E.s.c.a. studies of corona-discharge-treated polyethylene surfaces by use of gas-phase derivatization

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(Received 21 May 1984)

Chemically specific gas-phase reactions have been used to tag corona-discharge-induced chemical species on the surface of polyethylene. These tag reactions provide distinct moieties that can be detected via e.s.c.a. to provide a surface count of induced species. Hydroxyl, epoxy, hydroperoxy, carboxylic acid and carbonyl populations are discussed as a function of corona energy input, time after treatment and water washings.

(Keywords: X-ray scattering for chemical analysis; polyethylene surfaces; gas-phase derivatization)

INTRODUCTION

The modification of polymer surfaces by corona-discharge treatment (*CDT*) to improve adhesion has wide commercial use. Although there has been considerable research on *CDT* polymer surfaces, a basic understanding of the mechanism by which *CDT* improves adhesion is limited. One reason for this lack of understanding is the *CDT* process affects only the upper few hundred Angstroms of a polymer surface and, until recently, direct chemical analysis of a polymer surface had not been possible. The advent of X-ray photoelectron spectroscopy (X.p.s. or e.s.c.a.) has made it possible to directly analyse the upper 50 Å of a polymer surface.

Many theories have been proposed for the increased adhesion on *CDT* polymer surfaces, including electret formation[1-3], the elimination of weak boundary layers[4-8], increased surface roughness due to *CDT* pitting[9-11], and actual chemical changes such as oxidation. All of these may play a role in improving adhesion. We believe that the introduction of new reactive chemical species into the polymer surface is of prime importance. Most recently, the trend in the literature has been to identify these new chemical species and to relate them to changes in adhesive properties. Owens[12,13] attributed the strong self-adhesion of *CDT* polyethylene (PE) and poly(ethylene terephthalate) (PET) to the formation of enolic hydrogen bonds in the former and phenolic hydrogen bonds in the latter. These conclusions were based on the results of chemical and physical tests.

Briggs and co-workers[14-17] reported some of the earliest work in which X.p.s. was used to study *CDT* polymer surfaces. PE, PET and polypropylene (PP) were studied by use of a static-discharge treatment cell. In all cases, the polymer surface was oxidized. Their spectrometer was nonmonochromatic, resulting in relatively broad linewidths. In the C 1s spectra for the *CDT* PE and PP, a broad band at high binding energy indicated carbon–oxygen bonds. However, the assignment of this broad band to definite functional groups was inconclusive. For PET, the C 1s difference spectra gave a broad band in the high-binding-energy region, again indicating new carbon–oxygen bonds. Using deconvolution techniques, Briggs could see differences in the high-binding-energy C 1s region for PP by varying the corona conditions. But again the results were not definitive.

For identification of specific surface functional groups, derivatization reactions with group-specific reagents containing an X.p.s. tag have become increasingly popular. Everhart and Reilley[18] reported a series of derivatization reactions for plasma-treated PE. Their proposed reactions were all solution reactions needing long reaction times and in some cases high temperatures. These relatively severe reactions can be unreliable, as Everhart and Reilley reported[19,20]. The surface functional groups to be derivatized can be very mobile and may reorient into the bulk or become solubilized during these solution reactions. Briggs and Kendall[21] also used derivatization reactions to study *CDT* PE films. Except for the hydroperoxy functionality, solution reactions were used to identify surface species. Although the reaction conditions were milder than those of Everhart and Reilley, the problem of functional group mobility still remains. Hammond and co-workers[22,23] reported gas-phase derivatization reactions for surface epoxy (HCl) and hydroxyl (trifluoroacetic anhydride) functional groups. These reactions were tested on model copolymers, with excellent agreement between surface concentrations of hydroxyl and epoxy functional groups and bulk stoichiometry. In our work, we have used new gas-phase derivatization reactions along with those reported in the literature to tag the reactive oxygen-containing functional groups formed on the surface of *CDT* PE.

