

Electrical discharge treatment of polypropylene film

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The previously observed, but unexplained, deleterious effect of high relative humidity on the efficiency of electrical ('corona') discharge treatment for rendering polypropylene film printable has been re-examined. The effect of film temperature during treatment has also been studied. A consistent explanation of both effects based on the degree of surface coverage by physically adsorbed water is put forward, supported by X-ray photoelectron spectroscopy analysis of treated film surfaces.

Keywords Polypropylene; corona discharge treatment; X-ray photoelectron spectroscopy; polymer film treatment; adhesion; surface printability

INTRODUCTION

In a series of previous papers from this laboratory¹⁻⁴ the electrical ('corona') discharge treatment of polymer films has been studied with a view to increasing our understanding of (a) the mechanism(s) of polymer surface modification, (b) the precise chemical composition of the modified surface and (c) the nature of adhesive bonding to the treated polymer. X-ray photoelectron spectroscopy (XPS) has played a crucial role in these investigations by providing surface compositional information, particularly *via* derivatization techniques^{2,4} developed specially for this work. To date low density polyethylene (LDPE)^{1,2,4} and poly(ethylene terephthalate) (PET)³ have been studied. In both cases the mechanism of discharge treatment induced enhanced autoadhesion has been shown to depend on H-bonding between carbonyl groups and -OH groups: specifically enolic -OH in the case of LDPE or phenolic -OH in the case of PET. It has also been shown that the adhesion of a commercial nitrocellulose-based printing ink to discharge treated LDPE involves H-bonding *via* enolic -OH in the treated surface². Crosslinking *via* alcoholic -OH groups in the LDPE treated surface has also been studied⁴.

With the exception of the measurement of electrical parameters, particularly the true energy per cycle dissipated in the discharge, these studies have not included variables thought to be important in commercial discharge treatment. These have recently been summarized by Briggs⁵. Two obvious variables are the composition of the ambient atmosphere and temperature (of film and ambient atmosphere). It has been known for many years from the work of Levitzky *et al.*⁶ that discharge treatment of polypropylene (PP) film as a means of improving ink adhesion is significantly affected by relative humidity (r.h.) in the discharge region. These workers found that the discharge energy required to produce printability increased with increase in r.h. More recently r.h. has been shown to be important in the

discharge treatment of LDPE⁷. It is also well known that ozone and oxides of nitrogen are formed in the discharge and that their concentration will depend on air flow rate through the discharge region. There are reports that the thermal history of LDPE and PP film are important to discharge treatment efficiency (thought to be due to morphology effects)^{8,9} and there are numerous references in the patent literature to the effect of film temperature, at the point of discharge treatment, on final surface properties.

In view of the fact that the detailed results of Levitzky *et al.*⁶ on r.h. effects have never been explained we decided to study the above mentioned variables using similar film, namely biaxially oriented polypropylene homopolymer film.

EXPERIMENTAL

Discharge treatment apparatus

The discharge treatment apparatus was purpose built for this study and represents a significant advance on our previous parallel-plate designs¹⁻⁴. The cylindrical treatment cell is shown in *Figure 1*. The film is tightly wrapped around the earthed aluminium core and held in place using a strip of double sided sticky tape attached to the metal. This block is electrically isolated and supported by a PTFE base machined to form an annular plenum chamber from which gas will flow evenly over the film surface. This assembly is surrounded by a glass tube (acting as the dielectric) so that a fixed air gap is created. A spacing device (not shown) can be attached to the top of the Al block to help maintain uniformity of this gap. Alternatively, a PTFE cap which also fulfills this function can be fitted so that the exit gas can be collected or monitored. The high voltage electrode is a thin aluminium plate held tightly around the glass by wire hoops to which the HT lead can be connected. The aluminium core can be electrically heated from within and carries an embedded thermocouple.

