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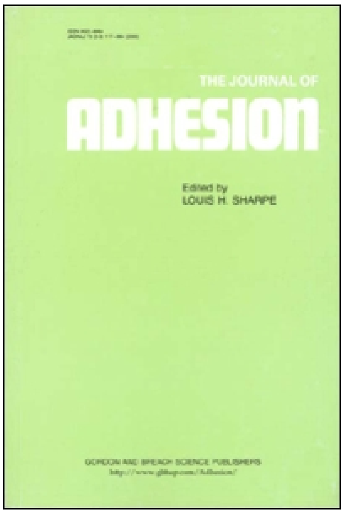

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XPS Studies of Polymer Surface Modifications and Adhesion Mechanisms

D. Briggs[a]
[a] Petrochemicals and Plastics Division-Welwyn Garden City, Imperial Chemical Industries Limited, Herts, U. K.

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XPS Studies of Polymer Surface Modifications and Adhesion Mechanisms

D. BRIGGS
Imperial Chemical Industries Limited, Petrochemicals and Plastics Division—Welwyn Garden City, Herts, U.K.

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XPS has been used to elucidate the mechanisms of surface modification of low density polyethylene by electrical ("corona") discharge treatment and by chromic acid treatment. The use of derivatisation techniques for improving the precision of functional group analysis is described. These techniques also allow the role of specific interactions in adhesion to discharge treated surfaces to be investigated. The role of residual Cr on the adhesion of deposited metal to polymer surfaces is discussed.

INTRODUCTION

The rapid growth in the use of plastics owes much to the relative ease, compared with conventional materials, with which they can be processed. However, many products having ideal bulk properties have non-ideal surface properties which would restrict their ultimate range of application. Most importantly the surfaces of many polymeric materials, especially polyolefins, pose several problems in adhesion situations. Although the reasons why this should be so are still the subject of debate,[1] empirical solutions have been developed. These "pre-treatments" are poorly understood in terms of how they modify the polymer surface and why they improve adhesion.[2] During the last few years Briggs and co-workers have undertaken[3–11] a systematic re-examination of pre-treatment effects using XPS; some aspects of two of these studies will be discussed.

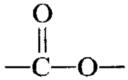
Presented at the Annual Meeting of The Adhesion Society, Savannah, GA, U.S.A., February 22–25, 1981.

Electrical discharge treatment

Electrical ("corona") discharge treatment of polyethylene and polypropylene film has been used for many years in order to render these surfaces printable and suitable for lamination or coating. In this process the polymer film is passed over an earthed metal roller covered with a "dielectric" (insulating) material. Separated from the film by $\simeq 2$ mm is an electrode bar to which a high voltage is applied (typically 15 kV at 20 KHz). Air in the film-electrode gap is ionised, the corona discharge thus formed is stable and this "treats" the film surface.

Discharge treatment of low-density polyethylene (LDPE) has been studied by many workers, particularly with reference to the autoadhesion enhancement effect. LDPE autoadheres when two surfaces are contacted under pressure at temperatures above $\simeq 90°C$. However after fairly low levels of discharge treatment, treated surfaces will autoadhere at significantly lower temperatures ($\simeq 70°C$). Two theories had been proposed to account for this effect. The first, due to Canadian workers,[12] suggested that electret formation was involved—the resulting increased adhesion being electrostatic in nature. The evidence for this was that discharge treatment in both "active" (air, O_2) and "inert" (N_2, Ar, He) gases gave the effect, its magnitude being related to the power dissipated in the discharge irrespective of which gas. Moreover the maximum effect was achieved in oxidising atmospheres before ATR-IR spectroscopy could detect any surface oxidation. The second, diametrically opposed theory due to Owens,[13] suggested that hydrogen bonding between polar groups formed by the discharge treatment was responsible. The effects of reacting treated surfaces with specific chemical agents and noting subsequent adhesive characteristics suggested a specific interaction between carbonyl (keto, aldehydo) and tautomeric enol functions across the interface. However, only LDPE treated in air was studied.

