An e.s.c.a. study of the gas-phase derivatization of poly(ethylene terephthalate) treated by dry-air and dry-nitrogen corona discharge

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Gas-phase derivatization has been used along with e.s.c.a. to determine corona-discharge-induced chemical species on poly(ethylene terephthalate) (PET). Dry-air and dry-nitrogen coronas were studied. We showed that: (1) if the corona discharge treatment (CDT) power level is kept low enough, few water-soluble species are created; (2) 4% of oxygen is added to the surface with dry-air corona; (3) 75% of the oxidation products are identified as hydroperoxy, epoxy, hydroxyl, carboxylic acid and isolated carbonyl species (with hydroxyl and isolated carbonyl the prevalent species). Short-term time-dependent ageing studies show a one-to-one correspondence between the decrease in hydroperoxy species and the increase in hydroxyl and isolated carbonyl moieties. Reaction sequences are proposed to explain these data. At longer times these surface populations decrease. In general, the results from nitrogen coronas and dry-air coronas are similar.

(Keywords: electron spectroscopy for chemical application; corona; poly(ethylene terephthalate); derivatization; nitrogen; air; ageing; kinetics; X-ray photoelectron spectroscopy)

INTRODUCTIONS

Corona-discharge treatment (CDT) of polymer surfaces to improve adhesion and wettability has wide industrial application. Until recently, little scientific effort has been devoted to understanding the chemical process taking place during CDT. Since such chemistry usually takes place in the upper few hundred angstroms of a polymer film, e.s.c.a. analysis is one of the few tools that can be used to study this phenomenon.

A variety of causes have been proposed for the increased adhesion of CDT polymer films[1-9], but it is generally thought that the introduction of new chemical species via oxidation of the polymer surface is of prime importance. Recently, much effort has been made to identify these species and correlate their appearance with an increase in adhesion or autoadhesion. Owens attributed strong self-adhesion and corona-discharge treated (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[8,9]. His conclusions were based on chemical and adhesive testing of CDT PE and PET. Identification of the adhesive-promoting species was based on influence rather than direct identification of the structure. Briggs and co-workers[10-12] reported the earliest e.s.c.a. work on CDT of PE, PET and polypropylene. Various oxidation states of carbon were identified; however, specific species could be identified only by deconvolution of the obtained spectra. Clark and co-workers[13-15] have done similar experiments (surface oxidation) on a variety of polymers, using the deconvolution technique to ascertain species created by surface oxidation.

The derivatization technique, first reported by Everhart and Reilley[16], provided a means of identifying the corona-created species. By this method, in a series of substituent-specific reactions, each species is labelled with an identifiable XPS tag. Unfortunately, these initial derivatizations required long reaction times and high temperatures, and stability of the CDT surfaces, physically or chemically, could not be ensured. Briggs and Kendall also used derivatization reactions to ascertain the surface composition of CDT PE[17]. Most of their derivatizations were solution reactions, and the problems of surface reorientation and solubility still remained. Hammond and co-workers[18,19] developed gas-phase reactions to ascertain the surface concentration of hydroxy (trifluoroacetic anhydride treatment) and epoxy (HCl treatment) groups. Known compounds were tested, and agreement between bulk and surface compositions was obtained. Much of this work has been reviewed[20].

Recently, we presented work on CDT PE in which *only* gas-phase reactions were used to analyse the surface[21]. We believe that gas-phase treatment will eliminate: (1) problems associated with surface plasticization and reorientation caused by solution derivatization; (2) dissolution of low-molecular weight material created by CDT and (3) the possibility of solvent reacting with the species created on the surface. The reactions (see *Figure 1*) were used to identify (via e.s.c.a.) hydroperoxy, hydroxyl, carbonyl, epoxy and carboxyl moieties. About 70% of the oxidized species were identified as the above materials, with the remaining considered, by influence, to be ether linkages and ester groups. In that work, we studied time dependence (population after CDT treatment) and noted

