Characterization of radical defects from abrasion and u.v.-photolysis in poly(ethylene terephthalate) fibres

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Radical products in poly(ethylene terephthalate) fibres are characterized using electron paramagnetic resonance (e.p.r.) spectroscopy. Different radical species are detected depending upon whether mechanical abrasion or ultraviolet (u.v.) light is used to degrade the fibre samples. From u.v.-photolysis at 77 K (liquid nitrogen) e.p.r. signals consistent with carbon-centred radicals are observed having a line shape centred at $g = 2.0034$. (The g factor is a scalar which depends upon the environment of the unpaired spin. For a free electron $g = 2.0023$.) From mechanical abrasion at 77 K a completely different e.p.r. pattern of two peaks is recorded consistent with an oxygen-centred species. The spectrum has one component centred at $g = 2.0318$ and another component centred at $g = 2.0094$. At room temperature only one signal is detected after decay of overlapping components for both abrasion and u.v. signals.

(Keywords: poly(ethylene terephthalate); electron paramagnetic resonance; free radicals; abrasion)

INTRODUCTION

Poly(ethylene terephthalate) (PET) is used as a substrate for microelectronic circuitry and other applications. A PET film can be irradiated with ultraviolet (u.v.) light to produce a surface on which electroless deposition occurs with metals such as copper or nickel[1]. In this way intricate microcircuit patterns can be achieved. The mechanism of sensitization of the film's surface by u.v. light is thought to involve the production of radical sites followed by formation of carboxyl and hydroxyl groups that are acidic and hydrophilic. Carboxyl groups can form from proton addition to cleaved ester linkages. Hydroxyl formation might accompany the cleavage of an ethylene linkage. Specific details about radical formation are important in understanding the catalytic effect of u.v. light on the PET surface.

PET is also the most commercially important polyester fibre, finding wide application as an industrial yarn, as well as in textiles. Structural changes in PET fibres may be induced mechanically. When fibres are stretched, primary end-of-chain radicals can form[2]. These radicals can decay to secondary centre-of-chain radicals by mechanisms such as proton transfer. The locus of chain scission in mechanically deformed PET is unknown. Thermal decomposition mechanisms have been widely studied, however, with cleavage of the C–O ester bond the most probable origin for thermal degradation. In this study, we show that there is a clear distinction between mechanically induced and u.v. radiation induced radical products in PET fibres at 77 K.

EXPERIMENTAL

PET fibres (1000 denier, 300 filaments per fibre) were obtained from the Allied Signal Co. They were partially crystalline with a density of $1.386\,\mathrm{g\,cm^{-3}}$. Biaxial oriented films of PET (Mylar from DuPont) were also used and gave comparable e.p.r. results to the fibres. A test sample consisted of several fibres having a weight of *c.* 100 mg. The fibres were placed in a ceramic container in liquid nitrogen and the abrasion process carried out using a power drill with a metal or sandstone bit. When the drill contacted the fibres, the sample was immediately transformed from highly oriented, uniform filaments into an entangled mass of filaments. As milling continued, the fibres tended to wrap around the drill bit. Further stress was placed on the sample by touching the end of the bit, containing the wrapped fibres in liquid nitrogen, against the ceramic container. Care was taken to avoid milling off particles of ceramic; to ensure that no artifact signals were being introduced, the absence of e.p.r. signals at both 77 K and room temperature from the ceramic itself was verified. The abrasion of each fibre sample was carried out for about 1 min under liquid nitrogen. Although O_2 was not purged from the liquid nitrogen, the sample was not exposed to air (all handling of the sample in liquid nitrogen) until after the e.p.r. spectrum was recorded. The abrasion process was reproducible; an e.p.r. signal was always detected from an abraded fibre.

Fibre samples having different degrees of orientation, produced by variation of their drawing conditions, were tested. The radical species observed in e.p.r. were identical, although with the present methodology no assessment of the efficiency of radical formation during abrasion of the various fibres was attempted.