In our work[7] discharge treatment was carried out in a model apparatus with static film samples and at low frequency (50 Hz). As Figure 1 demonstrates, XPS showed[7] that treatment in air, N_2 and Ar (at atmospheric pressure) leads to surface chemical changes including oxidation in all cases. Clearly treatment in Ar requires longer but power dissipation measurements confirmed the earlier result[12] that the power required to achieve a given level of autoadhesion (peel strength) was independent of the gas. It is also clear from Figure 1 that this corresponds roughly to the same degree of surface oxidation. Experiments were also carried out using a hydrogen discharge; this did not produce the autoadhesion enhancement effect and XPS did not detect surface oxidation. On the basis of these results the electret theory can be discounted, but the Owen's theory is given a firmer foundation. Figure 2 shows typical spectra for LDPE discharge treated in air.[7] A simple deconvolution of the high binding energy shoulder on the C1s peak gives three peaks which can be ascribed to $—CH_2O—$ (*e.g.*, alcohol, ether, ester, hydroperoxide) at ≃286.5 eV, $>C{=}O$ (*e.g.*, aldehyde, ketone) at ≃288.0 eV and



$$—\overset{\overset{\large O}{\|}}{C}—O—$$

(carboxylic acid or ester) at ≃289.5 eV. The O1s peak is even less informative. Most oxygen functional groups give O1s BE's of ≃532 eV, the exception is the ester oxygen in carboxyl groups at ≃533.5 eV. The shift in the O1s peak, shown in Figure 2, with increasing oxidation reflects the increasing relative concentration of carboxyl groups. Clearly this information is not specific

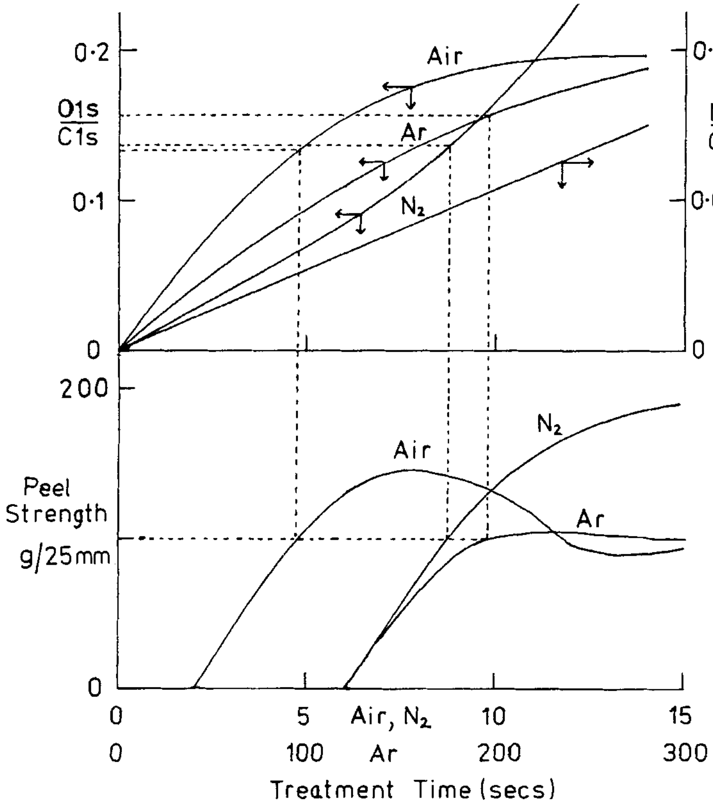


FIGURE 1 Variation of autoadhesion of LDPE (peel strength for seals made at 75° (2 sec, 15 psi)) and surface chemistry with discharge treatment time in air, nitrogen (50 Hz, 13.7 kV) and argon (50 Hz, 2.2 kV). The O1s : C1s intensity ratio is a qualitative measure of surface oxidation. Note the similar values of this parameter for surfaces giving 100 g peel strength—dotted lines. The N1s : C1s ratio was measured for films treated in N_2 only.