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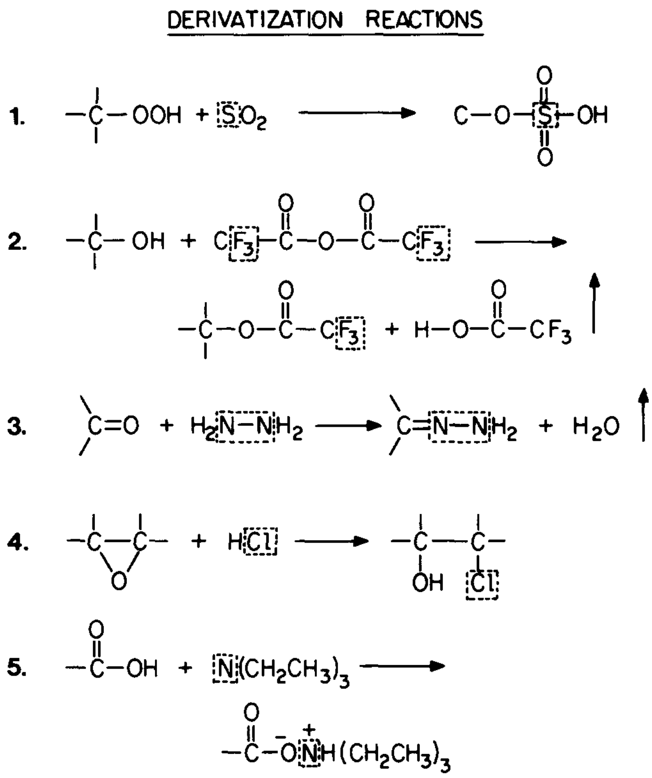


Figure 1 Schematic of derivatization reactions

some change in the oxidative species after CDT. We also showed that special low-temperature experimental techniques were needed to ascertain any useful information concerning carboxylic acid population.

We now present data on one study of the effect of air and nitrogen corona on CDT-induced species in PET, using the previously described gas-phase derivatization reactions.

EXPERIMENTAL

The XPS spectra were obtained on a Hewlett-Packard 5950A (e.s.c.a.) spectrometer with a monochromatic AlKα X-ray source. The use of a monochromatic precludes sample radiation damage, especially important for polymers. All the samples we used were stable in the X-ray beam and showed no evidence of X-ray damage during measurements. The pressure in the spectrometer during analysis was typically 5×10^{-9} torr. The data were collected with a Hewlett-Packard 9836 computer and stored on disc. Angular-dependent measurements were made with a Surface Science Laboratories Model 259 angular-rotation probe. Typically, the full width at half maximum (*FWHM*) for the individual components of the C 1s spectrum of a clean PET surface 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 from one another. The distance from glass surface to treated material was 0.066 cm. Samples could be moved through the assembly at various power levels and speeds. Energy input was varied from ~2150 to 43 000 J m^{-2}. A housing and feed-line system was put around the electrode arrangement so that dry air (<7% r.h.) and pure nitrogen (<2% O_2) could be used during corona application. Advancing water-contact angles were used in this study according to standard procedures[22].

The PET samples were commercial (0.254 cm) Kodak film base, washed consecutively in a series of solvents (pentane, dichloromethane, and ethanol) and dried in a vacuum oven to eliminate surface contamination. XPS evaluation of the washed samples showed oxygen–carbon stoichiometry consistent with pure PET. The power level chosen for these studies was determined as follows. A series of CDT power levels were run on the PET samples. Water-contact angles were measured before and after a 30 s wash with distilled water. When these contact angles did not change, indicating that little of the oxidized species could be washed from the surface, the corresponding power level was used to produce the samples for derivatization experiments. This provided for the maximum surface oxidation with little chance of low-molecular weight oxidation products being removed during derivatization and in the high vacuum of the e.s.c.a. experiment. The power level in this case was ~2150 J m^{-2}. At this level of treatment, angular-dependent e.s.c.a. measurements indicate a gradient of incorporated oxygen in the top 50 Å of the sample surface.

The effect of overtreatment and surface cleaning is seen in *Figures 2* and *3*. In the examples shown, cleaned PET and 'dirty' PET (a PET film that e.s.c.a. showed to be contaminated with a partial layer of hydrocarbon) were exposed to 43 000 J m^{-2} air CDT, and incorporated oxygen and water-contact angles were monitored as a function of time after treatment. At this high CDT level, oxidized material can normally be washed from the surface and angular-dependent e.s.c.a. measurements indicate a uniform incorporation of oxygen in the top 50 Å of the PET surface even after a water rinse. *Figure 2* shows that the incorporated oxygen level decreased as a function of time. The dirty sample, which could give lower-molecular weight oxidation products than clean PET, decreased much more rapidly in surface-oxygen content. A concomitant change in water-contact angle is shown in *Figure 3*, with the surface of the material becoming more hydrophilic with age. Note that ageing the clean PET at two different r.h.'s does not affect the observed ageing curve (*Figure 3*). The data in *Figures 2* and *3* are cross plotted in *Figure 4*, which shows a direct correlation between the amount of incorporated oxygen

