Surface modification of polyethylene by electrical discharge treatment and the mechanism of autoadhesion

A. R. Blythe, D. Briggs*, C. R. Kendall, D. G. Rance and V. J. I. Zichy

Imperial Chemical Industries Limited, Plastics Division, Welwyn Garden City, Hertfordshire UK.
(Received 11 April 1978)

A reexamination of previous studies concerning the electrical ('corona') discharge treatment of poly-
ethylene and the resulting enhancement of autoadhesion has been carried out. X-ray photoelectron
spectroscopic data provide new insight into the phenomenon by showing surface oxidation to result
from treatment in 'inert' gases. Treatment in hydrogen is an exception and results in no autoadhesion
enhancement even though energy input into the film is more efficient than in air. Autoadhesion
theories based on electret formation are rejected; those based on hydrogen bonding are largely up-
held and shown to be more generally applicable than at first imagined.

INTRODUCTION

So-called corona discharge treatment of polymer films is a
very widely used industrial process for enhancing their
adhesive properties. However, relatively little definitive
work has been reported to explain the effect of this treat
ment, especially in chemical terms, and the available litera-
ture concentrates on the phenomenon of increased auto-
adhesion of polyethylene. Even within this restricted area
there exists considerable disagreement over experimental
results and their interpretation, this disagreement deriving
in part from the different procedures used. Thus Owens[1]
has reported results from polyethylene treated on a com-
mercial machine for continuous treatment of film whilst
Canadian workers[2-4] have used a specially constructed dis-
charge cell for treating small stationary samples (and have
also investigated the effect of discharge in gases other than
air). The latter workers have rejected several mechanisms
in favour of increased autoadhesion via electret formation,
as the only mechanism capable of explaining *all* their re-
sults. Owens, working only with an air discharge gave good
evidence for a hydrogen bonding mechanism via polar
groups (enolisable carbonyl) introduced into the surface.

Previous spectroscopic investigation of discharge treated
polyethylene has relied solely on internal reflection infra-
red methods (often referred to as a.t.r. or m.i.r.) although
there has been a brief report of X-ray photoelectron spec-
troscopy (X.p.s. or e.s.c.a.) studies of nitrogen discharge
treatment[5]. Previous studies of polymer film surfaces by
Briggs, Brewis and Konieczko[6-9] have demonstrated the
unique contribution which this latter technique can make
to our understanding of adhesion phenomena. In parti-
cular their study of the polyethylene surface resulting from
melting the polymer against aluminium showed[7] that oxida-
tion took place at the interface to a degree correlatable
with the bond strength achieved with an epoxy adhesive.
The absence of any such information in reflection i.r. spec-
tra was one of the reasons for Schonhorn and Ryan's pro-
posal[10] that the elimination of a weak boundary layer (by

means of transcrystallization) explained the increased adhe-
sion to these surfaces. The success of X.p.s. lies in its sur-
face sensitivity. Although the overall sampling depth is
$\sim 10^2$ Å (compared with 10^4–10^5 Å for reflection i.r.)
surface groups constituting <1% monolayer can be detect-
ed. The technique is also highly versatile from a sample
handling viewpoint.

In this paper we attempt to resolve the differences noted
in the literature. Polyethylene film has been discharge
treated in a specially constructed cell using air, nitrogen,
argon and hydrogen (to repeat the Canadian experiments)
and on a commercial machine (for direct comparison with
the 'real life' situation and Owens' experiment). Besides
obtaining heat-seal data we have characterized the surfaces
by X.p.s., m.i.r. and water contact angle.

EXPERIMENTAL

Materials

Polyethylene film used in the discharge cell experiments
was ICI 'Alkathene' 33, a LDPE with an *MFI* of 0.3. The
film examined after treatment on a commercial discharge
treater was ICI 'Alkathene' 47, a LDPE with an *MFI* of 2.0.
Both materials are free of additives. All gases were high
purity (not less than 99.9%) grades from BOC Ltd, used
directly from cylinders.

Method of discharge treatment

A circular parallel-plate electrode cell was adopted, as
shown in *Figure 1* with an electrode diameter of 75 mm.
A pair of 1 mm thick glass plates, 100 mm in diameter,
were used as insulators one adjacent to each electrode,
with three glass blocks acting as spacers to maintain a fixed
air gap of 2 mm. In assembling the cell the film sample
was laid on the lower glass plate and any trapped air
squeezed from underneath it by spraying the top surface
with charge from a 'zerostat' gun (this led to no detectable
effect on the surface properties of the film). The electrodes
were enclosed under a bell jar which could be evacuated
(0.05 torr) and filled with various gases. Typically the
apparatus would be evacuated and purged three times be-

