Physico-chemical modifications of superficial regions of low-density polyethylene (LDPE) film under corona discharge

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Using e.s.r., ATR and d.s.c., data on the chemical and structural superficial modifications of LDPE films under corona discharge in the presence of air have been obtained. The results show that the electrical discharge creates superficial ethylenic bonds ($1630 \, cm^{-1}$) and carbonyl groups ($1720 \, cm^{-1}$), the amount of which varies inversely with the main power supply. The treated samples when stored in the presence of light and air undergo marked structural and chemical changes. Formation of a thin waxy layer rich in $> C=O$ and $> C=C <$ bonds with almost total absence of $-CH_2-CH_2-$ groups characteristic of LDPE is observed.

INTRODUCTION

It is well known that corona discharge treatment in the presence of air, or action of oxidizing mixtures, entails substantial morphological and chemical modifications in a surface region of a polymer, such as alteration of external appearance and formation of functional groups[1,2]. Although the magnitude and the nature of these modifications seem to depend on treatment technique and polymer used, the overall aim of these processes is to enhance the adhesive properties of polymers[3].

For corona discharge, which is widely used in industry for polymer treatments, the basic knowledge underlying the modification of material and its influence on adhesion is still lacking and the relevant literature is most controversial[4].

Early studies by Goring et al.[5,6] of discharge-treated LDPE in air, nitrogen and argon, suggested that the increased auto-adhesion is due to electret formation. This theory, however, was rejected by ICI researchers[7]. Using ESCA spectroscopy, they did not observe any surface oxidation of discharge-treated LDPE in hydrogen nor any increase in its autoadhesion after this treatment. The same authors[7] showed that the O/C ratio obtained by ESCA depends on treatment time and that for air discharge-treated samples the uptake of nitrogen (N/C

ratio) is very small. Clark[8] confirmed these results and attributed the effect of LDPE oxidation during the air discharge treatment to
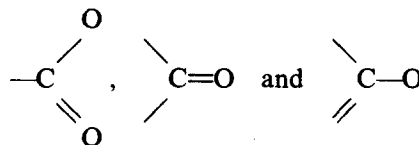
structural features. All these results are also consistent with the work of Amouroux et al.[9], who reported a relation between the treatment time, interelectrode gap-spacing, current intensity, polar component of the polymer, surface free energy (γ_s^p) and the O/C ratio of the air discharge-treated LDPE.

Owens[10] proposed a hydrogen bonding mechanism via enolizable carbonyls, to explain the self-adhesion between corona-treated LDPE films. He demonstrated, using different chemical reactions, that when the weakly acidic terminal hydrogen is substituted by another group, the surface will not adhere to itself. The Owens' theory was confirmed by Briggs and Kendall[11] and by Baszkin and Ter-Minassian-Saraga[12] in their study of the self-adhesion of ($KClO_3 + H_2SO_4$)-treated LDPE surfaces.

Although all these results provide evidence of surface

oxidation during corona treatment of LDPE, more work is required to identify the role of strong interactions occurring in adhesion processes.

Schonhorn and Hansen[13,14], using the surface-treatment technique CASING (cross-linking by activated species of inert gas), demonstrated that a considerable improvement of adhesive joints is primarily due to increasing the mechanical strength of the polymer in the surface region through formation of cross-links and unsaturated groups. The formation of the gel matrix does not affect the wettability of the polymer. It seems, therefore, that interfacial contact is a necessary but not a sufficient condition to form strong joints. Elimination of the weak boundary layer was shown to be necessary to form strong adhesive joints[15].

In previous work[16], paramagnetic probe ions Mn (II) in electron spin resonance spectroscopy (e.s.r.) and attenuated total reflection (ATR) in infrared spectroscopy were used to study the surface modification of LDPE films treated with ($KClO_3 + H_2SO_4$) oxidizing mixtures. It was shown that both techniques are well adapted to investigate the reactivity of ketone $\left(\diagup\!\!\diagdown\!\!C\!\!=\!\!O \right)$ groups created in the surface region of LDPE films before and after their annealing and adhesive joint formation in a heated mechanical press.

In the present paper these two techniques together with differential scanning calorimetry (d.s.c.) were chosen to characterize the superficial region of LDPE treated in a corona discharge in air.

EXPERIMENTAL

Material

Low-density polyethylene, Polyane, film (LDPE) used in this work was additive free but contained 300 ppm of antioxidant. The film is a product of "la Cellophane" (France). It has a thickness of 100 μm and a degree of crystallinity of $\approx 30\%$. Its density at 23°C is 0.918–0.934 g cm^{-3}.

Before corona-discharge treatment, all the samples (150 mm × 150 mm strips) were washed with acetone for 30 min to remove the surface impurities introduced during the processing and handling of the polymer. Then the samples were dried overnight in a desiccator under reduced pressure.