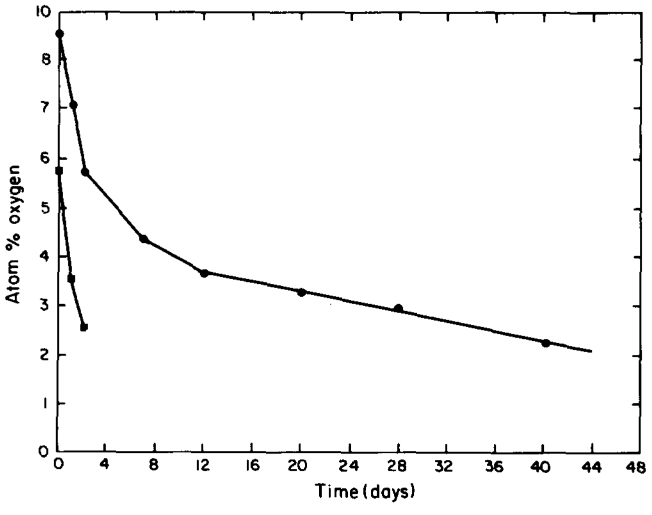


Figure 2 Incorporated oxygen *versus* ageing time for CDT (43 000 J m^{-2}) dirty (■) and clean (●) PET

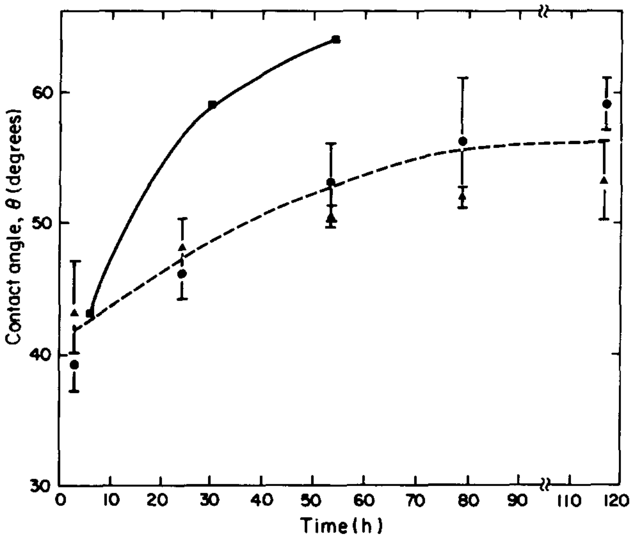


Figure 3 Water-contact angle (θ) *versus* ageing time for CDT (4300 J m^{-2}) dirty (■) and clean (▲, 0% r.h.; ●, 65% r.h.) PET

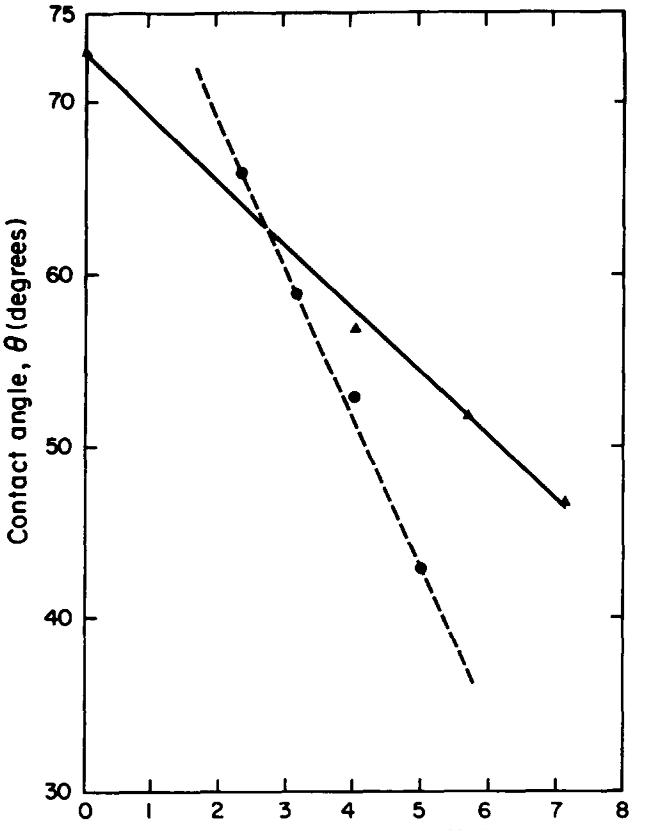


Figure 4 Water-contact angle (θ) *versus* excess incorporated oxygen for CDT PET; (▲) clean (average of 0% and 65% r.h.), (●) dirty

