These results can be framed into a simple model by supposing that τ_3 decrease at the highest exposures is due to shrinking of the free volume holes. The specific volume v is written as a weighted mean

$$v = v_a(1 - \chi) + v_c\chi, \tag{1}$$

where v_a (v_c) is the specific volume in the amorphous (crystalline) phase. v_a is decomposed into an occupied volume v_0 (assumed for simplicity to be equal to v_c) and into a free volume, given by the product of the (constant) hole number density N times the average hole volume v_h (obtained from τ_3 through the Tao–Eldrup equation [4, 5]):

$$v_a = Nv_h + v_0. \tag{2}$$

It follows:

$$v = \frac{1}{\rho} = N(1 - \chi)v_h + v_0. \tag{3}$$

Equation (3) for the pristine sample as well as for the sample exposed to 11000 hours reads

$$\frac{1}{\rho_{\text{prist}}} = N(1 - \chi_{\text{prist}})v_{\text{h,prist}} + v_0,$$

$$\frac{1}{\rho_{11000}} = N(1 - \chi_{11000})v_{\text{h,11000}} + v_0$$

and we can obtain the two parameters v_0 and N or, equivalently, $Nv_{\text{h,prist}}$:

$$Nv_{\text{h,prist}} = \frac{1/\rho_{\text{prist}} - 1/\rho_{11000}}{(1 - \chi_{\text{prist}}) - (1 - \chi_{11000})\frac{v_{\text{h,11000}}}{v_{\text{h,prist}}}}, \tag{4a}$$

$$v_0 = 1/\rho_{\text{prist}} - Nv_{\text{h,prist}}(1 - \chi_{\text{prist}}). \tag{4b}$$

By using again Eq. (3) for the sample exposed to 5928 hours we evaluate the density

$$\rho_{5928} = \left[Nv_{\text{h,prist}}(1 - \chi_{5928})\frac{v_{\text{h,5928}}}{v_{\text{h,prist}}} + v_0 \right]^{-1}, \tag{5}$$

which can be compared to the experimental result (Table II). Equations (4) and (5) contain the ratios $v_{\text{h,11000}}/v_{\text{h,prist}}$ and $v_{\text{h,5928}}/v_{\text{h,prist}}$. Their values were evaluated by averaging at all temperatures, in order to minimize the experimental uncertainties. It results $v_{\text{h,11000}}/v_{\text{h,prist}} = 0.83 \pm 0.02$, $v_{\text{h,5928}}/v_{\text{h,prist}} = 0.95 \pm 0.02$ and we get $\rho_{5928} = 0.885$ in agreement, within the errors, with the value found by density measurements. The proposed model can partly explain the decrease in I_3 with the exposure time, since the amorphous fraction available for Ps formation is reduced. However, the non-linear decrease in I_3 at low exposure times (Table III) requires also another mechanism which is Ps inhibition from carbonylic groups (absent in the pristine sample) whose presence is revealed by IR spectroscopy [6]: they are mainly localized in the amorphous zones. This agrees with the decrease in the melting temperature, representative of an increased heterogeneity of the exposed samples.

4. Conclusion

Outdoor degradation of a PE/PP copolymer was studied. A simple model assuming a constant nanoholes density can account for the main experimental results. These show a decrease in *o*-Ps intensity at low exposure times while *o*-Ps lifetime decreases only at the highest exposures where an increased crystallinity is evidenced by thermal and density measurements. Carbonyl groups present in the exposed samples partly account for the reduction of I_3 with the exposure time, while they should not influence *o*-Ps lifetime whose reduction at high exposure times is explained in terms of free volume holes reduction.

Acknowledgments

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