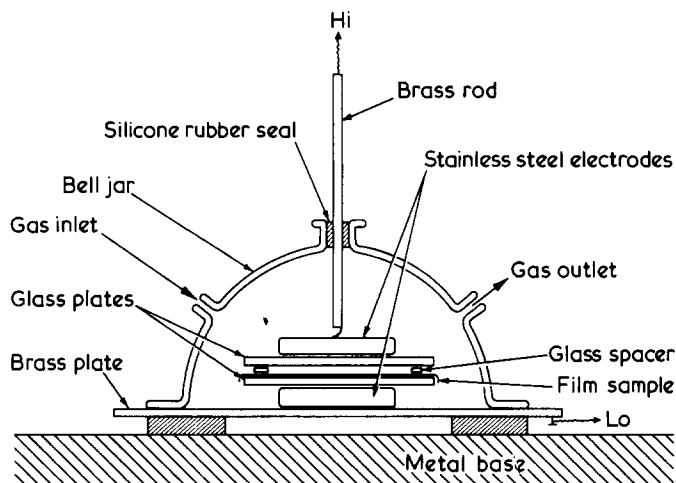* To whom all correspondence should be addressed.

Figure 1 Arrangement of discharge treatment cell

fore allowing gas to flow through the cell. Thus, all runs took place at atmospheric pressure.

The associated electrical circuit is shown in *Figure 2*. High voltage power was supplied by a step-up transformer controlled by a Variac on the mains input (50 Hz). The electrical energy dissipated per cycle in the discharge across the air gap was monitored on the oscilloscope using the method of Manley[11].

Below discharge inception voltages, the high voltage input was a pure sine wave. During discharge, however, the wave form was somewhat distorted by damped oscillations excited in the input circuit by the discharge pulses.

At the beginning of a run the phase between the X and Y inputs to the oscilloscope was adjusted to be zero below the discharge threshold—indicated by a straight line trace on the oscilloscope. After a considerable period of discharge treatment an apparent phase shift—indicated by an elliptical trace—was observed (but seen to disappear gradually). Phase alignment could be restored by dismantling and cleaning the cell. We tentatively conclude that the elliptical trace is evidence of surface conduction over the glass plates brought about by prolonged exposure to discharge conditions.

When carrying out experiments under fixed electrical conditions, referred to as standard conditions below, gap voltages in the middle of the possible range were chosen. These were 13.7 kV (air, N_2), 2.2 kV (Ar) and 6.0 kV (H_2) expressed as peak voltages. The relative humidity of the laboratory air varied between 42–48%.

Measurement of water contact angles

Freshly distilled deionized water was used for all experiments. Constant volume droplets of 1 μl were delivered from the tip of a 5 μl syringe onto the film. 30 sec after dispersion a polaroid photograph was taken of the droplet. This time interval was considered sufficient for the droplet to attain an equilibrium contact angle (θ), yet short enough for evaporation at room temperature to be negligible. Depending on θ the base diameter of the droplet (d) ranged from 1.4–2.0 mm. θ was determined from $\tan \theta/2 = 2h/d$ where h is the drop height. This assumes that the drop forms a segment of a sphere and that gravity distortion is negligible. This is generally considered true for droplets where $d < 0.5$ mm and $\theta < 90°$ [12]. However, in this work, it still remains a good approximation so that an assigned error in θ of $\pm 2°$ takes account of both non-uniformity of the polymer surface and the non-sphericity of the droplets.

X-ray photoelectron spectroscopy (X.p.s.)

An AEI ES200B spectrometer was used which employs an MgKα X-ray source (1253.6 eV) operated at 300 W. Samples were stuck onto the probe tip with double-sided sellotape and trimmed to overlap the tip slightly (7 mm x 20 mm) without touching the area to be examined. The background pressure was $\sim 10^{-8}$ torr. The spectrometer was calibrated such that peaks excited by MgKα and AlKα (an *in situ* impurity line due to electron bombardment of the gun window) were separated by 233.0 eV, giving a Au 4f^7/2 binding energy of 84.0 eV. All peaks are referred arbitrarily to the Cls maximum from the polymer at 285.0 eV to correct for surface charging. *BE*'s are considered accurate to ± 0.2 eV. The analyser was operated in the fixed analyser transmission (*FAT*) mode with a pass energy of 65 V.

Internal reflection infra-red spectroscopy

Spectra were recorded on a Perkin–Elmer 580 double beam ratio recording grating spectrophotometer with ordinate expansion facilities, fitted with a Wilks 9T single beam multiple internal reflection (m.i.r.) attachment (25 internal reflections). A KRS-5 reflection crystal (52.5 x 20 x 2 mm with 45° face angle) was used at a nominal angle of incidence of 45°. Under these conditions the penetration depth is ~ 2.5 μm in the wavelength region of interest[13]. Both surfaces of the reflection plate were covered with a film sample cut to the same size, each backed by a filter paper pad of slightly smaller size. This pad distributes the load provided by the pressure plates of the sample holder, improving sample–element contact and giving increased band intensities. M.i.r. spectra reported below were recorded with an ordinate scale expansion of x5 with a scan speed of 1000 cm^{-1}/4 min and an appropriate instrumental resolution ('integrated scan mode'). Band intensities were measured with reference to non-treated film and an internal reference bond at 1380 cm^{-1} (the latter was recorded without scale expansion).