Methods

Corona-discharge treatment. The corona-discharge reactor cell used is shown in *Figure 1*. One of the electrodes is an iron rotating roller (B), 200 mm in diameter, overlapped with mica dielectric and earth
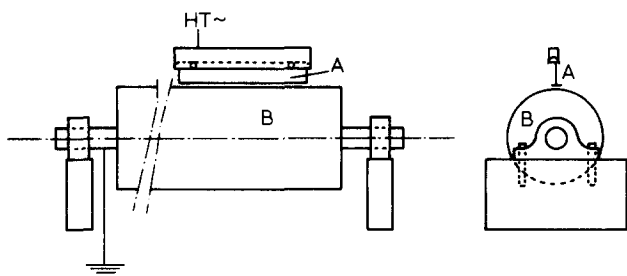

Figure 1 Electrical corona discharge cell. A, Aluminium T-shape electrode; B, iron roller overlapped with a mica dielectric

connected. The second electrode (A), an inverted T-shape aluminium section ($l = 2.5$ mm, $L = 390$ mm), is supplied with an alternating high voltage. LDPE film is stuck on one end of the roller by means of adhesive tape. The gap between the electrodes is adjusted to 1.5 mm, the frequency of the current is 20 kHz and the tension applied to the electrodes is 13 kV. The speed of the roller is 20 rev min^{-1}.

All the discharge experiments were carried out in ambient air, with an industrial-type corona-discharge cell and were as close as possible to the realistic conditions in which corona treatment is used in industry. The relative humidity was 45–55% and the temperature 20°C.

The samples were treated for 1 or 90 s on each face. The main power supply could be adjusted to between 4 and 7.6 W cm^{-2}.

D.s.c. analysis. The apparatus was a Dupont 990 thermal analyser; 5 mg samples and a heating rate of 20°C min^{-1} was used.

E.s.r. spectroscopy. The e.s.r. spectra were obtained using a Bruker BER 400 S spectrometer operating in X band (9.2–10 GHz). The apparatus sensibility being 1.5×10^{11} spin G^{-1}.

The treated samples were immersed in 10^{-1} M MnCl$_2$ aqueous solutions for 18 h then rinsed with methanol and dried.

I.r. spectroscopy (ATR). The infrared spectra were obtained with a Perkin–Elmer 421 spectrophotometer and with a single-beam Wilks Model 9 internal reflection attachment. The KRS-5 crystal of the Wilks attachment had the entrance and exit faces cut at 45° angles.

RESULTS

Electron spin resonance (e.s.r.)

Mn (II) ions were chosen as paramagnetic probes because of their high sensitivity to the electrostatic environment. It is possible from the analysis of their spectra to obtain some information on the covalent or ionic character of their bonding to a substrate.

When LDPE samples are chemically oxidized by a $KICO_3/H_2SO_4$ treatment, a certain number of carbonyl (ketone) groups bind Mn (II) ions through co-ordination bonds[16]. The e.s.r. spectrum (250 G wide) characteristic of such covalently bound Mn (II) ions to surface carbonyls is shown in *Figure 2* and is compared to the chemically oxidized LDPE not treated by MnCl$_2$ solution.

In contrast to the chemically oxidized LDPE and in spite of the fact that $\diagup\!\!\diagdown\!\!C\!\!=\!\!O$ groups are present, corona discharge samples did not bind Mn (II) ions. The e.s.r. spectra of samples treated by corona discharge and by corona discharge + MnCl$_2$ are almost identical. Moreover these two signals do not differ significantly from that of the control sample.

Infrared spectroscopy (ATR)