and the water-contact angle. These data indicate a direct correlation between PET overtreatment and the observed ageing phenomenon in PET.

Derivatization reactions (see *Figure 1*) were conducted as follows. Reactants that are room-temperature gases (SO_2 and HCl) were introduced into a flow-through vessel from lecture-bottle reservoirs (Matheson, Inc.). The other compounds [hydrazine and triethylamine (TEA) (Kodak Laboratory Chemicals); trifluoroacetic anhydride (TFA) (Aldrich gold label)] are room-temperature liquids. Derivatization reactions were run in a saturated atmosphere of these reactants. All specimens (~5 cm × 0.64 cm PET films) were exposed for 5 min to one of the reactants. This reaction time was determined from experiments in which exposure was varied from seconds to hours. In all cases (except triethylamine[21]) 100% labelling was achieved with model compounds (polymers or monomers with known concentrations of epoxy, hydroxyl, acid, etc. functionalities). For the time-dependent experiments, after CDT the samples were stored at 40% r.h. at room-temperature until derivatized.

RESULTS AND DISCUSSION

The derivatization reactions we used are shown in *Figure 1*. The e.s.c.a. labels are sulphur for hydroperoxy groups, fluorine for hydroxyl groups, nitrogen for carbonyls, chlorine for epoxy groups and nitrogen for carboxylic acid. Since some of the e.s.c.a. labels are highly reactive, there is no way to tell whether the hydroxy moiety is due to an isolated hydroxy or to an α-hydroxy olefin signal. Likewise, the carbonyl signal could be due to isolated carbonyls or to α-carbonyl olefin signals. Therefore, the total number of each species can be ascertained, but not necessarily its direct chemical environment. We had, in fact, attempted to ascertain the structural environment of carbonyls on CDT PE. Halogens were tried for derivatization of double bonds and methylene groups alpha to carbonyls. Treatment of CDT PE surfaces with Cl_2 gas produced totally chlorinated surfaces within seconds, whether experiments were run in light or darkness[21]. Evidently, the ease of formation of Cl free radicals in the gas phase and their ability to extract protons from the polymer made this test unusable.

Treatment with I_2 vapours produced no significant amount of reaction even after 24 h exposure. Br_2 gas reacted at a slower rate than Cl_2 gas but proceeded to totally brominate the PE surface after about 1 h reaction time.

Tables 1 and *2* show the results of our derivatizations. Data are shown for derivatization soon after CDT (30 min) and for various longer times after CDT (to ascertain any time dependence of the created species). Data are shown for air and N_2 CDT. Some general trends in the air–CDT data are obvious:

(1) In the 0 to 24 h time range, the epoxy and acid concentrations remain relatively constant.

(2) Hydroperoxy concentration decreases with time,

Table 1 Derivatized species (%) based on initially available carbon atoms for PET corona-treated in dry air

Species	30 min	3 h	24 h	338 h
C–O–O–H	0.18	0.10	0	0
$\overset{O}{C-C}$	0.28	0.25	0.28	0.08
C–OH	0.50	0.60	0.88	0.49
$C(=O)OH$	0.15	0.18	0.15	0.06
C=O	1.40	1.65	1.92	1.33
Total [O] tagged	2.84	3.06	3.38	2.02
[O] incorporated	4.0±0.2	4.0±0.2	4.0±0.2	3.1±0.2

Table 2 Derivatized species (%) based on initially available carbon atoms for PET corona-treated in dry nitrogen

Species	30 min	28 h	77 h
C–O–O–H	0.24	0.10	0
O / \\ C–C	0.28	0.27	0.18
C–OH	0.36	0.48	0.67
//O C \\OH	0.10	0.14	0.06
C=O	1.70	1.75	1.65
Total [O] tagged	3.02	2.98	2.62
[O] incorporated	4.0±0.2	4.0±0.2	3.5±0.2