Measurement of autoadhesion

Samples were sealed using a Sentinel Heat Sealer (Model No. 12AS) at 75°C for 2 sec at a jaw pressure of 15 p.s.i. ($\sim 10^5$ Nm^{-2}). Strips 25 mm wide were cut from the sealed samples, after cooling, and peeled (90°) at a rate of 305 mm/ min on an automatic peel strength testing machine. The reading taken was the maximum value recorded by the digital dynomometer. Average values from at least four such measurements are quoted, in g/25 mm.
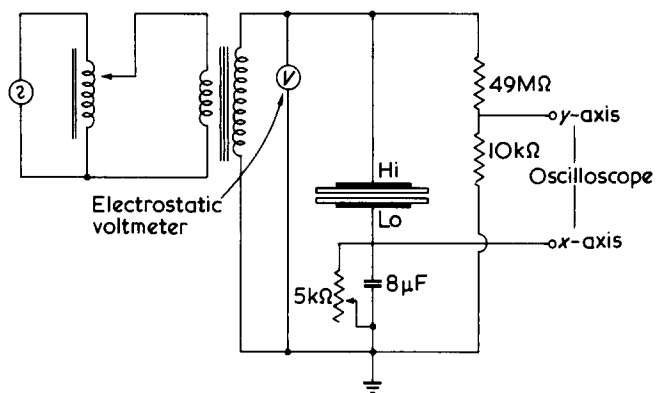

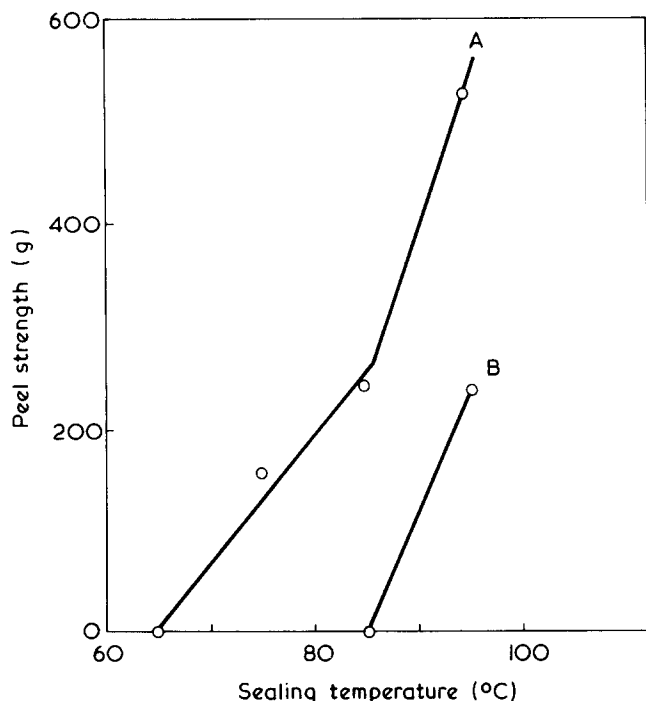*Figure 2* Electrical circuit diagram for discharge treatment system

Figure 3 Variation of peel strength (g/25 mm) with sealing temperature for LDPE film: (A) discharge treated; (B) untreated

RESULTS

Autoadhesion measurements

One point of contention in the literature is the effect of sealing temperature on the level of autoadhesion (hereafter referred to as peel strength). Owens[1] noted a marked dependence (air discharge under commercial treatment conditions) whilst Kim et al.[2] reported only a small dependence for air discharge and a marked dependence for nitrogen discharge treatments. In the latter case no treatment times were given. We carried out experiments with an air discharge under standard conditions for 12 sec. *Figure 3* shows the variation in peel strength with sealing temperature for these films and the untreated film. As will be made clear below these data should be reasonably comparable with Owens[1]; we suspect the data of Kim et al. (for air discharge treatment) result from overtreatment.

Owens' observation that application of H-bonding liquids at the junction of a seal drastically reduced the peel strength was confirmed for specimens treated in air *and* in nitrogen and argon. The reversibility of the effect was confirmed. We also confirmed that heating the treated films prior to sealing reduced autoadhesion. In our case the effect was completely destroyed by heating to 80°C for 3 min.