ATR spectra of a control (untreated) (A) and corona discharge (B) LDPE samples are shown in *Figure 3*. The examination of spectrum (B) shows a broad absorption band in the 3000–3500 cm^{-1} region which is related to OH hydroxyl groups. A band at 1630 cm^{-1} is assigned to
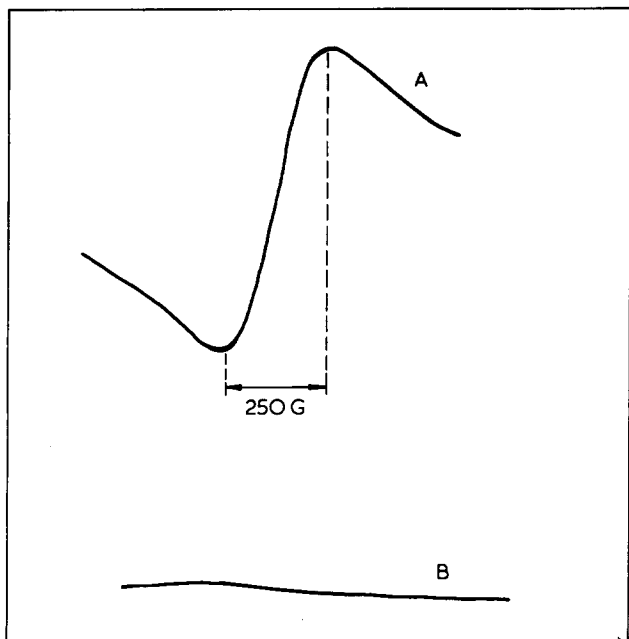
Figure 2 A, E.s.r. spectrum of $KClO_3/H_2SO_4$ oxidized polyethylene. $KClO_3$ concentration in the oxidizing mixture 0.09% (wt/wt); treatment time, 2 min; temp., 23°C; Mn^{2+} ions were adsorbed from $MnCl_2$ 10^{-1} M aqueous solution. B, E.s.r. trace from the same sample as in (A), but not treated by $MnCl_2$ solution
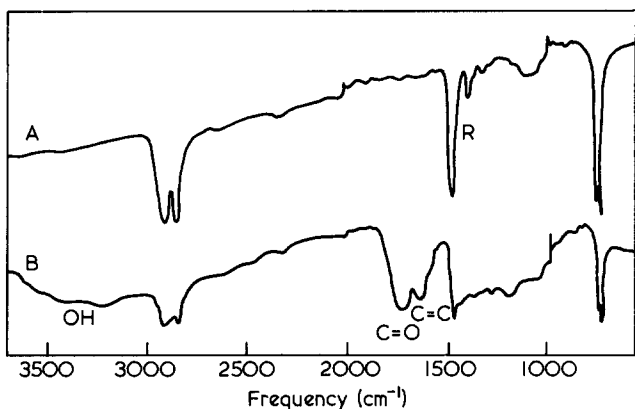

Figure 3 I.r. (ATR) apectra of LDPE films; A, control film; B, corona discharge film in air; treatment time, 90 s; mains power supply, 7.6 W cm^{-2}; R, reference peak

ethylenic double bonds $\left(\!\!\!\!\diagdown\!\!\text{C}\!=\!\text{C}\!\diagup\!\!\!\! \right)$ and the one at 1720 cm^{-1} is characteristic of carbonyl groups. Peak R in *Figure 3* represents the reference band chosen as an internal standard.

Figure 4 shows the absorption bands characteristic of $\diagdown\!\text{C}\!=\!\text{O}$ groups for chemically oxidized ($KClO_3/H_2SO_4$ mixtures) and corona discharge-treated LDPE films. It is noteworthy that the position of the peak at 1720 cm^{-1} for discharge-treated polyethylene is different from that observed (1710 cm^{-1}) in the case of chemically-oxidized sample.

Figure 5 shows the variations of carbonyl groups and ethylenic double bonds as a function of the main power supply in the discharge cell. The quantity of these groups is measured in arbitrary units by means of the ratio D/D_R

(D is the optical density of $\diagdown\!\text{C}\!=\!\text{O}$ or $\diagdown\!\text{C}\!=\!\text{C}\!\diagup$ bands and D_R is that of the reference peak R). The discharge treatment lasted 90 s and the measurements were carried out 1 h later (the time normally necessary to introduce the sample into the apparatus and to carry out the experiment). It is noteworthy that the decrease in $\diagdown\!\text{C}\!=\!\text{O}$ is initially very rapid and then slows. The curve relative to double bonds is similar.

The variation of carbonyl groups and double bonds for a discharge treatment time of 1 s is shown in *Figure 6*. Here the values are much lower than for 90 s treatment
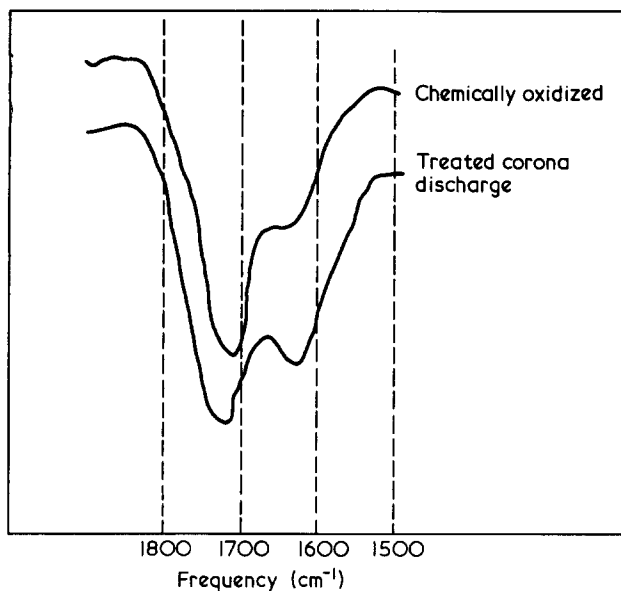