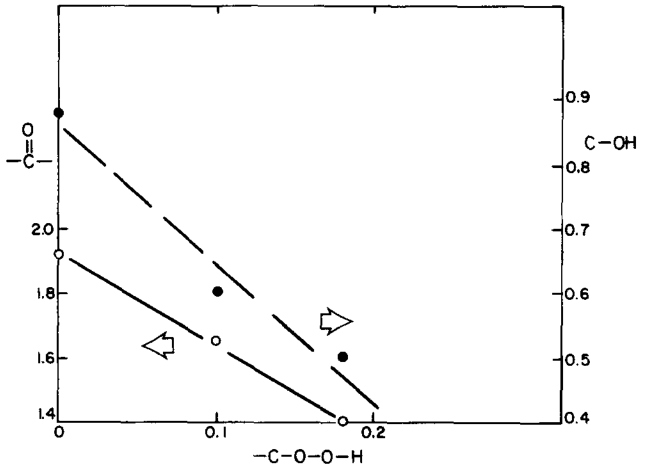


Figure 5 Carbonyl and hydroxyl populations *versus* hydroperoxy population for dry-air CDT PET. Numbers based upon initial surface carbon atom population

with a concomitant increase in the carbonyl and hydroxyl concentrations (0–24 h).

(3) The total assaysed oxygen increases, while the incorporated oxygen remains constant, within experimental error limits (0–24 h).

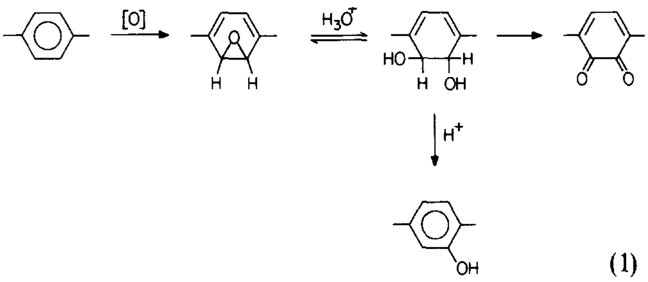
(4)At long times the population of all species decreases. This effect has also been observed in PE[21] and is believed to be due to either a slow reorganization of the oxidized PET surface into the bulk or buildup of a hydrocarbon contamination layer. Because of this latter effect, kinetic trends in the observed species can be discussed only for the data of the first 24 h.

With N_2 treatment, oxidized species are gradually lost, and there is a time-dependent decrease in hydroperoxy and epoxy species with a concomitant build up in hydroxyl population. Note that the total incorporated oxygen in both treatments is ~4% at short times. There was little evidence for incorporated nitrogen. In some cases ~0.1% nitrogen was detected in the form of an oxide (NO_x).

These results indicate that CDT creates high free-energy species on the surface of the polymer that continue to react after treatment and storage. Since the chemistries appear to be different, they will be addressed separately.

Dry-air CDT of PET

The largest changes observed with time are in the hydroperoxy, hydroxyl and carbonyl species. *Figure 5* is a plot of carbonyl and hydroxyl populations *versus* hydroperoxy population. The slope is linear and shows a one-to-one correspondence between the species. Therefore, reactions must be occurring that would increase isolated carbonyl and hydroxyl populations.



(1)

Equation (1) is a consecutive reaction, which could stop at diene diol formation when the highly reactive oxygen species is depleted. Such reaction sequences are plausible, but we have no way of determining if they are correct.

The reactive oxygen, [O], shown in equation (1) could actually come from a variety of sources other than hydroperoxy decomposition, such as atmospheric oxygen that has been excited via energy transfer with an excited surface-state species or u.v.-excited oxygen molecules. With our present experimental system, there is no way to determine where this excess [O] is derived to promote further oxidation.