Figure 4 shows the variation of peel strength with treatment time for the gases used. Note the longer time scale for argon treatment. No autoadhesion could be obtained by hydrogen discharge treatment.

Power consumption measurements

These were carried out in order to check the important conclusion of Stradal and Goring[4] that autoadhesion enhancement is controlled by the power consumed in the discharge, irrespective of the gas used (O_2, N_2, Ar or He). *Figure 5* shows our power *versus* peak voltage curves for air, N_2, Ar and H_2. The curve for air reproduced closely

that previously obtained by Rosenthal and Davis[14], whose experimental procedure we followed. Comparison of *Figures 4* and *5* and noting that peak gap voltages used for *Figure 4* are 13.7 kV (air, N_2) and 2.2 kV (Ar) shows that the energy required to achieve a peel strength of 100 g/ 25 mm is 127, 253 and 164 ml/cm^2 for air, N_2 and Ar, respectively. Thus, although the power consumed in the case of Ar is a factor of 44 lower than in the case of air the energy required to produce a given peel strength is almost the same. The overall variation of a factor of two for all three gases is similar to that found by Stradal and Goring[4]. Note, however, that for any given gap voltage the power consumed in the hydrogen discharge is higher than for other gases. although no autoadhesion can be obtained.

Spectroscopic and contact angle measurements

X.p.s. shows that oxygen is incorporated into the film surface for all the gases used in discharge treatment, except hydrogen. The variation with treatment time is shown in *Figure 6* in terms of the Ols:Cls peak intensity ratio. Also shown is the Nls:Cls ratio for the case of nitrogen discharge treatment (both oxygen and nitrogen introduced). Again, note the longer time scale for argon treatment. In the hydrogen discharge experiments oxygen uptake was insignificant after 30 sec. After 60 sec a trace could be detected, the highest Ols:Cls value observed was 0.02 (an extreme case).
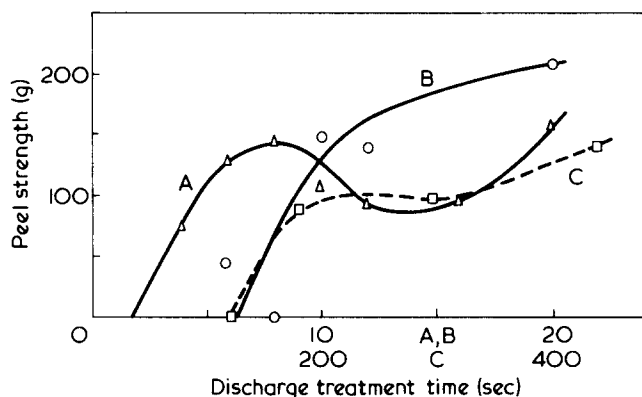

Figure 4 Variation of peel strength (g/25 mm) with discharge treatment time for discharge in air (A), nitrogen (B) and argon (C) (see text for treatment conditions)
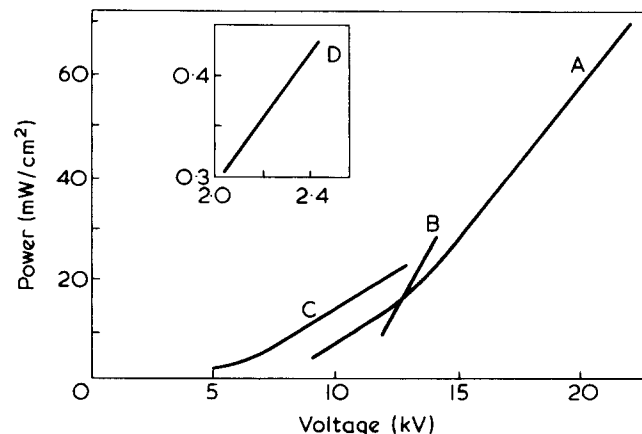

Figure 5 Power consumed in the discharge cell as a function of peak—peak gap voltage for air (A), nitrogen (B), hydrogen (C) and argon (inset (D))
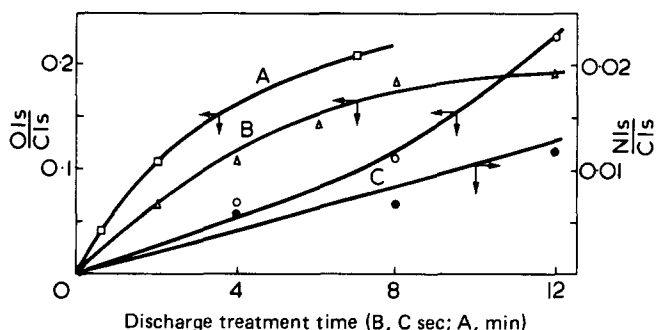
Figure 6 Uptake of oxygen and nitrogen by the polyethylene surface as a function of discharge treatment time for argon (A), air (B) and nitrogen (C). The degree of uptake is measured by normalizing the Ols or Nls peak intensity to that of the Cls peak from the polymer (from X.p.s.)