Figure 4 Comparison of the parts of i.r.(ATR) spectra corresponding to carbonyl groups for $KClO_3/H_2SO_4$ (conditions as those in *Figure 2*) and corona discharged in air LDPE film (conditions as those in *Figure 3*)
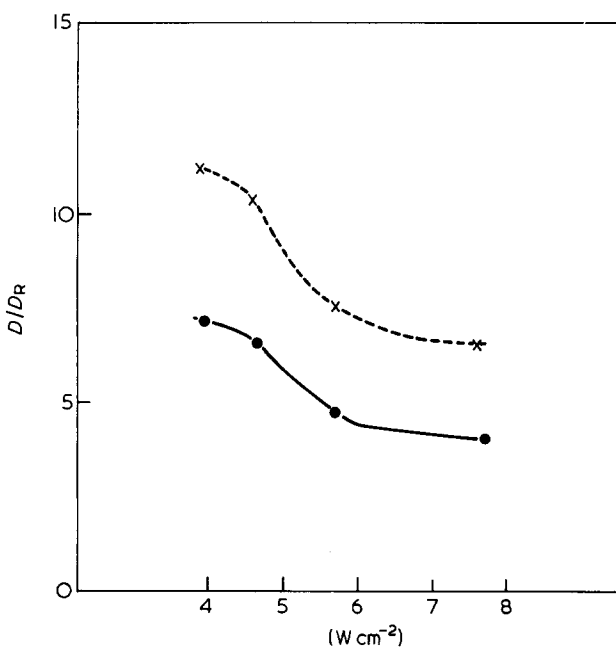

Figure 5 Variation of $>CO$ (×) and $>C=C<$ (●) groups as a function of the main power supply. Corona discharge-treatment time 90 s. Measurements carried out 1 h after treatment

(note that the ordinate scale is multiplied by 5 as compared with *Figure 5*). The curve relative to ethylenic double bonds has a maximum whereas that of carbonyl groups is monotonic with a very small slope.

Figure 7 shows the effect of ageing in air on discharge-treated samples. A marked decrease in the amount of carbonyl groups is observed during the first few days of storing (20°C, 45–55% r.h.). After 7 days an additional although weaker decrease is still observed. The variation in double bonds is insensitive to the storing time. This phenomenon is observed whatever the main power supply in the discharge cell.
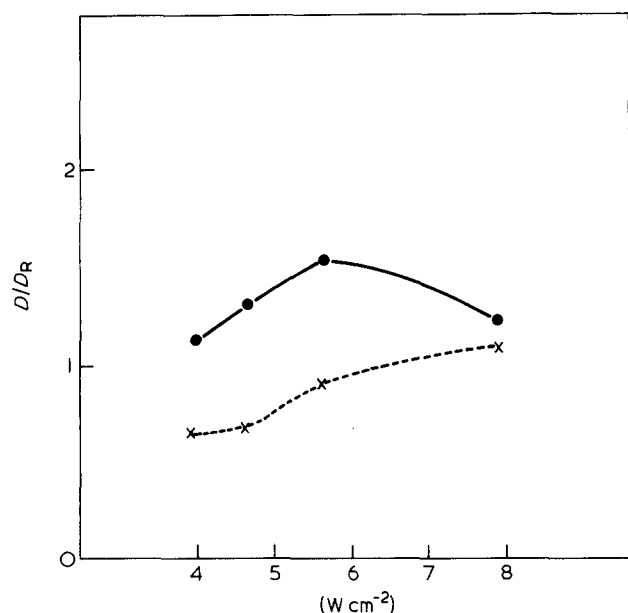

Figure 8 Effect of water immersion on chemical modification of corona discharge treated LDPE. A, I.r.(ATR) spectrum of corona discharge treated in air LDPE; treatment time, 90 s; main power supply, 7.6 W cm^{-2}. B, The same sample after immersion in water during 1 h