EXPERIMENTAL

The X.p.s. spectra were obtained on a Hewlett-Packard 5950A e.s.c.a. spectrometer with a monochromatic Al Kα X-ray source. The use of a monochromatic source precludes sample radiation damage, especially important for polymers. All our samples were stable in the X-ray beam and showed no evidence of X-ray damage during measurements. The data were collected with a Hewlett-Packard 9836 computer and stored on disc. Angle-resolved depth profiling was done with a Surface Science Laboratories model 259 angular-rotation probe. Typically, the FWHM for the C 1s peak in a clean polyethylene

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sample was 1.0 eV. All spectra were referenced to the C 1s peak for neutral carbon, which was assigned a value of 284.6 eV.

The corona unit was a 3 kHz Pillar system consisting of six glass-covered aluminium electrodes arranged in a hemispherical array equidistant from one another. The spacing from the glass surface to the treated material was 0.66 mm. Samples could be moved through the assembly at various powers and speeds. Energy input was varied from ~4000 to ~35000 J m^{-2}.

The PE samples were commercial 10 mm high-density polyethylene films. To eliminate surface contamination, we washed these films consecutively in a series of solvents (heptane, dichloromethane, ethanol and ethyl acetate) and vacuum dried them. These solvents were chosen so that polar and nonpolar impurities were removed. A similar study on poly(ethylene terephthalate) showed the necessity of this wash step, as various amounts of hydrocarbon contamination (as determined from e.s.c.a. by the O : C ratio) were observed on uncleaned samples[24]. After the samples were washed, e.s.c.a. measurements showed little oxidation on the surface of the polymer.

Advancing-water-contact angles were used in this study according to standard procedures[25]. 'Washed' samples were specimens that had been used for initial contact angles and were then rinsed for ~30 s with distilled water.

Derivatization reactions

Reactants that are gases at room temperature (SO_2, NH_3 and HCl) were introduced into a flow-through vessel from lecture-bottle reservoirs (Matheson, Inc.). The other compounds are liquids (hydrazine, diethylamine and triethylamine from Kodak Laboratory Chemicals and trifluoroacetic anhydride from Aldrich Chemical Co., gold label). Their vapour pressures were adequate to saturate a 500 ml jar by the use of about 5 ml of reactant liquid.

All specimens (5 × 0.6 cm PE films) were exposed for 5 min. We decided upon this reaction time by performing exposure-variation experiments from seconds to hours. In all cases (except the acid tag; see Discussion) 100% labelling was achieved with model compounds, e.g. polymers or monomers with known concentrations of epoxy, hydroxy, acid, etc. functionalities.

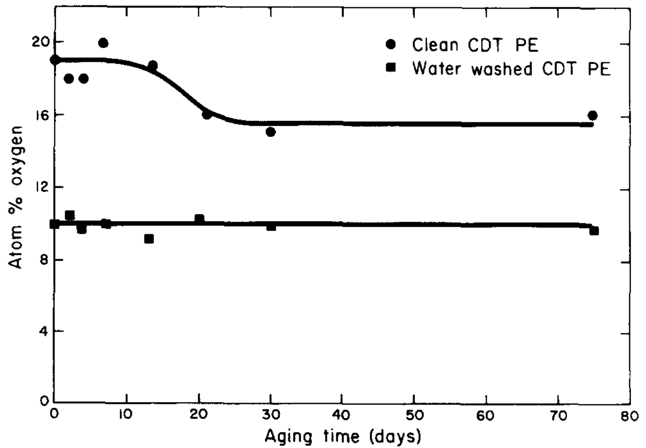


Figure 1 Atom% incorporated oxygen vs. time after *CDT* (35000 J m^{-2})