Table 1 Binding energies of Ols and Nls peaks from X.p.s. of polyethylene surfaces discharge treated under different conditions

Discharge gas	Treatment time (sec)	Binding energy (eV) Ols	Nls	
Air	2	532.3	–	
Air	12	532.5	407.7	
Air	30	533.3	401.5*,	407.8
	Commercial	532.9	400.1,	407.3
Nitrogen	12	532.0	399.9	
Argon	120	532.2	–	
Argon	420	533.2	–	

* Very broad, just detectable

Very small Nls peaks were also observed for air discharge treated samples. These showed a marked time dependence for cell treated samples i.e. rapid loss of intensity with time in the spectrometer. In all cases the Ols signal decreased in intensity during examination, but the effect was relatively slight. All spectra were obtained in a strict time sequence to take account of this effect. *Table 1* gives the binding energies (*BE*s) of these peaks from the different experiments, relative to Cls = 285.0 eV. When oxidation was significant, a high *BE* tail appeared on the side of the primary Cls peak due to carbon atoms in an oxidized form (see below). If surface modification is assessed in terms of oxygen incorporation then the commercially treated sample would correspond to a sample treated in the cell for ~15 sec.

Only in the case of air discharge treatment did m.i.r. detect changes in the film surface within a time scale appropriate to autoadhesion enhancement, in accord with previous literature. The minimum treatment time for which significant spectral changes could be observed (air discharge) was ~4 sec which represents a marked improvement in sensitivity compared with the previous best (as discussed below). Band intensity changes are presented in *Table 2*.

It is interesting to contrast the X.p.s. data with the contact angle curves shown in *Figure 7*. The unusual behaviour of the curve for argon discharge would seem to indicate that oxidation of the surface is much gentler in this case (in agreement with the power dissipation result). We conclude that a higher population of polar groups at the surface may be achieved compared with air and nitrogen discharge where the contact angle plateaus suggesting the occurrence of sub-surface modification. Hydrogen discharge led to only minor changes to θ from that of the pure polymer, the lowest value recorded after 60 sec discharge being 95° (an extreme case).

DISCUSSION

The most important aspect of this work is the discovery that discharge treatment of polyethylene in all gases except hydrogen leads to the incorporation of oxygen functions into the polymer surface, their number increasing with treatment time. Since treatment in hydrogen is unique in not enhancing autoadhesion, it is immediately apparent that this effect goes hand-in-hand with an increase in surface oxidation. Thus discharge treatment, even in nitrogen or noble gases, falls into line with all previous investigations by X.p.s. of treatments which enhance adhesion to polyethylene surfaces[6-9].

The spectroscopic data allow a more detailed picture to be obtained. The Ols binding energy for relatively short treatment times is 532 eV which is consistent with C=O, C–OH, C–O–C[8]. A shoulder begins to appear on the high *BE* side of the Cls peak (*Figure 8*). Its position is also consistent with these groups (Cls chemical shift values are ~1.5 eV for C–OH and ~3.0 eV for C=O[15]). After longer periods of time the Ols peak increases in *BE* which suggests

Table 2 Relative intensities and assignments of i.r. bands for polyethylene discharge treated in air for 4 and 12 sec compared with the untreated material

Band position (cm⁻¹)	Assignment	Relative intensity[a] Untreated	4 sec	12 sec
1720	–C=O	0.017	0.040	0.083
1631	–ONO₂[b]	0.008	0.012	0.038
1065	?[c]	0.076	0.132	0.207
908	–CH=CH₂	0.037	0.028	0.020
969	tr–CH=CH–	0.015	0.011	0.008
890	>C=CH₂	0.173	0.113	0.081