Figure 6 Variation of > C=O (×) and > C=C < (●) groups *versus* the main power supply. Corona discharge-treatment time 1 s. Measurements carried out 1 h after treatment
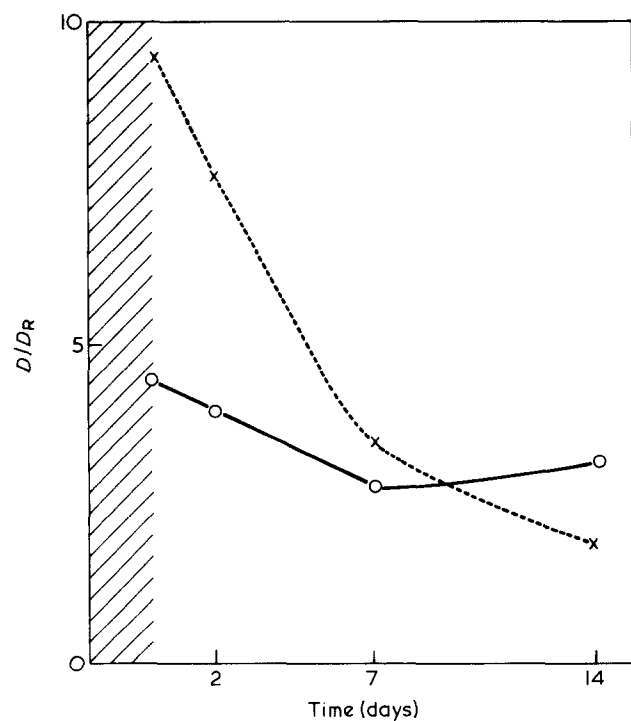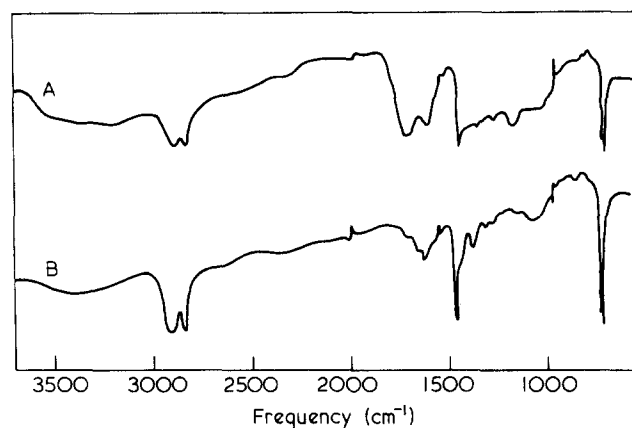
Notwithstanding the presence of carbonyl groups, the e.s.r. data show that Mn^{2+} ions do not bind to the surface of the treated polymer when in contact with the MnCl$_2$ aqueous solution. It appears, therefore, useful to obtain more information about the interactions which occur between water and this modified polymer.

In *Figure 8*, i.r. spectra of two discharge-treated samples are compared. One of these spectra corresponds to a discharge-treated sample examined after 1 h of *immersion* in distilled water and dried under vacuum before ATR measurement (B), while the second spectrum (A) is that of a usual discharge-treated specimen. For the sample immersed in water the bands at 3000–3500 cm^{-1} had not completely disappeared but the 1630 cm^{-1} band is highly attenuated.

If the corona-treated sample is immersed in water for longer, its ATR spectrum is similar to the control one (untreated sample).

Treatment with methanol gives similar results; however, in this case the decrease in the intensity of these bands is much faster.

Differential scanning calorimetry

Scans of control (untreated) and corona discharge-treated LDPE films are shown in *Figure 9*. Both samples present a peak at 109°C corresponding to the fusion of the polymer. Two endothermic transitions described as A and B are evident for the treated sample, while the control has only peak A.

Figure 10 shows the shift of the endothermic peak A during ageing of the treated sample at room temperature in air. Peak B appears to be independent of sample ageing. However, the temperatures at which the peak A appears are lower if the scans are carried out shortly after the discharge treatment.

Initially, the curve increases markedly and then slowly attains an equilibrium.

In *Figure 11* the temperature of endotherm B is plotted against the main power supply in the discharge cell for the treatment times 1 and 90 s. For both curves a rectilinear relation can be observed. It is noteworthy that these two straight lines are very similar.

It is also noteworthy that when an untreated LDPE film was heated in an oven for 1 h at 80°C, the same endotherm B appears as for the corona-treated samples.
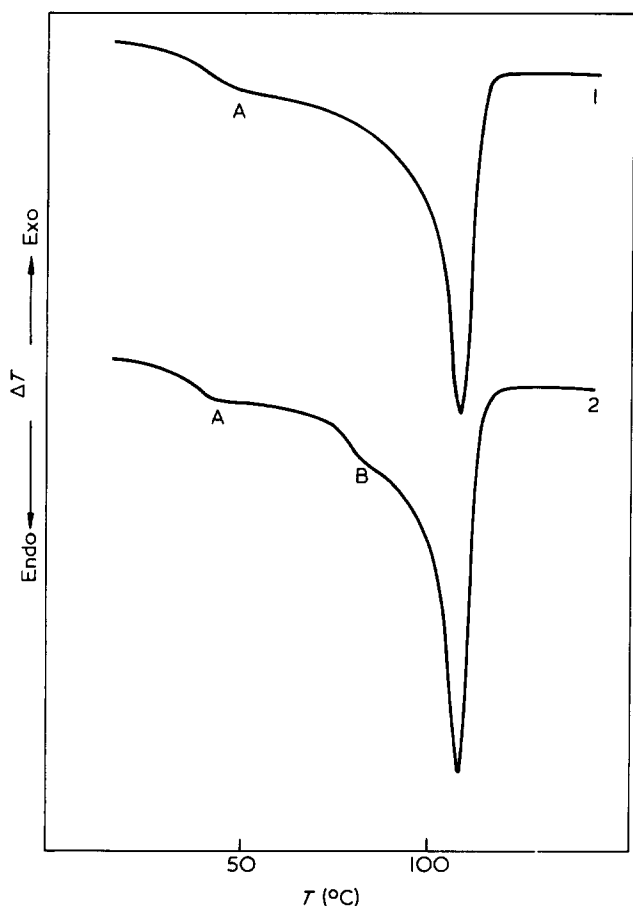