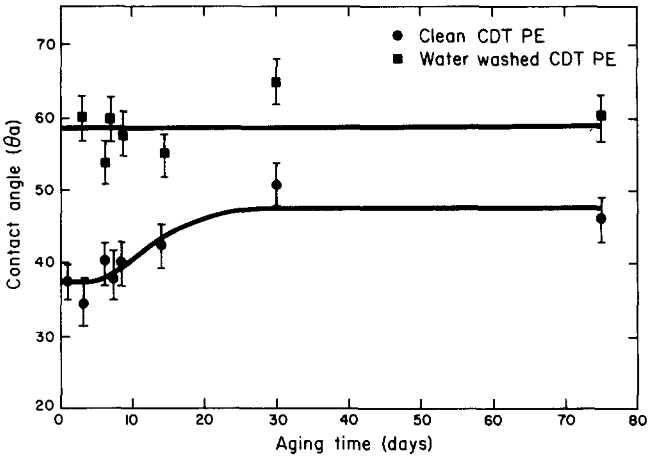


Figure 2 Advancing contact angle (H_2O) vs. time after *CDT* (35000 J m^{-2})

RESULTS AND DISCUSSION

X.p.s. shows that oxygen is incorporated into the surface of *CDT* PE. The amount of oxygen incorporated can be varied from 10 to 20 atom% with the power treatment levels we used. Small day-to-day variations in the amount of incorporated oxygen were also observed at identical power settings. Generally these differences were within ±10% of a given value. Angular-dependent X.p.s. showed that the distribution of the incorporated oxygen was homogeneous in the top 50 Å of the PE film surface with oxygen incorporation > 12 atom%. However, with lower oxygen incorporation a definite gradient existed in the top 50 Å, indicating an oxygen-rich surface. Also, at the higher oxygen incorporation, much of the oxidized polymer could be removed with a 30 s water wash (*Figures 1* and *2*). Water washing always gave 9–11 atom% incorporated oxygen and a contact angle of 55–60°, regardless of the initial oxygen level or the initial contact angle. Except for the intensity of the neutral carbon peak due to the PE backbone, the e.s.c.a. spectra before and after washing were nearly identical, showing that, within the limits of error, the water-soluble material and the insoluble surface material were identical. We believe that at higher powers considerably more chain scission occurs, giving water-soluble material. These short-chain species can produce boundary layers that can have significant effects on the adhesion properties of *CDT* PE.

The results of ageing on *CDT* PE treated at ~35000 J m^{-2} are shown in *Figures 1* and *2*. During ageing, the samples were stored in clean, sealed glass containers at ambient conditions. Both the oxygen level as measured by X.p.s. and the contact angle showed little change during the first 2 weeks after *CDT*. Between 2 and 4 weeks, the oxygen level dropped 15%, and the contact angle increased accordingly. After about 4 weeks, the surface stabilized. These changes could be due to reorientation of the surface polar groups into the bulk or to buildup of a hydrocarbon overlayer during storage of the films. Based on the inelastic mean free paths (IMFP) of the O 1s and C 1s levels, a drop of ~15% in the oxygen level is consistent with reorientation into the bulk of polar oxygen species on the order of 5 Å or the buildup of a 5 Å hydrocarbon overlayer.

Figure 3 shows the X.p.s. C 1s spectra for a clean PE film (A), a PE film that received *CDT* at 35000 J m^{-2} (B),

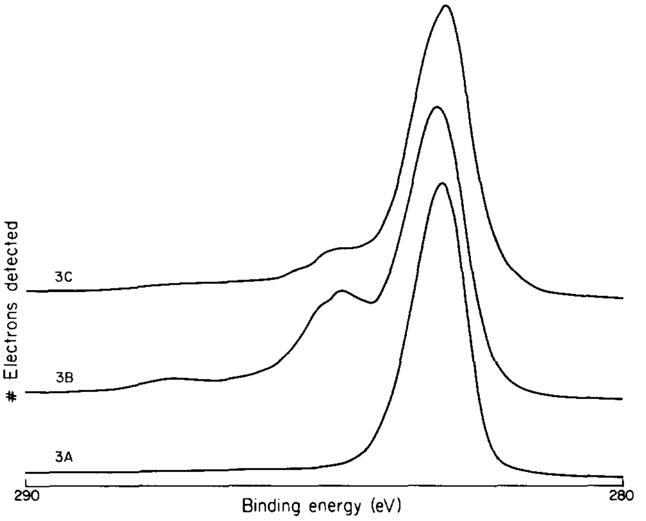


Figure 3 E.s.c.a. C 1s spectra for (A) clean PE, (B) *CDT* PE (100 J m^{-2}), (C) sample B after a 30 s water wash