To perform the e.p.r. measurements after abrasion, the samples were transferred in liquid nitrogen to a quartz dewar in the TM_{110} cavity in a Bruker ER200 spectrometer operating at x-band (9–10 GHz). The radical concentration of a typical sample was estimated as 10^{13} spins $\mathrm{mg^{-1}}$ based on comparison with a weak pitch standard (0.0033% in KCl). Thus, signal averaging by adding 1000 scans was required for each spectrum. This

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improved the signal-to-noise ratio by about a factor of 31 *versus* a single scan. Instrument settings were as follows: a central magnetic field of 0.333 T at frequency 9.33 GHz, sweep width of 20.0 mT, modulation of 0.1 mT, power 2 mW. To measure the g values a manganese marker (Mn^{2+}) was used. The sealed marker was contained in the sample tube with the fibre ensuring that the H_1 field was constant for the sample and the standard.

U.v. photolysis was carried out by keeping the samples under liquid nitrogen and photolysing for about 30 min. A 1000 W high pressure Hg–Xe lamp (unfiltered) was used. Our findings support low parent-to-radical conversion using u.v. because several minutes of photolysis of the fibres were required for adequate signal-to-noise ratios. This may be due to rapid decay of primary radicals to non-paramagnetic products yielding a lower concentration of secondary radicals. The conversion by 100 eV radiation of parent molecules into free radical products in PET is also reported to be low[10].

RESULTS

Abrasion experiments

The e.p.r. spectrum of free radicals formed by abrasion of PET fibres is shown in *Figure 1*. There are two overlapped spectra from different free radicals contributing to the spectral pattern. These are labelled A and B.

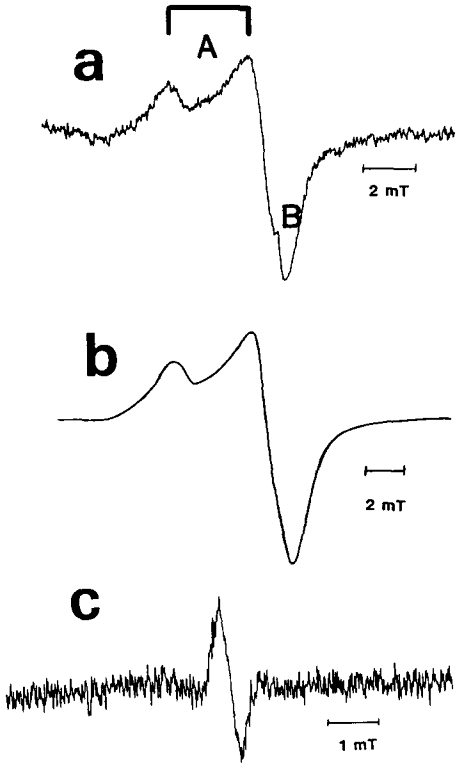


Figure 1 (a) The e.p.r. signal from PET fibres after abrasion in liquid nitrogen is shown. This signal was recorded at 77 K and is assigned to two spectral components. Component A is consistent with the benzoyloxy radical [C_6H_4–(CO)–O·. Component B is the sharp line near the free electron value. (b) The spectrum of a polycrystalline signal such as expected for the fibres was calculated using the g values for the benzoyloxy radical given in *Table 1*. The calculated spectrum is in good agreement with (a). (c) The signal of a radical species which remained after the sample of abraded PET fibres was warmed to room temperature