Figure 7 Effect of storing time on amount of > C=O (×) and > C=C < (●) groups. Corona discharge-treatment time, 90 s; main power supply, 4.6 W cm^{-2}

Figure 9 Parts of thermograms corresponding to 1, control, (untreated LDPE sample); 2, corona-discharge treated sample, (conditions as described) in *Figure 3*
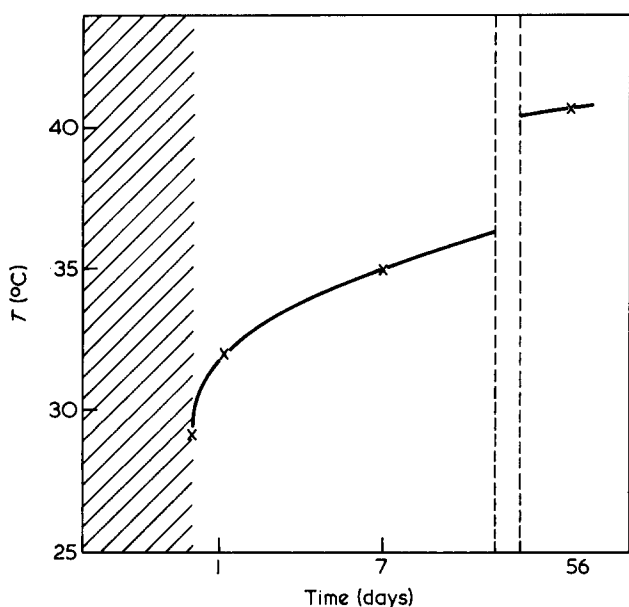

Figure 10 Variation of endotherm A (see *Figure 9*) as a function of storing time. Corona discharge treatment conditions as described in *Figure 3*

DISCUSSION

The results show that under the operating conditions used in this work the action of corona-discharge treatment produces $\diagdown$C$=$C$\diagup$ double bonds and $\diagdown$C$=$O carbonyl

groups represented, respectively, by the appearance of the absorption bands at $1630 \, cm^{-1}$ and at $1720 \, cm^{-1}$ in i.r. spectra. The band at $1720 \, cm^{-1}$ assigned to carbonyl groups is located at a different position from that appearing ($1710 \, cm^{-1}$) on LDPE films treated by a $KClO_3/H_2SO_4$ mixture (see *Figure 4*).

It can be assumed that a part of $\diagdown$C$=$O groups formed during the corona-discharge treatment is of aldehyde or ester type.

In the case of a $KClO_3/H_2SO_4$ oxidation of LDPE, the surface functionality consists of $\diagdown$C$=$O ketone groups.

The e.s.r. results confirm this. For chemically-oxidized LDPE, strong co-ordinated bonds with Mn (II) ions are observed (*Figure 2*).

As the amount of carbonyl groups and ethylenic double bonds varies inversely to the main power supply for 90 s treatment (*Figure 5*), a maximum of polar sites should be obtained, therefore, for the lowest power supplies applied.

Competition effects between oxidizing reactions and decarboxylation of the polymer through chain breaking and CO_2 evacuation may explain the role of the power supply in the discharge process in presence of air[17].