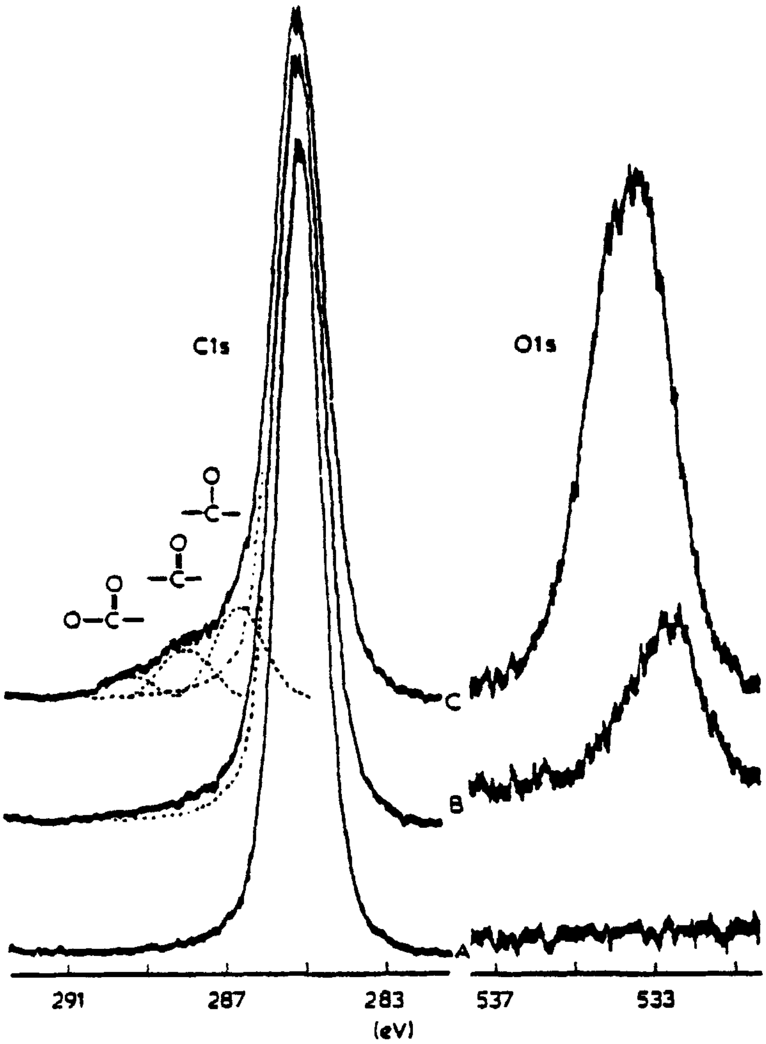


FIGURE 2 C1s and O1s peaks for LDPE treated at 50 Hz, 13.7 kV in air for (a) 0 sec (b) 8 sec and (c) 30 sec respectively.

enough to probe the detailed structure of the oxidised layer or to allow correlations to be made with the autoadhesion results. To overcome this problem a series of derivatisation reactions have been devised to label specific functional groups. The criteria for successful derivatisation are rather stringent and can be listed as follows:

1) the reagent must undergo a specific reaction with a particular functional group and introduce into the surface a heteroatom "label", preferably an element with a high cross-section for X-ray photoemission;

2) the derivatising reaction should proceed rapidly under mild conditions;

3) solvents, if necessary, must be benign.

Conditions (2) and (3) are the most difficult to meet. Reactions which proceed rapidly at room temperature in the solution phase are often sterically hindered in the polymer surface layers. Solvents which permeate into the polymer are likely to aid reaction but may, at the same time, give rise to surface reorganisation, *e.g.*, functional group migration into the bulk.

These effects have recently been studied by Everhart and Reilley.[14] Solvents may also extract lower molecular weight material produced during the surface modification process.

The solvent-type reaction conditions described above are to some extent a compromise between achieving complete derivatisation of the modified surface (which angular variation XPS experiments show to have a thickness comparable with the sampling depth of the technique) and avoiding solvent attack on the very material under study. They are the result of many experiments, which also showed that reproducibility was very dependent on the use of fresh solutions of the derivatising agent. We believe that derivatisation has reached a high degree of completion (compared with the "infinity" result under the conditions used).