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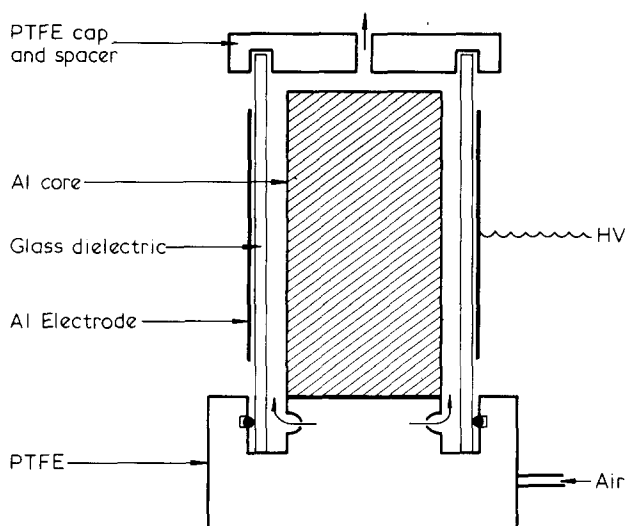


Figure 1 Design of discharge treatment cell

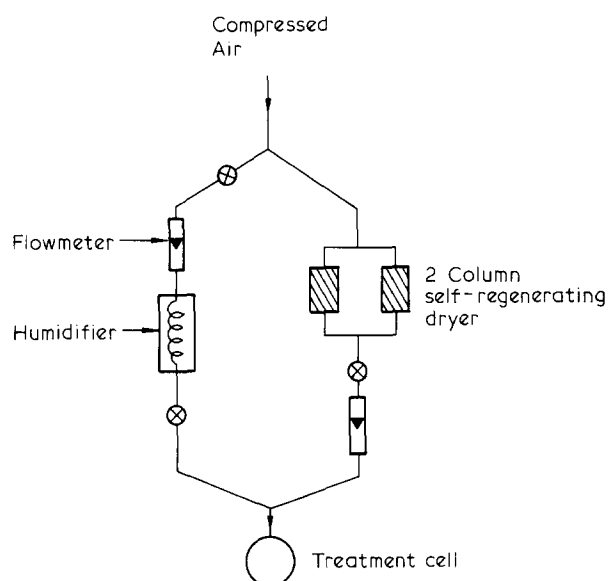


Figure 2 Method for providing air of variable relative humidity to the cell

A compressed air line was set up as shown in Figure 2 to supply air at up to 50 l min^{-1} to the cell. A drying unit reduces the r.h. to $\approx 10\%$ at the cell. Higher r.h. can be produced by admixing a stream of air passed through a humidifying column. R.h. was measured by disconnecting the pipe on the entrance to the cell and attaching a glass tube containing wet and dry thermocouples connected to a 'Comark' temperature recorder. The temperature of the gas entering the cell can be raised by heating the humidifier and pipework to the cell.

Figure 3 shows the electrical circuit associated with the apparatus. A low voltage signal generator (Wayne Kerr S121 AF oscillator) provides a sine-wave input to the power amplifier (Amcron M600) which in turn supplies a variable current/voltage to the primary of the step-up transformer. This was essentially home built using a ferrite core and a secondary winding originally designed for an X-ray generator. The ferrite core gaps can be adjusted to tune the transformer to operate over a range of frequencies, in this case at $\approx 12 \text{ kHz}$.

The power dissipated in the discharge was measured using the oscilloscope technique described previously¹.

X-ray photoelectron spectroscopy

Discharge treated sample surfaces were examined with a VG Scientific Ltd ESCALAB spectrometer using $\text{Mg K}\alpha$ radiation (300W). The electron take-off angle with respect to the sample surface (θ) was $\approx 80^\circ$. Angular variation was restricted by the close proximity of an ion gun to the sample. However, examination of the least oxidized sample (see below) using an AEI ES200B spectrometer showed identical O1s:Cl1s intensity ratios at $\theta = 25^\circ$ and $\theta = 80^\circ$. Thus the surface is homogeneous with the sampling depth of the technique ($\approx 40 \text{ \AA}$). Cl1s and O1s signals were recorded with an analyser pass energy of 6 eV. The much weaker N1s signals were recorded at 25 eV, giving lower resolution but sensitivity greater by a factor of 12. The background pressure during operation was $\approx 10^{-9}$ torr. Charging effects were corrected by referencing all peaks with respect to the Cl1s maximum, assigned to binding energy (BE) = 285.0 eV. Deconvolution was carried out with a Du Pont 310 curve resolver.