I.r. and d.s.c. data suggest that chemical and structural modifications of corona-treated samples depend on their storage time in ambient air (*Figures 7* and *10*). For chemical modification, i.r. spectra indicate a marked
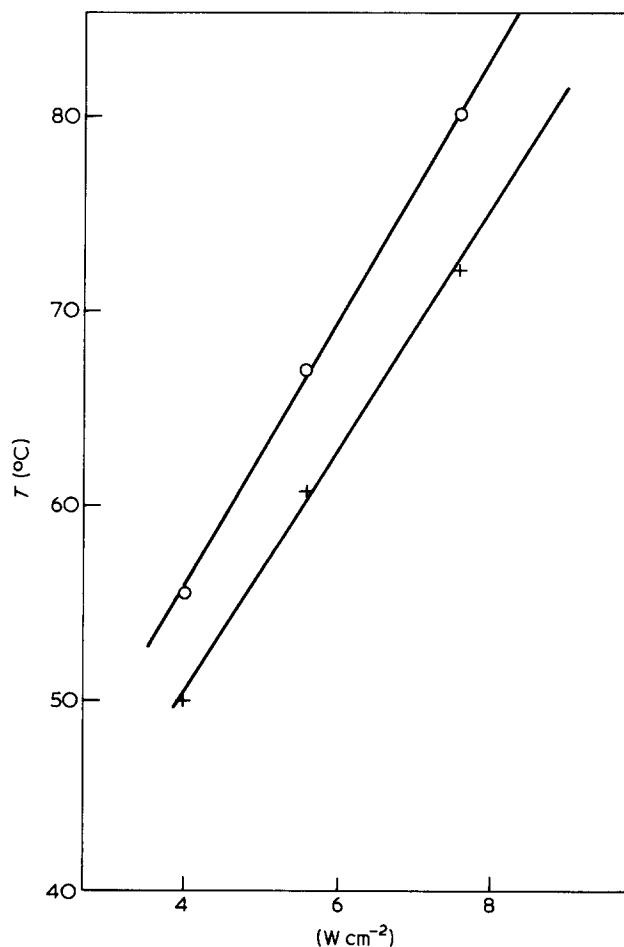

Figure 11 Variation of endotherm B (see *Figure 9*) versus the main power supply for two different treatment times: +, 1; O, 90 s

decrease in the number of $\diagdown$C=O groups after a few days as shown by the decrease in characteristic peak intensity; the ethylenic bonds seem more stable.

Such a phenomenon may be explained by a slow decarboxylation at room temperature and in presence of light and air.

As far as thermal behaviour of treated samples is concerned, the d.s.c. data indicate that the temperature of the A endotherm increases with ageing of the treated sample in ambient air. This endotherm, already present in untreated LDPE samples, originates most probably from partial quenching of the polymer during manufacture. It disappears after the fusion of the polymer followed by slow cooling. Indeed, the fusion temperature of the LDPE is 109°C which suggests a high degree of branching.

It is possible to speculate that the corona-discharge treatment disrupts a certain number of intermolecular bonds, especially in the low-organized microdomains rich in branching. In ambient air and under influence of light a type of 'annealing' occurs probably coupled with cross-linking of the polymer substance. The shift of the temperature of peak A is very rapid at the beginning and then slows. The B endotherm is relatively independent of the treatment time. This suggests that a very rapid trans-formation of the polymer substance takes place under the corona discharge (see *Figure 11*). The observation made during the control test in an oven with untreated LDPE samples confirms this hypothesis. A considerably long annealing time is required to obtain an effect similar to that obtained with a very short corona treatment.

In spite of the fact that the population of polar groups (as shown by i.r. analysis) is high, the manganese ions do not adsorb on corona discharge-treated samples. More-over, the treated surfaces after immersion in H-bonding liquids did not reveal the presence of carbonyl groups (ATR). Thus, it appears that the modification of the superficial regions observed on the LDPE sample during corona treatment have mostly disappeared by action of H-bonding liquids.

Also a thin waxy layer sticks to the KRS5 crystal surface during the i.r. examination and remains on it after the polymer sample is detached from the crystal. This layer can also be stripped off the polymer with a razor blade. The i.r. spectrum and the d.s.c. thermogram of this material are given in *Figure 12*: although the bands at 1720 cm^{-1} ($\diagdown$C=O) and 1630 cm ($\diagdown$C=C$\diagup$) are present, no characteristic band of (–CH$_2$—CH$_2$–) groups can be detected. The d.s.c. thermogram of that waxy layer (*Figures 12* and *9*) demonstrates a marked decrease of the fusion peak of polyethylene (109°C) as well as the presence of an endothermic accident. The second thermo-gram was obtained after stripping of the waxy layer. It is similar to the thermogram of the total treated sample before stripping. Thus, it appears that the heat effect of the discharge will affect not only the superficial region of the polymer but also deeper layers.