Table I summarises the reactions taking place with the reagents used in this study. The derivatisation of aldehydo- or keto-carbonyl groups with pentafluorophenylhydrazine (PFPH), or hydrogen atoms in methylene groups adjacent to these carbonyls (α—H) with Br_2 and of carboxylic acid groups with NaOH have been discussed previously.[8] Br_2 also reacts with unsaturation in the polymer and in quantification the "blank" value for Br uptake was subtracted from that of the modified polymer (assuming discharge treatment does not affect double bonds). Full experimental details for the other reactions can be found in Ref. 11.

Acid chlorides react potentially with alcoholic —OH and also with the enol tautomer of the above-mentioned carbonyl groups (the equilibrium would normally be heavily in favour of the carbonyl). Under the conditions used with chloroacetylchloride (CAC) it seems that the —OH reaction is predominantly with the enolic —OH (see below). The search for a mild derivatising reagent for alcoholic —OH eventually led to the reagent di-isopropoxide titanium bisacetylacetonate (TAA) which is sold as an adhesion promoting, OH cross-linking, agent. The evidence from carrying out multiple reactions, discussed below, is that this reagent does not derivatise enolic —OH. Prior reaction of a surface with NaOH to remove carboxylic —OH did not markedly affect the

TABLE II

Quantification of functional groups

Reaction	XPS ratio† (core level/C1s)	Atomic ratio (element/carbon)	Number of functional group per original Surface —CH2—
PFPH	(F1s) 0.205	5.5×10^{-2}	>C=O, 1·1 × 10^{-2}
Br_2/H_2O	(Br3d) 3.6×10^{-2}	10.6×10^{-3}	CH_2C=O, 5.3×10^{-3}
CAC	(C12p) 1.3×10^{-2}	6.0×10^{-3}	C—OH, 6.0×10^{-3}
TAA	(Ti2p3/2) 6.2×10^{-2}	1.5×10^{-2}	C—OH, 1.5×10^{-2}
NaOH	(Na1s) 8.8×10^{-2}	1.1×10^{-2}	—COOH, 1.1×10^{-2}
SO_2	(S2p) 7.6×10^{-3}	4.7×10^{-3}	C—OOH, 4.7×10^{-3}
None	(O1s) 0.209	8.7×10^{-2}	

† Estimated error ±5% for a given sample, ±15% for the complete experiment.

be comparable, as is observed. The raw C1s spectra tend to show broadly similar intensities for the C—OH (etc.), >C=O and —COOH regions which is also borne out by these results. The total assay of >C=O, C—OH and COOH groups would give an atomic O:C ratio of 5.7×10^{-2}, where "C" is the carbon atoms in the original surface. This compares with the actual value of 8.7×10^{-2} from the discharge treated surface. Considering that ether and ester groups are also likely to be present, in numbers comparable to the groups which have been derivatised, this assay is seen to be entirely reasonable. The apparent internal consistency of these results is additional evidence for the essential reliability of the derivatisation procedures used.

We previously used these techniques to show[8] that hydrogen bonding between carbonyl and enol functions on opposite discharge treated LDPE surfaces was responsible for autoadhesion, as postulated by Owens.[13] The results also showed that the required keto-enol tautomerisation occurred. In this work we also showed[8] that the blocking of enol functions prevented adhesion between discharge treated LDPE and a commercially obtainable printing ink. We now extend this investigation of the role of specific interactions using the autoadhesion between discharge treated LDPE surfaces.

It should be emphasised that under the conditions of heat sealing used (at 85°C) untreated LDPE surfaces do not autoadhere, in other words an interdiffusion mechanism is unlikely.