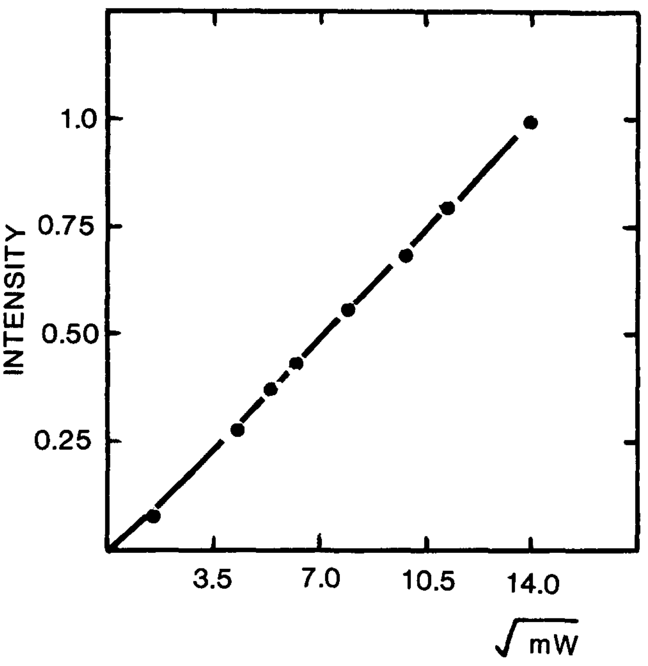


Figure 2 The saturation curve of the two prominent peaks of radical A shown in *Figure 1a*, recorded at 77 K. Both peaks have identical saturation characteristics indicating that the peaks are from the same radical species. The maximum power of 200 mW was not sufficient to saturate the e.p.r. signal

Radical B is centred at $g = 2.0024$, very near the free electron value. Radical A has two dominant peaks. One peak is centred at $g = 2.0318$ and a second peak is centred at $g = 2.0094$. The saturation profile of these two peaks is given in *Figure 2*. Both peaks have identical saturation behaviour suggesting that the peaks belong to the same radical species. The range of g-values encompassed by the pattern is typical of many oxygen centred radicals. For example, *Table 1* shows e.p.r. constants for oxygen centred radicals. The range of g values is from *c.* 2.00 to 2.03. Of these radicals the benzoyloxy radical (line 3 *Table 1*) has values similar to the spectrum which we observe in *Figure 1*. This is demonstrated by the simulated pattern using the isotropic average of the g tensor, and the principal values given in *Table 1* for the benzoyloxy radical (spectrum 1b). This spectrum was computed assuming a random distribution of radical orientations, in accordance with the random orientation of the fibres arising from the abrasion process. The calculated spectrum indicates that the e.p.r. data from the mechanically abraded PET fibres is consistent with the formation of a benzoyloxy type of radical structure, C_6H_5–(CO)–O·.

The structure of the PET repeat unit is shown below.

$$\left[(CO)\underset{d}{-}C_6H_4\underset{c}{-}(CO)\underset{b}{-}O-CH_2\underset{a}{-}CH_2-O\right]$$

The possible locations for bond cleavage of the PET monomer unit are indicated as (a) the ethylene bond, (b) the ester bond, (c) the carboxy bond, and (d) the phenylene–carbonyl bond. To form a benzoyloxy type radical, cleavage of bond b is required. Based on comparison to bond strengths of model compounds[7] one predicts the ester bond to be slightly weaker than the ethylene bond, favouring dissociation at b. Cleavage of the ester bond is also consistent with pyrolysis products of PET[6] and model compounds such as ethylene

Table 1 *g* Values of oxygen centred radicals

	g_{iso}	g_x	g_y	g_z	Ref.
O=C(OH)–CH=CH–CO–O·	2.0119	2.0261	2.0061	2.0035	3
HOOC–C=C–CO–O·	2.0141	2.0348	2.0073	2.0043	3
C_6H_4–COO·	2.0117	2.0228	2.0041	2.0082	4, 5
$[$(CO)–C_6H_4–COO·	2.0159	2.0320	2.0094	2.0063	This study

dibenzoate (I), vinyl benzoate (II) as shown by the following schemes[8]:

$$\text{I}\quad C_6H_5\text{–(CO)–O–}CH_2\text{–}CH_2\text{–O–(OC)–}C_6H_5 \xrightarrow{\Delta} C_6H_5\text{–(CO)–OH} + C_6H_5\text{–(CO)–O–CH}{=}CH_2$$