Sample transfer from the treatment cell to the instrument was effected as follows. On removal from the metal core the film was immediately doubled (treated side inwards) to avoid dust pick-up on the treated surface. A piece of film cut from the centre of the sample was then stored temporarily under cover (in a petri dish) before being mounted on the sample stub using double-sided adhesive tape. The surface was finally subjected to an air blast before insertion into the instrument. Examination took place within 30 mins of treatment. Care was taken to ensure that each sample came from the same position within the cell to avoid any inhomogeneity of treatment, although very extensive previous studies of LDPE treatment had shown this only to be a problem around the edge of the film. These studies⁴ also showed very reproducible trends in surface composition with degree of treatment which confirms that adventitious contamination during sample transfer is not significant.

Materials

The polymer film was specially made from ICI 'Propathene' homopolymer, being biaxially oriented with a thickness of $21 \mu\text{m}$. The final draw ratios were $\approx 7:1$ (MD) and $\approx 6:1$ (TD).

Discharge treatment assessment

The effectiveness of discharge treatment was monitored by the printability of the film (to parallel the work of Levitzky *et al.*⁶). This was assessed with a commercial nitrocellulose-based ink and the 'sellotape stripping test'¹⁰. Ink retention of 90% or more was designated as adequate printability for the purpose of the experiments discussed herein. Treatments were carried out under fixed conditions of applied voltage (7.5 kV rms) and frequency

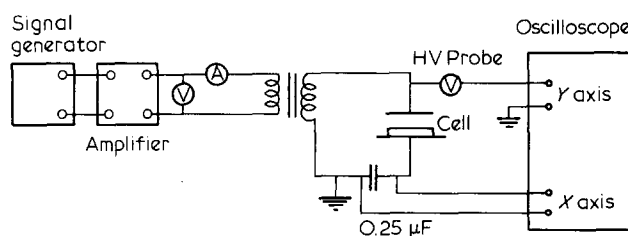


Figure 3 Electrical circuit of the discharge treatment apparatus

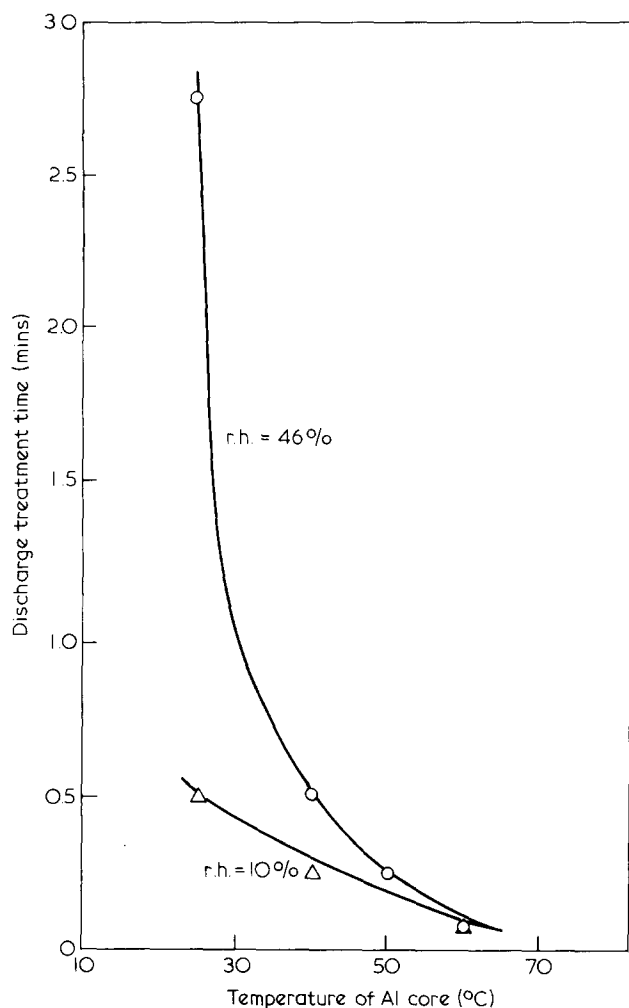


Figure 4 Effect of film temperature on discharge treatment time needed to achieve printability; (O) air at 46% r.h., (Δ) air at \approx 10% r.h. See text for treatment conditions

(12 KHz), the total energy dissipated then being a function of discharge time. Preliminary results under a variety of frequency/voltage conditions suggested that printability depended on air flow-rate through the cell, though in a complex way. Certainly at low frequency (long discharge treatment times) an increase in air flow was beneficial. In this work a gas flow rate of 50 l min^{-1} was used for all gas compositions. Under these conditions the power dissipated in the discharge was 1.3 W cm^{-2} .