Table III shows the effect on adhesion of reacting the surfaces with PFPH and TAA. As reported earlier PFPH prevents adhesion by eliminating enolisable carbonyl groups. On the other hand reaction with TAA actually increases adhesion above that of the discharge treatment alone. This would be consistent with the opening of another specific adhesion "channel", namely cross-linking of —OH groups *via* the Ti complex. Since the above XPS

TABLE III

XPS and autoadhesion measurements from derivatised surfaces

Treatment	Cls (3×10^4)	Ols (10^4)	Fis (10^4)	Ti2p3/2 (3×10^3)	Peel strength† g/25 mm
DT	20.4	12.8	—	—	250
DT—PFPH	20.0	7.5	12.3	—	0
DT—PFPH—TAA	18.7	11.2	9.7	15.2	241
DT—TAA	19.8	12.9		15.3	390
DT—TAA—PFPH	18.8	15.0	9.1	11.6	180

† Estimated error ±5% for discharge treated samples, ±10–15% for deravitised samples.

analysis suggests that enolic and alcoholic —OH groups can be separately derivatised, then reaction with PFPH and TAA should give independent control over these two sites for specific interaction. This is clearly seen in the case of sequential reaction with the two reagents. Despite the increased error involved in carrying out two solvent based derivatisation reactions the XPS data are reasonably self-consistent also.

Table IV gives similar results for the reactions with CAC and TAA. This time CAC reacts directly with the enolic —OH. Also shown are the water contact angles. Clearly there is no correlation between contact angle and adhesion. Broadly speaking the contact angle hysteresis is constant (the error here is ±4°) indicating that no major changes in surface roughness or heterogeneity are introduced by the chemical treatments.

Although the adhesion values are from single experiments many series of experiments confirmed the observed trends. Both the discharge treatment and the heat sealing stages of the experiment are subject to significant variability and best results were always obtained for a complete set of data obtained on any single day. It should be noted from Tables III and IV how consistent the XPS and peel strength data are when these are comparable. The TAA reaction is the most novel extension of this investigation and Figure 3 shows that the

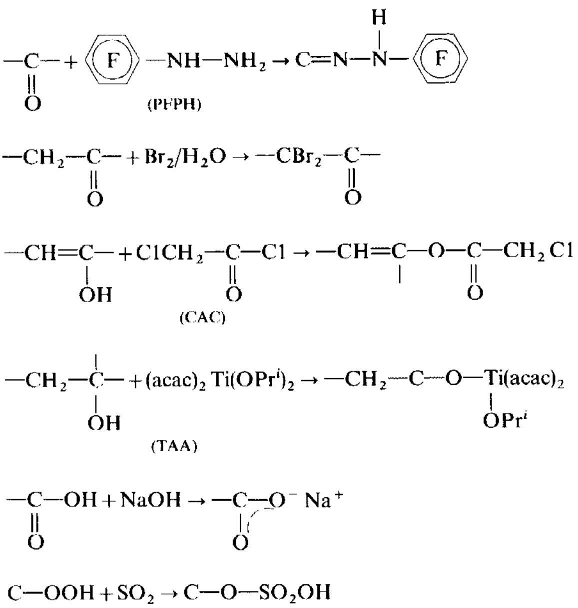
TABLE IV

XPS, contact angle and autoadhesion measurements for derivatised surfaces

Treatment	Cls (3×10^4)	Ols (10^4)	C12p3/2 (10^3)	Ti2p3/2 (3×10^3)	Water contact angle θ_a	θ_r	Peel strength g/25 mm
None					104	96	0
DT	20.4	12.8	—	—	68	63	220
DT—TAA	19.4	12.7	—	11.6	86	73	393
DT—CAC	20.0	11.4	7.9	—	90	87	12
DT—CAC—TAA	18.0	10.6	8.2	11.8	79	73	283

TABLE I

Derivatisation reactions employed



$$-\underset{\underset{O}{\|}}{C}- + \text{(F)}-NH-NH_2 \rightarrow C{=}N-\overset{\overset{H}{|}}{N}-\text{(F)}$$

$$-CH_2-\underset{\underset{O}{\|}}{C}- + Br_2/H_2O \rightarrow -CBr_2-\underset{\underset{O}{\|}}{C}-$$

$$-CH{=}\underset{\underset{OH}{|}}{C}- + ClCH_2-\underset{\underset{O}{\|}}{C}-Cl \rightarrow -CH{=}\underset{|}{C}-O-\underset{\underset{O}{\|}}{C}-CH_2Cl$$

$$-CH_2-\underset{\underset{OH}{|}}{\overset{|}{C}}- + (acac)_2Ti(OPr^i)_2 \rightarrow -CH_2-C-O-\underset{\underset{OPr^i}{|}}{Ti}(acac)_2$$

$$-\underset{\underset{O}{\|}}{C}-OH + NaOH \rightarrow -\underset{\underset{O}{\|}}{C}-O^- Na^+$$