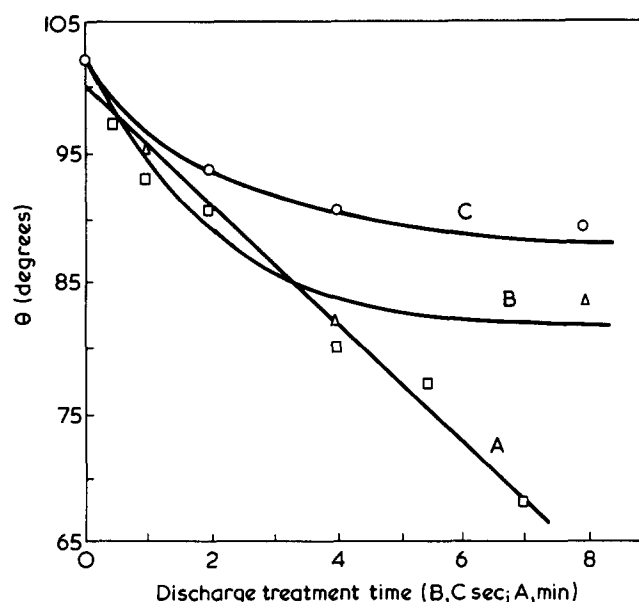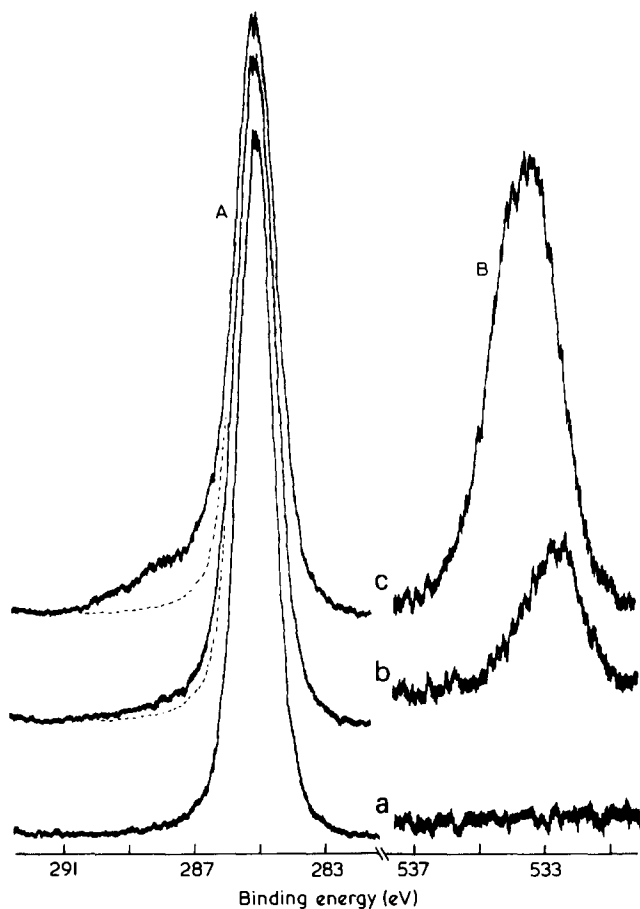[a] See experimental section
[b] N=O asym stretch mode
[c] See discussion

Figure 7 Variation of equilibrium contact angle (θ°) with discharge treatment time for argon (A), air (B) and nitrogen (C) discharge

Figure 8 Binding energies of Cls (A) and Ols (B) peaks for LDPE: (a) untreated; (b) 8 sec discharge in air; (c) 30 sec discharge in air; Count rates are 3×10^3 counts/sec (Cls) and 10^3 counts/sec. (Ols), (high resolution spectra)

higher levels of oxidation, e.g. $-COOH$, esters, since the Ols BE for

$$\underset{-C-O-}{\overset{\overset{\displaystyle O}{\parallel}}{}}$$

is ~ 1.5 eV higher[16] than the oxygen functions mentioned above;

$$\underset{-C-O}{\overset{\overset{\displaystyle \bar{O}}{\parallel}}{}}$$

also occurs at ~ 532 eV. An additional shoulder on the Cls peak (separation ~ 4.5 eV) becomes more apparent which tends to confirm[15]

$$\underset{-C-O-}{\overset{\overset{\displaystyle O}{\parallel}}{}}$$

The nitrogen species observed for treatment in nitrogen has a BE consistent with $-NH_2$ (~ 400.0 eV)[17]. This species is also observed in much lower quantities after air treatment (on the commercial treater only) but under these conditions the main nitrogen species has a much higher BE (~ 407.6 eV). This is too high for $-NO_2$[17] and is thought to be $-ONO_2$. The Nls peak intensity is about 1/30th that of the Ols peak from such a surface.

Relevant portions of the m.i.r. spectra are shown in *Figure 9*. The obvious changes are formation of carbonyl

(keto/carboxyl) and nitrate ester ($-ONO_2$) groups, the growth of a strong band at ~ 1065 cm^{-1} and the reduction in intensity of unsaturation bands (quantified in *Table 2*). Initially (4 sec treatment) the striking feature is the reduction in concentration of vinylidine ($>C=CH_2$) groups, the major unsaturation in LDPE, accompanied by the appearance of a band at 1065 cm^{-1}. The assignment of this band is uncertain. Primary alcohols give a C–OH band in the region of 1050 cm^{-1}. An attempt to confirm this assignment was made by deuteration with D_2O. No band shift was detected, although this is not conclusive since the predicted shift of 5 cm^{-1} is marginal. We postulate the band to be due to an oxygen containing group, possibly a cyclic ether. Support for this assignment comes from Hays'[18] observation of a broad band between 1000 and 1100 cm^{-1} formed when ozone (from a discharge source) reacts with linear polyethylene. This band was ascribed to ozonide groups from reaction with vinyl end groups. Similar groups and/or more stable cyclic ethers formed by crosslinking might be expected from our experiments. The amorphous polymer gives an absorption pattern in the 1070 cm^{-1} region. A change in morphology tends to be ruled out, however, by the fact that annealing a treated sample does not affect this new band; moreover no significant change in polymer surface crystallinity (assessed by the relative intensities of bands at 2016 and 1898 cm^{-1})[19–22] was observed within this time scale.