and film B after a 30 s water wash (C). The C 1s spectrum for the clean PE film surface shows a single peak indicative of the carbon–carbon bonds in PE. This particular sample had ~1% oxygen on the surface before *CDT*. After *CDT*, 18% oxygen was incorporated into the PE surface, and the C 1s spectrum shows new peaks to high binding energy, indicating the formation of carbon–oxygen functionalities (*Figure 3B*). After water washing, a large decrease in the high-binding-energy region of the C 1s spectrum was observed (*Figure 3C*), consistent with removal of the carbon–oxygen functionalities. A simple deconvolution of spectrum 3B is shown in *Figure 4*. The high-binding-energy region of the C 1s spectrum can be fitted with three peaks corresponding to carbon atoms with a single bond to oxygen at 286.2 eV (e.g. alcohol, epoxy, ether, ester, hydroperoxy, peroxide), carbon atoms with two bonds to oxygen at 287.5 eV (e.g. aldehyde or ketone), and carbon atoms with three bonds to oxygen at 289.0 eV (e.g. carboxylic acid or ester). Unfortunately, from the C 1s spectrum alone, one cannot be more specific about the functional groups formed. The O 1s spectrum is even less informative, giving one broad peak at about 532.8 eV, in the middle of the range for O 1s spectra of carbon–oxygen functionalities. The O 1s binding energies range from 531.6 eV for a carbonyl oxygen in a carboxyl group to 533.1 eV for an ester oxygen in a carboxyl group, with most other carbon–oxygen species at ~532.5 eV.

For probing the detailed structure of this oxidized layer, gas-phase derivatization reactions have been developed to tag specific functional groups. The reactions we chose (*Table 1*) represent what we believe to be the best choice for a given functional group, based on reproducibility on model polymer surfaces and on the *CDT* PE and the fact that no detectable artifacts are introduced during the reaction. All of these reactions were run on blanks (clean non-*CDT* PE) to ensure that physisorption does not occur. In all blanks, either none of the tag material was detected or it was orders of magnitude lower in concentration than on the treated PE. Reaction 1, gaseous SO_2 with hydroperoxy to form the sulphonic acid, has been described by Mitchell and Perkins[26] and was used by Briggs and Kendall[21] as a tag for surface hydroperoxy on *CDT* PE. A suitable model compound is not available for this reaction; however, the S 2p binding energy after derivatization was 169.2 eV, equivalent to that of the S 2p peak in a sulphonic acid, showing that the reaction proceeds as expected. Also, after derivatization, the increase in oxygen content was twice that of sulphur, again consistent with reaction 1. Reaction 2, the esterification of hydroxyl with gaseous trifluoroacetic anhydride to form trifluoroacetate moieties, has been described by Hammond and co-workers[22,23]. We tested this reaction with a copolymer of known hydroxyl content, (40/60) *N*-isopropylacrylamide / *N*-(2-hydroxypropyl) methacrylamide, and observed ~100% reactivity. Angular-dependent X.p.s. showed homogeneous reactivity in at least the top 50 Å of the polymer surface. Isolated carbonyls, i.e. those with no adjacent oxygen groups, can be tagged by reaction with gaseous hydrazine to form the hydrazone (reaction 3). A suitable model compound was not found for the isolated carbonyl; however, after derivatization, the N 1s binding energy was 399.7 ± 0.1 eV, consistent with the formation of a hydrazone. The X.p.s. data also showed a loss of oxygen corresponding to about half of the amount of nitrogen incorporated, consistent with reaction 3. Epoxy functionalities were tagged using gaseous HCl to open the epoxy ring and form a chlorohydrin (reaction 4). This derivatization reaction was originally proposed by Hammond[22]. We tested this reaction on a model epoxy compound [1,2-epoxy-3-(*p*-nitrophenoxy)-propane] and found ~100% reactivity. Angular-dependent X.p.s. showed homogeneous reactivity in at least the top 50 Å of the model compound surface. The reaction apparently proceeds as expected, since the oxygen concentration does not change after derivatization.