$C-OOH + SO_2 \rightarrow C-O-SO_2OH$

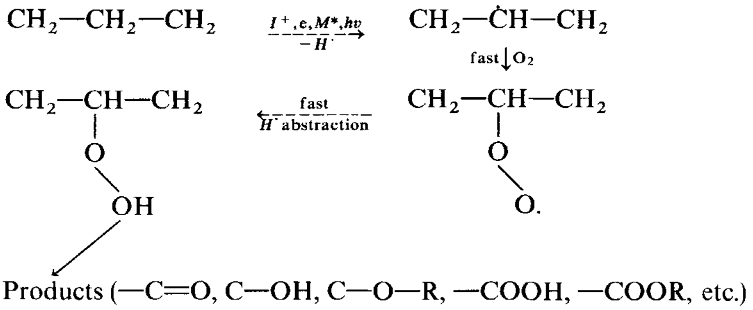
Abbreviations:
PFPH = pentafluorophenylhydrazine
CAC = chloroacetylchloride
TAA = di-isopropoxytitanium bisacetylacetonate.

TAA reaction, so the reagent does not apparently react with carboxylic acid groups either.

The specific reaction of SO_2 with hydroperoxides has previously been described[15] and this is used, with *IR*, as a diagnostic tool for bulk R—OOH assay. Being a gas-phase reaction it is admirably suited to the XPS derivatisation technique.

The level of discharge treatment used in this study is quite high, but not by any standards excessive. (Experimental details can be found in Ref. 11.) It corresponds to the level of maximum autoadhesion under the heat-sealing conditions employed in this study (Figure 3). It also corresponds to a level at which the film used would pass a searching printability test. The surface energy measured using the ASTM wipe test was 55 dyne cm^{-1}.

The consensus view in the literature for the likely mechanism of oxidation during discharge treatment of LDPE is the following:



Products (—C=O, C—OH, C—O—R, —COOH, —COOR, etc.)

Both chain scission and cross-linking take place. The key intermediate is the hydroperoxide group, whose stability and decomposition has been the subject of much research. Hydroperoxides in polyethylene can have long lifetimes so if this mechanism is correct these groups should be detectable. The SO_2 reaction is positive identification and, we believe, the first direct evidence for this mechanism. Of the groups likely to be produced by hydroperoxide decomposition, derivatisation techniques have therefore identified —C=O, C—OH and —COOH.

The XPS data can be quantified, as previously described,[11] to give the data in Table II. The value for the population of CH_2C=O groups assumes that on average two α—H atoms will be replaced during bromination. Since this group can tautomerise to give one enol —OH the population of —CH_2C=O assessed by Br_2 uptake and enolic —OH assessed by the CAC reaction should

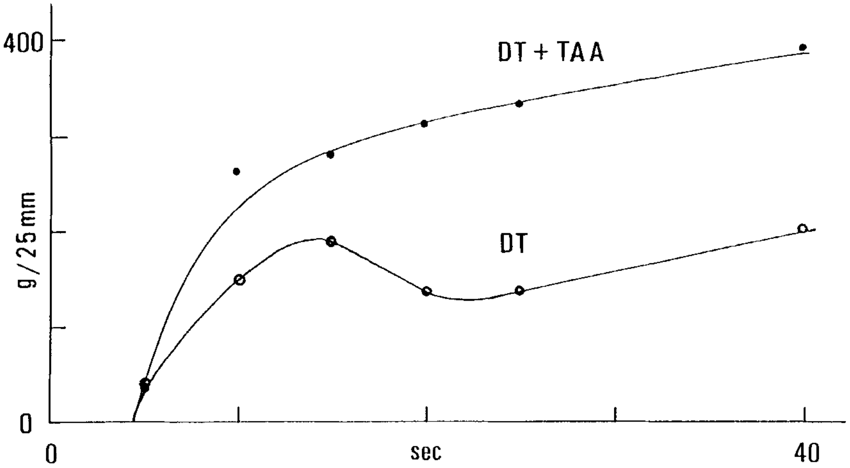


FIGURE 3 Variation of autoadhesion of LDPE (peel strength for seals made at 85°C (2 sec, 15 psi) after discharge treatment in dry air at 12.6 mW cm^{-2} (DT) and after subsequent treatment with di-isopropoxytitanium bisacetylacetonate (DT + TAA), as a function of discharge treatment time.