After 12 sec treatment the carbonyl band and nitrate ester bands are clearly defined (confirmation of the latter's assignment comes from the detection of the accompanying weaker band at 1274 cm^{-1} after longer discharge times). Unsaturation, other than vinylidine, has virtually disappeared.

X.p.s. and m.i.r. data are therefore in good overall agreement as to the chemical nature of the groups produced during discharge in air. M.i.r. data especially focusses attention on the initial attack at points of unsaturation. Over an extended time scale (up to 30 sec treatment) there is a clear correlation between the decrease in intensity of the vinylidene band (890 cm^{-1}) and the increase in intensity of the 1065 cm^{-1} band, which points strongly to this being due to an oxygen function, as discussed above.

The observation of carbonyl groups after air discharge by reflection infra-red spectroscopy is not new. However, it has been shown[4] that this evidence of surface oxidation
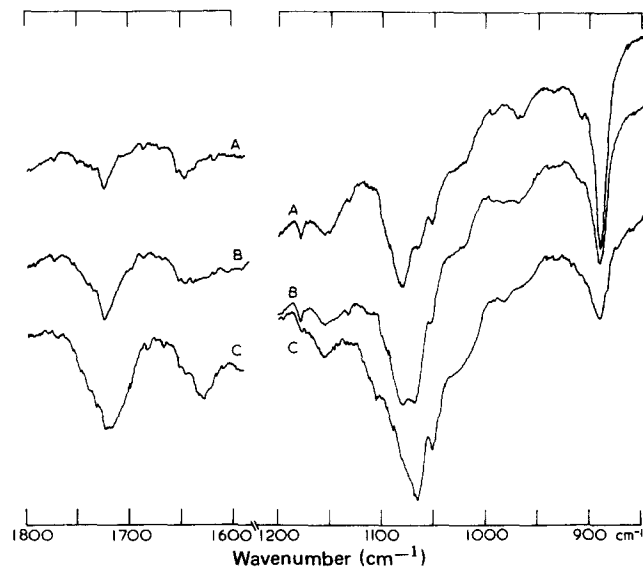
Figure 9 M.i.r. spectra of LDPE: untreated (A), 4 sec discharge in air (B) and 12 sec discharge in air (C)

appears only *after* the optimum level of autoadhesion has been reached. The present data show that this result was an artifact of the method used. The superior m.i.r. spectra from our work show that significant spectral changes can be followed in the range of sub-optimal treatment. X.p.s., however. is even more positive. It follows the change in surface chemistry at very low treatment levels with ease and also detects oxidation during discharge in ·inert· gases where m.i.r. certainly cannot detect any surface modification.

Stradal and Goring[4] have firmly established the dependence of the level of autoadhesion on the power consumed in the discharge, irrespective of the gas used (O_2, N_2, Ar, He). Our own data confirm their results. However, we and others[2] have shown that hydrogen is a major exception. This highly significant result has received scant attention by those workers who propose that electret formation[2,3] is responsible for the autoadhesion effect. Taken together with all the X.p.s. data this result would appear to reject the electret theory completely.

However, it is necessary to discuss the source of oxygen which gives rise to oxidation in inert' atmospheres (neglecting for the moment the possible role of nitrogen containing groups). Although we made no attempt to remove traces of oxygen containing impurities from our gases our observations are quite compatible with those of other workers who did. Therefore we conclude either that their methods were not sufficiently effective or that the oxygen can come from a source other than the gas supply. The only remaining possibilities are the polymer itself and the apparatus. The former contains dissolved oxygen which may not be completely removed by the evacuation and flushing procedures adopted in this work. The latter is usually constructed of glass. Moreover, the electrodes are usually covered with glass plate dielectrics and this material is a ready source of absorbed water molecules. Note that the partial pressure of oxygen containing molecules need only be very small: glow discharge at pressures of ~0.1 torr (even in 'inert' gases) efficiently introduces oxygen functions into polymer surfaces[23].