Tagging the acid groups was the most difficult. We tried many of the proposed ionic solution reactions, including NaOH[21], $AgNO_3$[27] and $CaCl_2$. All of these were non-reproducible. The amount of tag material on the surface varied, depending on the wash conditions after reaction.

We used various bases in an attempt to complex the carboxylic acid moiety via the formation of the base salt. Polymers of known acid contents were exposed to saturated atmospheres of ammonia, diethylamine and triethylamine. These polymers included polyacrylic acid, a 20% polyacrylic acid/80% polyethylene copolymer and poly(4-carboxystyrene). This series gives a range of ~9–33% of the carbon atoms as acid groups. The lower value would more closely approximate the amount of acid groups observed on *CDT* polyethylene. From a deconvoluted C 1s spectrum of the *CDT* PE (*Figure 4*), we can place an upper limit on the amount of carbon atoms as acid groups at 2–3%. Reaction of the above bases with these polymers always gave ~10–15% complexation of

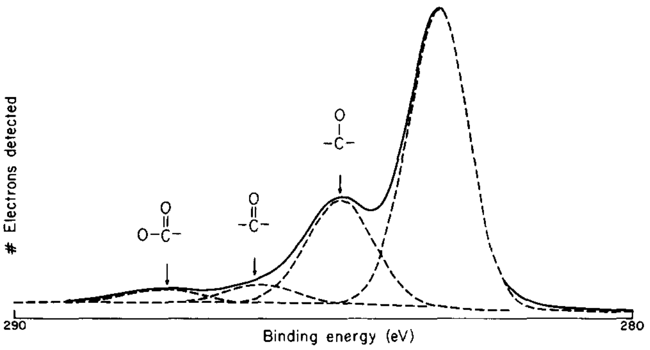
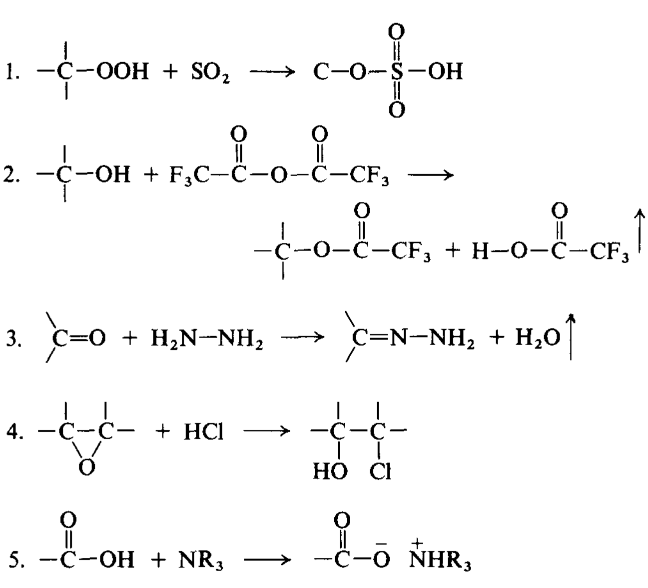