These two latter results lead to the conclusion that in these conditions of corona-discharge treatment a thin layer, rich in carbonyl ($\diagdown$C=O) and double bond ($\diagdown$C=C$\diagup$) groups and poor in (–CH$_2$—CH$_2$–) groups,
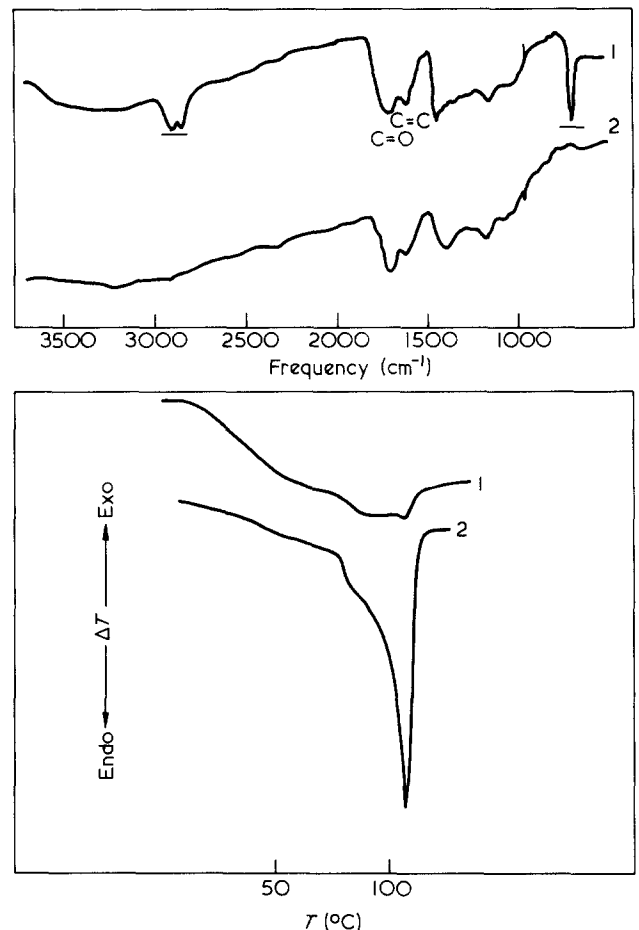

Figure 12 (a) l.r. (ATR) spectra of 1, corona-discharged LDPE sample (conditions as described in *Figure 3*); 2, superficial waxy layer stuck on KRS5 crystal after removing of this sample. (b) D.s.c. Part of thermograms of: 1, corona-discharged LDPE sample superficial layer stripped off the polymer; 2, corona-discharged LDPE sample free of the superficial layer

is formed in the superficial region of the polymer. The substance of this layer would be amorphous while the structure of deeper layers is thermally modified (probably by crystallization).

CONCLUSION

The data obtained using e.s.r., d.s.c. and ATR techniques clearly show the difference between the purely chemical modifications of the material under corona discharge and those relative to the thermal effect.

Only superficial areas of the polymer are chemically modified whereas deeper layers are affected by the thermal contribution of the discharge. Moreover, the treated samples are highly sensitive to storage in the presence of light and air at room temperature.

REFERENCES

1   Mittal, K. L. in 'Microscopic Aspects of Adhesion and Lubrica-tion. Tribology Series 7' (Ed. J. M. Georges), Elsevier, Amster-dam, 1982, p. 153
2   Blais, P., Carlson, D. J., Csullog, G. W. and Wiles, D. M. *J. Colloid Interface Sci.* 1974, **47**, 636
3   Kaelble, D. H. 'Physical Chemistry of Adhesion', Wiley Inter-science, New York, 1971, Ch. 13, p. 456

4   Brewis, D. M. and Briggs, D. *Polymer* 1981, **22**, 7
5   Kim, C. Y., Evans, J. and Goring, D. A. I. *J. Appl. Polym. Sci.* 1971, **15**, 1365
6   Stradal, M. and Goring, D. A. I. *Can. J. Chem. Eng.* 1975, **53**, 427
7   Blythe, A. R., Briggs, D., Kendall, C. R., Rance, D. G. and Zichy, V. J. I. *Polymer* 1978, **19**, 1273
8   Clark, D. T. in 'Polymer Surfaces' (Eds. D. T. Clark and W. J. Feast), J. Wiley, Chichester, 1978, Ch. 16, p. 344
9   Amouroux, J., Goldman, M. and Tran, M. *J. Chim. Phys.* 1978, **75**, 662
10 Owens, D. K. *J. Appl. Polym. Sci.* 1975, **19**, 265

11 Briggs, D. and Kendall, C. R. *Polymer* 1979, **20**, 1053
12 Baszkin, A. and Ter-Minassian-Saraga, L. *Polymer* 1978, **19**, 1083
13 Hansen, R. H. and Schonhorn, H. *J. Polym. Sci.* 1966, **B4**, 203
14 Schonhorn, H. and Hansen, R. H. *J. Appl. Polym. Sci.* 1967, **11**, 1461
15 Schonhorn, H. in 'Polymer Surfaces' (Eds. D. T. Clark and W. J. Feast), J. Wiley, Chichester, 1978, Ch. 10, p. 224
16 Catoire, B., Bouriot, P., Baszkin, A., Ter-Minassian-Saraga, L. and Boissonnade, M. M. *J. Colloid. Interface Sci.* 1981, **79**, 143
17 Hansen, R. H., Pascale, J. V., de Benedictis, T. and Rentzepis, P. M. *J. Polym. Sci. A* 1965, **3**, 2205