The lack of oxidation in H_2 suggests either that the oxidizing species present in the system are effectively removed (reduced) or that radicals present on the surface after treatment, which could react on subsequent exposure to air, are quenched. The latter possibility is discredited by the observation that quenching an Ar discharge with hydrogen (simply by switching the gas flow and using the fact that the discharge in H_2 cannot be sustained at the gap voltage used for Ar) gave the same oxidation level (by X.p.s.) as observed for a normal Ar discharge treatment after the same time. A discharge experiment was also carried out in an Ar/H_2 mixture (the relative concentrations were not measured, but the ratio was restricted by the very narrow range of applied voltage over which discharge could be obtained). Although the voltage used was the standard one for Ar discharge the oscilloscope trace was typical of a H_2 discharge (each gas gave a 'fingerprint' trace). The oxidation level after the same time as the other experiments noted above remained the same. This experiment, therefore, casts no further light on the origin of the oxidizing species.

It should be noted at this point that X.p.s. (and m.i.r.) showed that heating air discharge treated films to 80°C for 3 min does not result in a loss of oxygen functions, even

though autoadhesion is lost. Thus, the data presented in this paper are not inconsistent with Owens' theory[1] of autoadhesion, namely that carbonyl groups are produced which can enolise to give hydrogen bonding across the interface, but which H-bond internally if preheated leading to loss of autoadhesion. This is true for discharge in 'inert' gases as well as for air discharge (the only case studied by Owens[1]). However, the driving force behind enolisation is far from obvious. The X.p.s. data suggest that several other H-bonding situations, e.g. involving –OH (non-enolic) or –COOH should be considered (also –NH_2 in the nitrogen discharged surface). We are now attempting a more detailed characterization of the oxygen functions by systematic derivatization experiments.

Although the present work has firmly established the correlation between the changes in surface chemistry brought about by discharge treatment and the degree of autoadhesion, it still leaves open the question of the mechanism by which the discharge produces the chemical change. It should be mentioned however, that the apparent area of treatment is closely bounded by the edges of the metal electrodes. This suggests that exposure to electron or ion bombardment, rather than mere exposure to active species, like atomic oxygen or ozone, is necessary.

REFERENCES

1   Owens, D. K. *J. Appl. Polym. Sci.* 1975, 19, 265
2   Kim, C. Y., Evans, J. and Goring, D. A. I. *J. Appl. Polym. Sci.* 1971, 15, 1365
3   Evans, J. M. *J. Adhes.* 1973, 5, 1 and 29
4   Stradal, M. and Goring, D. A. I. *Can. J. Chem. Eng.* 1975, 53, 427
5   Courval, E. J., Gray, D. E. and Goring, D. A. I. *J. Polym. Sci. (Polym. Lett. Edn)* 1976, 14, 231
6   Briggs, D., Brewis, D. M. and Konieczko, M. B. *J. Mater. Sci.* 1976, 11, 1270
7   Briggs, D., Brewis, D. M. and Konieczko, M. B. *J. Mater. Sci.* 1977, 12, 429
8   Briggs, D., Brewis, D. M. and Konieczko, M. B. *Eur. Polym. J.* 1978, 14, 1
9   Brewis, D. M., Konieczko, M. B. and Briggs, D. 'Adhesion 2' (Ed. K. W. Allen) Applied Science, 1978, p. 77
10 Schonhorn, M. and Ryan, F. W. *J. Polym. Sci. (A-2)* 1968, 6, 231
11 Manley, T. C. *Trans. Electrochem. Soc.* 1943, 84, 83
12 Bartell, F. E. and Zuidema, H. H. *J. Am. Chem. Soc.* 1936, 58, 1449
13 Harrick, N. J. 'Internal Reflection Spectroscopy' Interscience, 1967, p. 30
14 Rosenthal, L. A. and Davis, D. A. *IEEE Trans. Ind. Appl.*, 1975, 1A-11, 328
15 Lindberg, B. J. *J. Electron Spectrosc.* 1974, 5, 149
16 Clark, D. T. and Thomas, M. R. *J. Polym. Sci.* 1976, 14, 1671
17 Siegbahn, K. *et al.* 'ESCA, Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy', Vol 20 Nova Acta Regiae Soc Sci Upsaliensis, Ser. IV, 1967. [NB We have previously shown our *BE*'s to be systematically lower by 1.6–1.7 eV than these (ref 6)]
18 Hays, D. A. 'Dechema-Monographien', Verlag Chemie, 1974, 72, 95
19 Nielson, J. R. and Woollett, A. M. *J. Chem. Phys.* 1957, 26, 1391
20 Krimm, S. *Fortschr. Hochpolym. Forsch.* 1960, 2, 51
21 Okada, T. and Mandelkern, L. *J. Polym. Sci. (A-2)* 1967, 5, 239
22 Nielson, J. R. *J. Polym. Sci. (C)* 1964, 7, 19
23 Yasuda, H., Marsh, H. C., Brandt, S. and Reilley, C. N. *J. Polym. Sci. (Polym. Chem. Edn)* 1977, 15, 991