RESULTS

Figure 4 shows the effect of film temperature on discharge treatment efficiency (time of treatment required to achieve printability) for two values of r.h.: nominally dry ($< 10\%$ r.h.) and typical of ambient air in the UK (46% r.h.). The dramatic effect of increasing r.h. can be cancelled out by increasing the film temperature.

Figure 5 shows the effect of r.h. over a wide range for various combinations of film and ambient gas temperature.

It has previously been demonstrated that the important electrical parameter in discharge treatment is the total energy dissipated in the gas discharge. Since Figures 4 and 5 are plotted in terms of treatment time, it is important to determine whether the true power dissipation in the discharge is independent of humidity or temperature.

Measurements showed that the power dissipation was constant over the range 30–70% r.h., but slightly lower at very low r.h. (by $\approx 15\%$). As expected the film temperature had no effect on power dissipation at constant r.h.

Figure 6 shows the X-ray photoelectron spectrum in the Cls, Ols and Nls regions from film surfaces treated (7.5 kV rms, 12 kHz) for 5 s in flowing (50 l min^{-1}) or static air both with r.h. of $\approx 10\%$ and 46%. This time was chosen as being the minimum for accurate repetition, the aim being to study the initial changes in surface composition. The same overall trends were observed at higher levels of treatment. The Cls peak has been deconvoluted to reveal the relative contributions to the high BE shoulder, as discussed previously¹. For the untreated surface the Cls peak is symmetrical and oxygen and nitrogen are not detected. The Ols region in all cases contains only a single broad peak which is structurally uninformative. The Nls peaks at $\approx 407.8 \text{ eV}$ and $\approx 406.3 \text{ eV}$ can be confidently assigned to $-\text{ONO}_2$ and $-\text{NO}_2$ groups respectively¹⁴. Lower BE features in this region span the range 399–402 eV and have relatively low intensity except for the case of treatment in flowing dry air. This range covers groups such as $-\text{C}=\text{N}$, $-\text{NH}_2$, $-\text{CONH}_2$, $-\text{CONH}-$ and NH_3^+ , in increasing order of Nls BE^{14,15}. The NH_3^+ function appears to dominate the Nls region ($\approx 401.7 \text{ eV}$) after treatment in flowing dry air. The high BE Nls component was found to be unstable with respect to the instrumental conditions (high vacuum and/or X-ray flux) over a period of some 30 min. The spectra from each sample were