N_2 CDT of PET

N_2 CDT of PET produces a system with kinetics quite different from those observed for dry-air (see *Table 2*). Within the limits of measurement error, the carbonyl and carboxylic acid populations are constant. The hydroperoxy and epoxy are decreasing, and hydroxyl is increasing. Such differences are probably caused by the conditions of the experiment. In dry-air CDT, direct oxidation of the surface can take place in the corona. In the N_2 CDT the oxidative chemistry is caused either by N_2 excitation of the polymer surface followed by oxygen addition or by direct oxidation caused by the impurity oxygen in the nitrogen gas. The populations of the various tagged species are not very different in either case. The data of *Table 2* can be rationalized by equation (2).

$$\text{C–O–O–H} \quad \text{C–OH} + [\text{O}] \qquad (2)$$

Equation (2) indicates a 1:1 correspondence between these species, and the data in *Figure 6* confirm such a correspondence. Additional hydroxyl could be formed by hydrolysis of the epoxy ring. Unfortunately, a reaction such as equation (2) would be expected to further oxidize the PET surface. Our data show no evidence of such oxidation. Perhaps chain scission occurs, creating volatile PET species by this degradation mechanism.

DISCUSSION

Comparison of the results from air and nitrogen corona treatment shows that the reaction pathways after corona treatment are quite different. However, in general, the populations of chemical species are similar. This similarity may be due to the ageing of both materials in an air environment after CDT.

We saw no evidence for directly bonded nitrogen as $-NH_2$ or $-NR_2$, as Amouroux *et al.*[23] observed. However, they used extremely long treatment times (tens

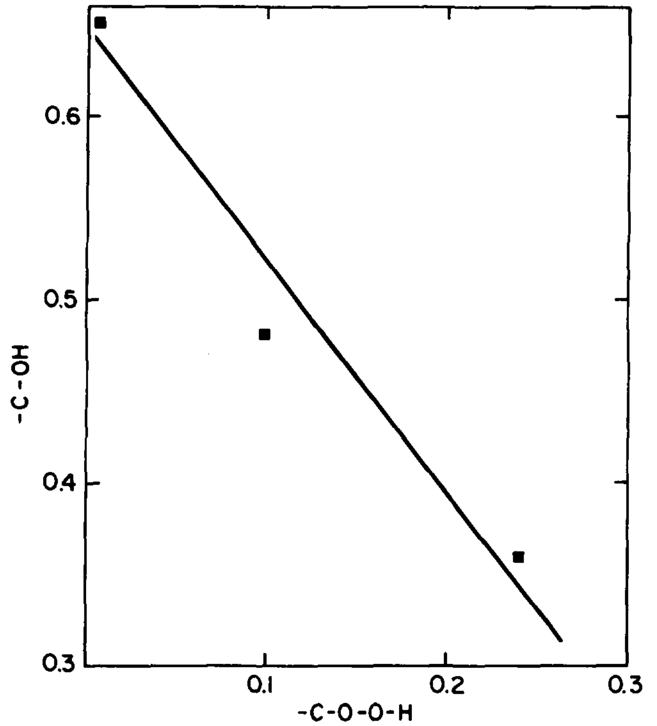


Figure 6 Hydroxyl population *versus* hydroperoxy population for dry-N_2 CDT PET. Numbers based upon initial surface carbon atom population

of minutes) compared with the hundredths of seconds in our experiments. Unfortunately, these derivatization techniques do not account for all of the excess incorporated oxygen. In both cases, ~70% is tagged. We believe that the untagged species are esters and ethers, for which we have not been able to develop a gas-phase e.s.c.a. assay. Halogenation reactions could not be used because of their tendency totally to halogenate the surface of the film.

These results show that corona power high enough to cause oxidation, but not loss of material, or reorientation of surface groups (owing to water washing) incorporates ~4% oxygen. Most of this oxygen is in the form of isolated carbonyl and hydroxyl groups. With long storage of CDT materials, excess surface oxygen is lost.

It is also possible that ring opening can occur, which would create further oxidation sites in PET[12].

CONCLUSIONS

Gas-phase derivatization has been used along with e.s.c.a. to determine corona-discharge-induced chemical species on PET. Dry-air and dry-nitrogen coronas were studied. We showed that: (1) if the CDT power level is kept low enough, few water-soluble species are created; (2) ~4% oxygen is added to the surface with dry-air corona; (3) 75% of the oxidation products are identified as hydroperoxy, epoxy, hydroxyl, carboxylic acid and isolated carbonyl species (with hydroxyl and isolated carbonyl the prevalent species). Short-term time-dependent ageing studies show a one-to-one correspondence between the decrease in hydroperoxy species and the increase in hydroxyl and isolated carbonyl moieties. Reaction sequences are proposed to explain these data. At longer times these surface populations decrease. In general, the results from nitrogen coronas and dry-air coronas are similar.

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