Figure 4 Best-fit deconvolution of spectrum in *Figure 3B*

Table 1 Derivatization reactions



$$1.\ -\overset{|}{\underset{|}{C}}-OOH + SO_2 \longrightarrow C-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

$$2.\ -\overset{|}{\underset{|}{C}}-OH + F_3C-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CF_3 \longrightarrow -\overset{|}{\underset{|}{C}}-O-\overset{\overset{O}{\|}}{C}-CF_3 + H-O-\overset{\overset{O}{\|}}{C}-CF_3\uparrow$$

$$3.\ \rangle C=O + H_2N-NH_2 \longrightarrow \rangle C=N-NH_2 + H_2O\uparrow$$

$$4.\ -\overset{|}{C}\underset{O}{\diagdown\!\diagup}\overset{|}{C}- + HCl \longrightarrow -\overset{|}{\underset{\underset{HO}{|}}{C}}-\overset{|}{\underset{\underset{Cl}{|}}{C}}-$$

$$5.\ -\overset{\overset{O}{\|}}{C}-OH + NR_3 \longrightarrow -\overset{\overset{O}{\|}}{C}-\overset{-}{O}\ \overset{+}{N}HR_3$$

the observed acid groups. The N 1s binding energy after reaction was 401.4±0.2 eV, consistent with the formation of the ammonium salt. We verified this binding energy by measuring the N 1s binding energy for the ammonium salt of benzoic acid. Numbers such as 10–15% complexation could suggest monolayer surface reactivity of these bases; however, angular-dependent depth profiling showed homogeneous reactivity throughout the sampling depth (~50 Å).

The fact that derivatization of the reference polymers shows incomplete complexation could be explained in terms of chemical equilibrium. The carboxylic acid/base equilibrium under these experimental conditions (initial gas-phase treatment plus 10^{-9} Torr vacuum at ~20°C) could be such that 10–15% of the acid groups are the limit of complexation. If this is the case, there is little hope of complete complexation at ambient; however, lowering the temperature might decrease the probability of dissociation. To check this possibility we immediately loaded derivatized samples onto the e.s.c.a. sample probe and cooled them to 150 K with liquid nitrogen. During this cool-down period, the sample probe was enclosed in a glove bag purged with dry nitrogen. Cooling to 150 K took 2–3 min. Under these conditions, the NH_3 derivatization complexed ~50% of the acid groups. If the sample was allowed to remain at ambient for 15 min before cooling, the amount of complexation dropped to ~30%. Cooling after 24 h at ambient gave ~20% complexation. Warming the sample to room temperature in the vacuum system decreased the complexation to 10–15%, as observed for the samples run at room temperature. These results show that the ammonium salt is unstable at room temperature and degrades to a value of ~20% complexation. Under high vacuum conditions, even more degradation occurred. Essentially the same results were found for diethylamine and triethylamine. From these results, we can place an upper limit on the amount of complexation at ~50% with this derivatization reaction.

Table 2 shows results of the derivatization reactions on a *CDT* PE sample treated at 35000 J m^{-2}. Except where noted, the derivatization reactions were run within 1 h after treatment. The results before and after a 30 s water wash are also listed. Interestingly, the predominant species initially was the epoxy group. Also, a large amount of hydroperoxy was found, showing the long lifetime of this species in *CDT* PE. A nitrogen peak at 407.6 eV was detected; this peak is assigned to an NO_3 group[28]. From the total of the oxygen in the tagged functional groups and the NO_3 group, we can account for about 76% of the incorporated oxygen. This is reasonable, since ether and ester functionalities have not been tagged (and would probably account for most of the remaining oxidative species). From the deconvoluted C 1s spectrum (*Figure 4*), one can determine that ~85% of the unaccounted-for oxygen is present as ether functionalities and 15% as ester functionalities. Thus, the ether functionality has the largest population of any species, ~3.4×10^{-2}. After a 30 s distilled water rinse, about 45% of the incorporated oxygen was removed. The derivatized functional groups showed a corresponding decrease in concentration, ranging from 25% for hydroperoxy to 52% for epoxy. Except for hydroperoxy, water washing gave a nearly uniform decrease in all species. This result might suggest that the hydroperoxy functionality is not at the immediate polymer surface where it could react chemically, but rather is below the surface in an environment that shields it from reacting.