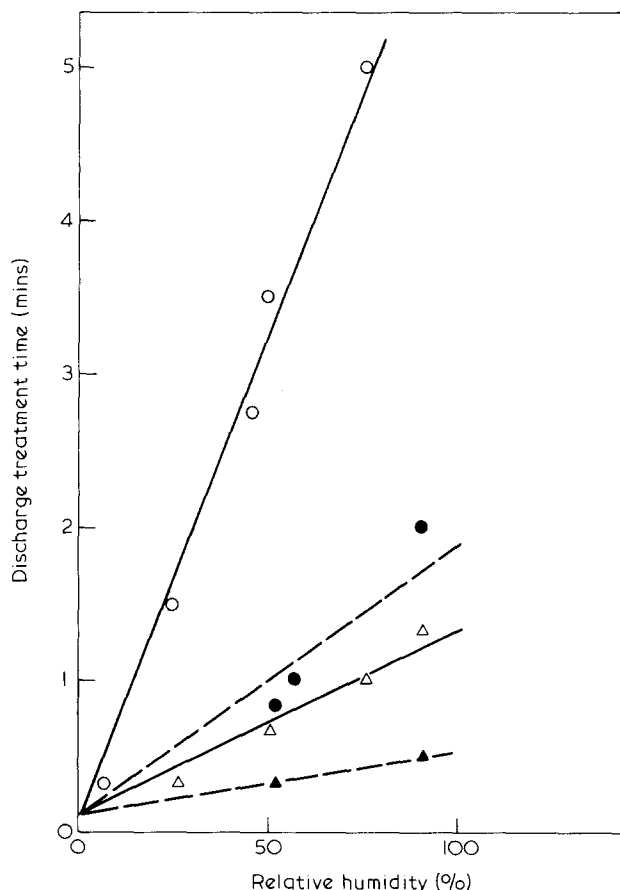


Figure 5 Effect of relative humidity on discharge treatment time needed to achieve printability for various combinations of film and air temperature; (O) film and air $\approx 11^\circ\text{C}$; (●) film 50°C , air $\approx 46^\circ\text{C}$; (Δ) film 50°C , air $\approx 11^\circ\text{C}$; (\blacktriangle) film 50°C , air 36°C . See text for treatment conditions

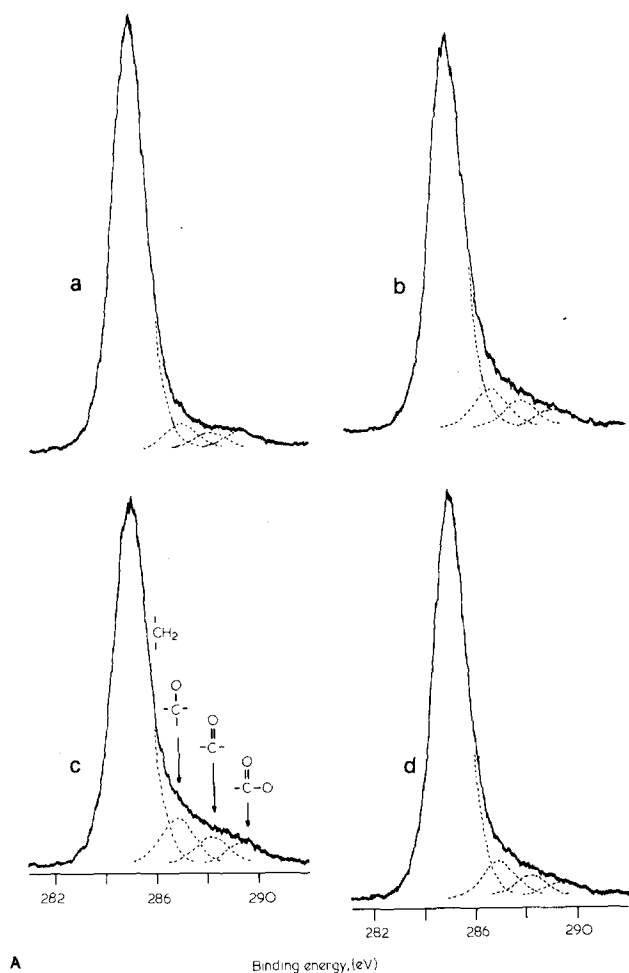
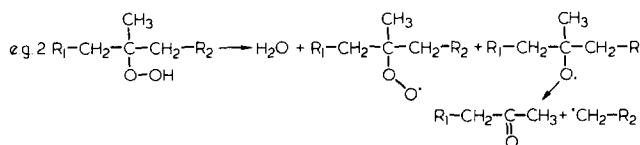
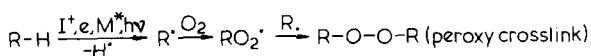


Figure 6A C1s peaks from polypropylene surface after 5 seconds discharge treatment (see text for full conditions). (a) Flowing air, 10% r.h.; (b) static air, 10% r.h. (c) flowing air, 46% r.h., (d) static air, 46% r.h. Count rate = 3×10^3 counts s^{-1} (FSD)

recorded in a strict sequence taking in all ≈ 10 mins. XPS also showed that exposing treated surfaces to alcohol for 1 min removed most (up to 90%) of the oxidized material.