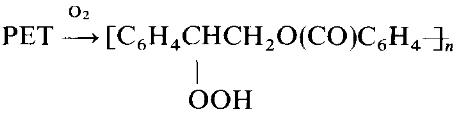
$$\text{II}\quad C_6H_5\text{–(CO)–O–CH}{=}CH_2 \xrightarrow{\Delta} C_6H_5\text{–(CO)–OH} + HC{\equiv}CH$$

$$\text{III}\quad \text{PET} \xrightarrow{\Delta} [C_6H_5\text{(CO)OH}$$

$$+ \text{ low molecular weight oligomers}$$

$$+ \text{ unsaturated esters}$$

This assignment is also consistent with the proposed mechanism of oxidation of PET[9].



$$\text{PET} \xrightarrow{O_2} [C_6H_4\underset{\text{OOH}}{\underset{|}{\text{CH}}}CH_2O(CO)C_6H_4]_n$$

$$\longrightarrow [C_6H_4\text{–(CO)–O}\underset{\bullet}{\text{C}}\text{H}CH_2\text{–O(CO)–}C_6H_4]_n$$

$$+ \cdot\text{OOH} \longrightarrow [C_6H_4\text{–(CO)O}\cdot$$

$$+ CH_2{=}CH\text{–O–(CO)}C_6H_4]$$

Radical B is more difficult to assign due to the lack of *g* anisotropy and unresolvable hyperfine interactions. The signal of radical B sometimes appeared more intense than the signal from radical A in samples only slightly abraded. At room temperature the signal of the benzoyloxy radical decayed leaving a weak signal which may be different from radical B (*Figure 1c*).

U.v. radicals

The alteration of the u.v. treated surface of PET is important to the understanding of photo-grafting experiments in which a metal such as copper is shown to preferentially bond to the u.v. treated PET surface. Studies using sensitizers such as benzophenone suggest that u.v. irradiation of PET films creates a surface region rich in PET free radicals as a result of hydrogen abstraction by the $^3n\pi$ excited state of benzophenone. The free radicals initiate graft polymerization of unsaturated monomers from solution[1]. The PET fibres in our study were not treated with a sensitizer but, as shown in *Figure 3*, free radical signals centred near $g = 2.0024$ are observed after u.v. photolysis of the fibres at 77 K.

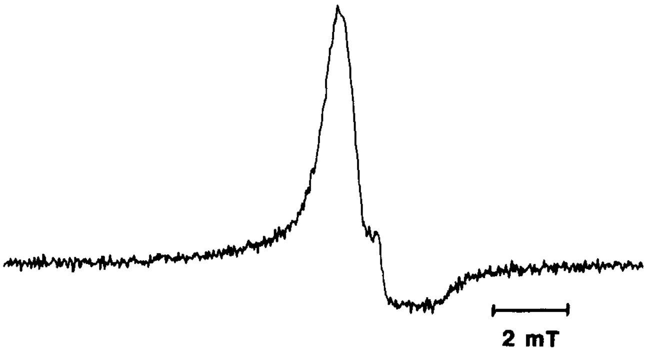
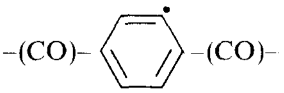


Figure 3 This spectrum was recorded at 77 K from a PET fibre sample which was irradiated at 77 K with unfiltered u.v. light from a Hg–Xe source. The pattern is characteristic of carbon-centred radicals which are randomly oriented to give a powder pattern. There are no resolvable hyperfine interactions. The sharp feature near the lower part of the spectrum may be the same species as noted in *Figure 1a* as radical **B**. This signal decayed when the sample was warmed to room temperature

The spectrum in *Figure 3* has an asymmetric line shape because of the lack of macroscopic alignment of the fibres. (Experiments which would probe the molecular orientation of the fibres were not performed in this study.) The e.p.r. signal is composed of spectral components from all possible orientations of the radicals. γ-Irradiated PET is reported to form carbon-centred radicals most likely by hydrogen abstraction from the ethylene group or from the aromatic ring as shown in the following structures[10].

$$\text{–}C_6H_4\text{–(CO)–O–}\dot{C}\text{H–}CH_2\text{–O–(CO)–}C_6H_4\text{–}$$



The overall e.p.r. signal in *Figure 3* differs, however, from the free radical signal produced in PET fibres exposed to 100 eV γ rays[11]. A sharp peak near the free electron *g* value does appear in the spectrum of reference 11, as well as in our spectra, suggesting that a trapped electron or trapped ion is formed by the u.v. or γ radiation.