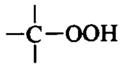
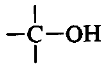
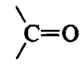
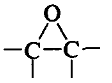
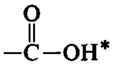
Preferably, samples should be studied at *CDT* levels where the oxygen incorporation is about 10%. At this level, water washing did not alter the PE surface; with the water rinse there was always ~10% oxygen incorporation regardless of the starting oxygen level. Oxygen incorporation of about 10% was obtained by operating the corona unit at ~4000 J m^{-2}. *Table 3* shows results of derivatization on such a sample. Except for large decreases in the epoxy and carbonyl functionalities, the results are similar to those found at 35000 J^{-2}, (*Table 2*). NO_3 was not detected at these conditions. Oxygen

Table 2 *CDT*-induced surface functionalities in polyethylene (~35000 J m^{-2})

Functional group	Group conc. × 10²* Initial	Group conc. × 10²* Water-washed
$-\overset{\vert}{\underset{\vert}{C}}-OOH$	1.2	0.9
$-\overset{\vert}{\underset{\vert}{C}}-OH$	1.7	1.1
$\rangle C=O$	1.8	0.9
$-\underset{\vert}{C}\overset{O}{\frown}\underset{\vert}{C}-$	2.3	1.1
$-\overset{\overset{O}{\Vert}}{C}-OH$†	1.6	0.8
NO_3	0.8	0.4
Total [O] tagged	13.8	7.7
Actual [O] incorporated	~18	~10

* Moles of functional species per unreacted initial carbon atom
† Twice the actual tag value (see text)

Table 3 *CDT*-induced surface functionalities in polyethylene (~4000 J m^{-2})

Functional group	Group conc. × 10^2		
	Initially	Aged 16 days	Water-washed
 $-\overset{|}{\underset{|}{C}}-OOH$	1.1	1.1	1.3
 $-\overset{|}{\underset{|}{C}}-OH$	1.8	1.2	1.2
 $>C=O$	1.1	1.0	0.8
	0.9	0.4	0.4
 $-\overset{\overset{O}{\|}}{C}-OH^*$	1.6	0.8	0.8
Total [O] tagged	9.2	6.4	6.6
Actual [O] incorporated	~12	~10	~10

* Twice the actual tag value (see text)

incorporation was down to 12%, and again we can account for about 76% of the oxygen. *Table 3* also lists the results for derivatization after the samples were aged for 16 days and after a 30 s water wash immediately after *CDT*. (The oxygen incorporation changes significantly in 16 days; see *Figure 1*.) The aged and the water-washed samples are similar, showing large decreases in the epoxy and acid functionalities, intermediate change in the hydroxyl functionality, and little or no change in the hydroperoxy and carbonyl functionalities. These data suggest that oxidized PE molecules containing the acid, epoxy and hydroxy functionalities are either diffusing into the bulk of the PE or slowly subliming during ageing. These results also suggest that many of the hydroperoxy and isolated carbonyl groups are bound to less-mobile molecular species.

CONCLUSIONS

Gas-phase derivatization techniques and e.s.c.a. were used to identify corona-produced oxidative species in polyethylene. Five species were identified directly: hydroperoxy, hydroxyl, isolated carbonyl, epoxy and carboxylic acid. Ether and ester species were also inferred from the e.s.c.a. spectra. The former account for ~76% of the oxygen incorporated into PE. Water-soluble surface species were produced at powers > ~4000 J m^{-2}. Above this level, e.s.c.a. showed homogeneous oxidation within the top 50 Å of the PE surface. Below this level, a gradient of oxidation exists, with the oxygen-rich material at the surface. Water washing samples treated at powers >4000 J m^{-2} removed material to ~10% incorporated oxygen. Population distributions of the incorporated species are discussed in light of ageing, washing and *CDT* power.

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