DISCUSSION

It is commonly assumed in the literature that surface oxidation during discharge treatment is *via* a free radical process of the following type:



There is a significant body of evidence, spectroscopic and otherwise, for the introduction of oxygen-containing groups into polymer surfaces consistent with such a mechanism⁵. Recently the key hydroperoxide intermediate has been detected following surface derivatization⁴. This mechanism only involves oxygen as

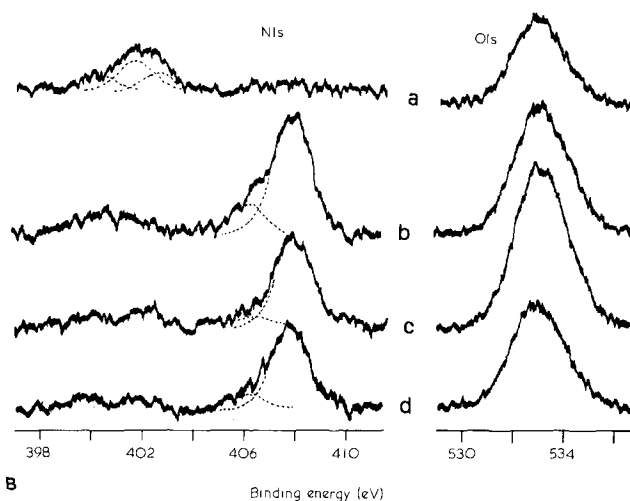


Figure 6B N1s and O1s peaks from treated polypropylene surfaces, as in Figure 6A. Count rate = 3×10^3 counts s^{-1} (FSD). Relative to C1s and O1s peaks the N1s peak was obtained under conditions of higher sensitivity (X 12)

a reactive species but clearly other possibilities exist for the introduction of oxygen functionalities into the surface, namely through reaction with water, ozone, oxides of nitrogen, nitric acid and radicals derived from them.

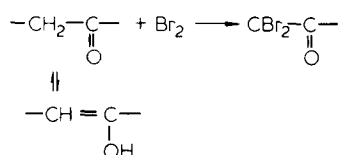
It is clear from Figure 6 that the composition of the gas in the discharge markedly affects the chemistry of the modified polymer surface. In particular, there is least oxidation when a dry air flow is used and the high BE Cls structure indicates that the incorporation of carboxyl groups, as a proportion of all oxygen functions, is greatest in this case. Oxidation is greatest in the case of flowing wet air, and the surface composition is then more similar to that obtained with static air (wet or dry). However, discharge treatment in wet air (static or flowing) leads to a proportionally higher concentration of groups containing C-O (alcohol, ether etc.) than does treatment in dry air. The introduction of oxidized nitrogen groups ($-NO_2$ and $-ONO_2$) shows that species formed in the discharge *via* radical or ion-molecule reactions interact with the film surface. This is to be expected under static conditions when a significant concentration of these species can build up. In flowing dry air these groups are not detected, but in flowing wet air they are detected and this points to nitration reactions occurring *via* nitric acid which is 'rained out' onto the film surface. It can reasonably be inferred from these observations that ozonolysis will occur, especially under static conditions, and that direct reactions with adsorbed water will also take place.

An attempt has been made to obtain a more quantitative picture. Using sensitivity functions derived from studies of pure polymers and taking into account the contribution of oxidized nitrogen functions to be O1s envelope the O:C atomic ratios (O only from groups with oxygen bound to carbon) corresponding to Figure 6 (a-d) are 0.11, 0.16, 0.21 and 0.13 respectively. Comparison of the total high BE portion of the Cls signal (C_0) with the O1s signal allows an overall stoichiometry for functional groups containing oxygen only to be calculated ($O:C_0$). In all cases this is between 1.2-1.3 (maximum value for flowing dry air), but it must be emphasized that the value is very sensitive to the corrections for $-ONO_2$ groups. (The highest level of N observed corresponds to N:C (atomic) ≈ 0.02 .) Besides contributing to the O1s signal the

group induces a shift in the Cls *BE* of ≈ 2 eV¹⁴, hence C-ONO₂ groups are contained within the high *BE* Cls envelope and must be subtracted. The crude deconvolution of the C₀ envelope allows a value of O:C₀ to be calculated assuming the peaks labelled C-O, C=O and $\begin{array}{c} \text{O} \\ \diagup \\ \text{C}=\text{O} \end{array}$ do derive only from groups with these stoichiometries. Again in all cases the values are between 1.2–1.3. This does little to clarify the situation since there is so much potential redundancy in the deconvolution. In particular (see below) it is not possible to distinguish between C-OH and C-O-O-C since both have a *BE* shift of ≈ 1.5 eV and O:C of 1.0. It does suggest however that groups such as C-OOH and -O-C-O- cannot be present at very high levels.