A firm assignment of the carbon-centred radicals will require electron-nuclear double resonance to look for unresolved proton hyperfine couplings. In the absence of such unresolved couplings, we note that carbon-centred radicals are consistent with fragmentation reactions to form end-of-chain radicals and other crosslinking species. Some possible mechanisms are shown below.

$$[\text{(CO)–}C_6H_4\text{–(CO)–O–}CH_2\text{–}CH_2\text{–O–(CO)–}C_6H_4]_n \rightarrow [C_6H_4\cdot + CO + \cdot OCH_2CH_2] \rightarrow \text{–}C_6H_4\text{–}OCH_2CH_2\text{–}$$

or

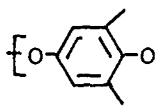
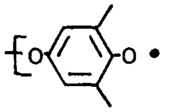
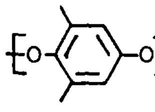
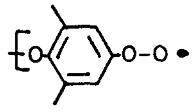
$$[C_6H_4\cdot + \cdot CH_2CH_2] + CO_2 \rightarrow \text{–}C_6H_4\text{–}CH_2CH_2\text{–}$$

or

$$\text{–}\dot{C}_6H_4\text{–(CO)–}OCH_2CH_2O\text{–}$$

$$+ \text{–}C_6H_4\text{–(CO)–O–}\dot{C}\text{H–}CH_2O\text{–}$$

Table 2 Other mechanically generated free radicals

Polymer	Radical	Ref.
		18
		18
$[-CH_2-CH_2-]$	$[-CH_2-\underset{\bullet}{C}H-CH_2-]$	2

DISCUSSION

A comprehensive treatment of fracture must relate the molecular processes which ultimately govern material failure to the macroscopic accumulation of defects. The chain scission mechanisms underlying fracture are influenced by the applied mechanical stress, temperature, bond strengths, as well as the supermolecular structure[12–15]. It is clearly necessary to probe molecular events during the course of fracture experiments if the understanding necessary for realizing optimal failure properties in materials is to be achieved.

Static loading experiments on nylon fibres have shown that there is a direct dependence of stress induced chain scission on temperature[16]. Detectable levels of free radicals in nylon fibres at room temperature can readily be produced by stress[17]. Mechanical abrasion at 77 K of poly(2,6-dimethyl-*p*-phenylene oxide) produces the 2,6-dimethyl phenoxy radical[18] (see *Table 2*). The counter radical formed during this process would be the phenyl radical. A peroxy radical formed by the reaction of the phenyl radical with oxygen was assigned. In cyclic tensile stress loadings of polyethylene followed by γ irradiation alkyl radicals are observed[16]. Poly-(*p*-(2-hydroxyethoxy)benzoic acid) fibres also form phenoxy-type radicals in stress–strain experiments at room temperature[19]. Our observation of the phenoxy-type radical in PET adds to the growing list of mechanically generated radical products that can be identified and thus directly studied. The effect of anisotropic deformation, particularly uniaxial extension, on radical formation in PET fibres is currently under study.

Carbon-centred radicals from u.v. photolysis support surface damage mechanisms via free-radical formation in PET. It has been shown that post-treatment of u.v. damaged PET with a neutralizing agent enhances metal deposition[20]. The formation of primary end-of-chain radicals would provide sites for oxidation to yield hydroxyl and carboxyl groups. A neutralizing agent would make these acidic sites neutral or alkaline while preserving the hydrophobic nature of the surface. This may help to explain the selective deposition of certain metals to u.v.-irradiated PET surfaces.

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