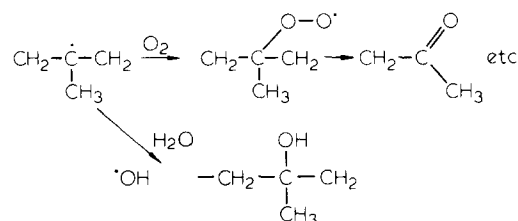
The physical adsorption of water onto a hydrocarbon surface (polyethylene) has been described in the literature¹¹, the surface coverage being a function of the partial vapour pressure of water above the surface. There is no reason to believe that polypropylene would behave differently. In our system where the air is never saturated surface coverage will therefore increase with r.h. for any given temperature of film and air. However, for film temperatures greater than the air temperature the surface coverage at any given r.h. will decrease as the film temperature increases. Whence we may conclude that the data in *Figures 4* and *5* are consistent with the assumption that the surface coverage of adsorbed water is important in controlling discharge treatment efficiency (for producing a printable surface). *Figure 4* is straightforward but *Figure 5* requires some explanation. The two solid lines again reflect the effect of increasing film temperature at constant r.h. For all three lower lines the temperature of the Al core was 50°C although the actual film surface temperature is governed by the temperature of the flowing air. Thus the 'film 50°C/air 11°C' experiment overestimates the film surface temperature by an unknown amount. This is counteracted by increasing the air temperature (two broken lines) but at the same time the water vapour partial pressure increases for any given r.h. Hence the relative positions of the two broken lines. These three lines for a nominal film temperature of 50°C serve to underline the changes in treatment efficiency produced by combinations of quite subtle changes which affect the adsorbed water coverage of the film surface.

It remains to explain why adsorbed water affects the efficiency of discharge treatment for making polypropylene film printable. XPS clearly shows that the surface chemistry is affected. In our previous studies of polyethylene discharge treatment we showed^{2,4} that enolic -OH groups, produced by enolization of ketonic or aldehydic carbonyl groups, are crucial to the adhesion of the printing ink used (the same ink was used in this work). The most rapid test of this effect is to react the discharge treated surface with Br₂/H₂O. The bromination reaction:



prevents enolization and the surface completely loses its printability. PP gives the same result as LDPE. There is a simultaneous drop in wettability which is undoubtedly

due to the removal of low molecular weight oxidized material (shown by XPS). However, exposure to the solvents used in the reaction and in subsequent washing of the film (water and ethanol) has the same effect on wettability *without* affecting printability. The carbonyl (whence enolic -OH) groups arising *via* the hydroperoxide mechanism noted above are therefore the critical functionality. It can easily be envisaged that reaction of chain radicals with oxygen will be prevented by the competitive reaction with water (or OH radical) which is on (or very close to) the polymer surface. This will lead to a greater proportion of alcoholic -OH groups in the surface:



This change in surface chemistry is consistent with the XPS data from surfaces treated in flowing wet and dry air. The alcoholic -OH groups are not involved in printing ink adhesion.

It is also necessary for good print adhesion that the enolic -OH groups be firmly attached to the surface. Therefore molecular weight changes which occur during discharge treatment play a crucial role too. The β -substituted back-bone in PP lends itself to chain scission during oxidation, but it is also known that PP crosslinks in oxygen containing plasmas¹². The balance of degradation and crosslinking will also be upset by competitive reactions of chain radicals with water. As the above schemes show the formation of peroxy cross links will be prevented. We have noted that high r.h. tends to promote the appearance of a frosted surface during discharge treatment of PP and a similar observation has been reported for LDPE^{7b}. Since film clarity is restored by surface washing, low molecular weight oxidized material is implicated. Microscopic evidence confirms this view^{7b,13}.

In summary, therefore, we believe adsorbed water can give rise to effects on surface chemistry and molecular weight both of which will be disadvantageous to achieving printable film. In view of the fact that much of the oxidized material is of low molecular weight (shown by XPS) it seems likely that the dominant role of water is the prevention of peroxy crosslinking reactions. The fact that increasing the discharge energy sufficiently can overcome the problem for high r.h. conditions (as discovered by Levitzky *et al.*⁶, and confirmed by these studies) suggests that the surface equilibrium is not maintained in contact with the plasma and that eventually the adsorbed water is removed by reaction or direct sputtering.

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