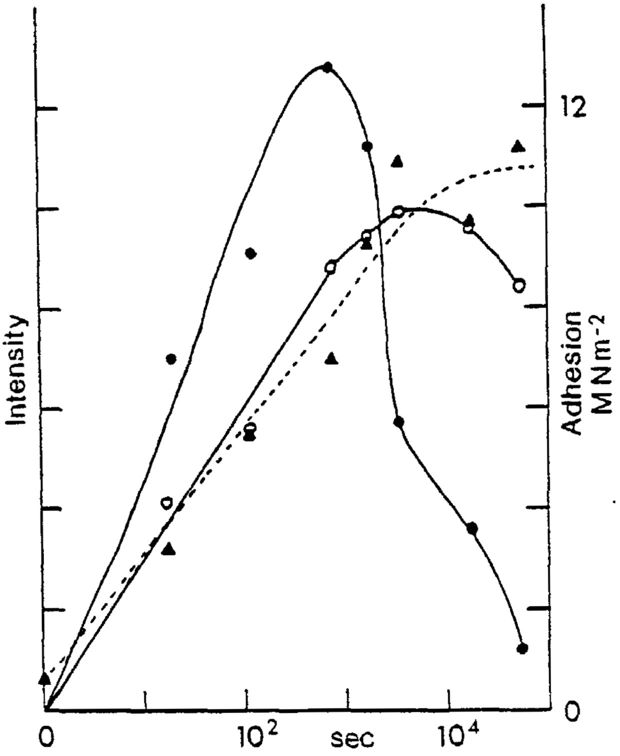


FIGURE 5 CrO_3—H_2O etching of LDPE as a function of time at 25°C. Open circles: O1s peak intensity (10^4 c/s fsd), full circles: Cr2p$_{3/2}$ peak intensity (10^3 c/s fsd), triangles: lap shear strength of adhesive joint to epoxide. Reproduced with permission from Ref. 9.

concentration. Figure 6 shows the changes in the high resolution C1s spectra from the same samples. The high BE shoulder grows until eventually a distinct carboxyl peak ($\simeq$289.5 eV) appears. These spectra show that as oxidation proceeds so the nature of the oxygen containing species changes from spectral domination by carbonyl ($\simeq$288 eV) to carboxyl ($\simeq$289.5 eV) groups. IR data confirmed this trend and also showed that unsaturation ($>C{=}C<$) was not affected. After 16 h etching the atomic concentration of oxygen determined by XPS is $\simeq$4%.

The Cr2p$_{3/2}$ BE was found to be 577.4 ± 0.3 eV. On the basis of Allen and Tucker's data[19] and on our own comparison with Cr(acac)$_3$ (using both BE's and spin-orbit splitting data) we assign the surface bound chromium to be Cr (III). From well-known mechanisms for hydrocarbon reactions we postulate the following course of oxidation:

$R_3CH + H_2CrO_4 \rightarrow R_3COH + Cr(IV)$ branch point attack

$R_2CH_2 + H_2CrO_4 \rightarrow R_2CHOH + Cr(IV)$ chain methylene attack

$Cr(IV) + Cr(VI) \rightarrow 2Cr(V)$

$R_2CHOH + Cr(VI)/Cr(V) \rightarrow R_2C = O + Cr(IV)/Cr(III)$, *etc.*

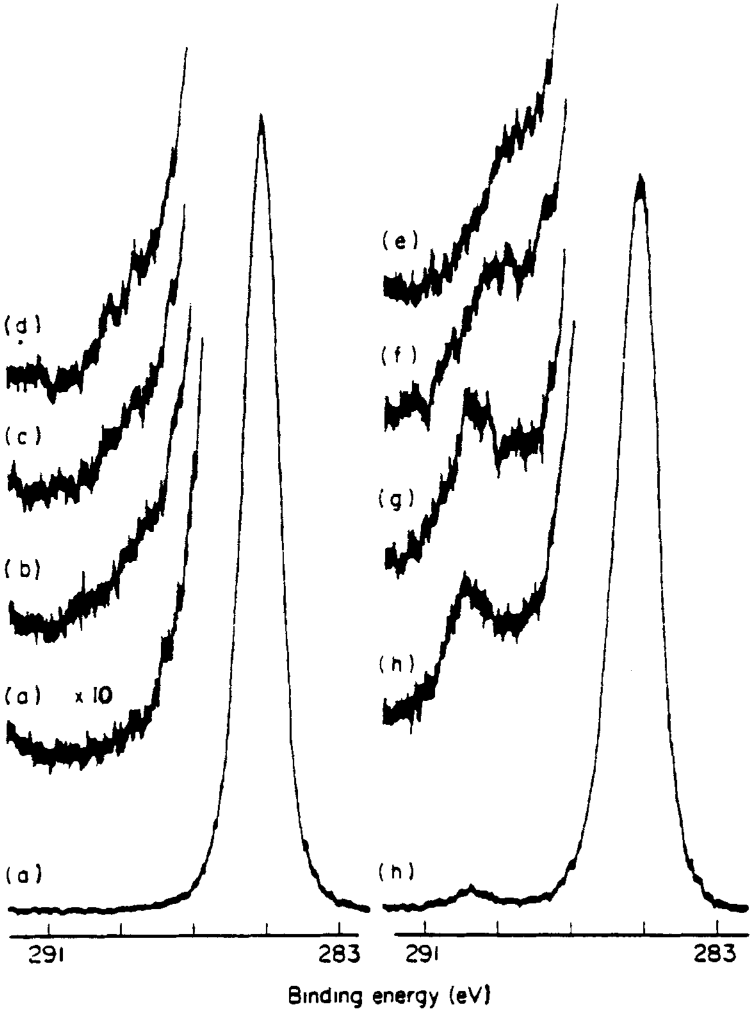


FIGURE 6 High resolution C1s spectra for LDPE etched with CrO_3—H_2O at 25°C for (a) 0 sec (b) 20 sec (c) 40 sec (d) 2 min (e) 10 min (f) 1 h (g) 5 h (h) 16 h count rate = 3×10^3 c/s fsd. Reproduced, with permission, from Ref. 9.

adhesion improvement is achieved across a wide range of discharge treatment level. Incidentally, we believe the smoothing out of the dip in the original autoadhesion curve is due to the solvent removal of low molecular weight oxidised material during the derivatisation reaction.

Similar experiments with SO_2 reacted surfaces showed that this had no effect on autoadhesion. Carley and Kitze[16] have recently speculated on the role of peroxidic groups in discharge treated surfaces. Their analysis of these groups, by reaction with diphenylpicrylhydrazyl (DPPH) and subsequent colorimetry, excluded the possibility of hydroperoxide reactions since these groups could not be detected by ATR. The results presented here must cast some doubt on the validity of their method.

In our previous paper we concluded[8] that NaOH reaction with discharge treated surfaces did not affect adhesion; thus carboxylic acid groups are not implicated in adhesion mechanisms. Although Owens observed[13] a similar result we now find that the situation is much more complex. Depending on the conditions of the NaOH reaction (concentration, exposure time and washing procedure) almost any value of adhesion from zero to an undiminished value could be obtained even though XPS showed derivatisation had taken place. We are therefore inclined to agree with Everhart and Reilley[17] that this reaction is unreliable and a better derivatising agent needs to be found for examining the role of carboxylic acid groups.

The quantitative XPS data shows that only a fraction of the polar groups which lead to the increase in surface energy (or wettability) of LDPE need be involved in giving adhesion values as high as 400 g/25 mm. In the case of hydrogen bonding *via* enolic —OH only 3×10^{12} groups cm^{-2} are involved (assuming 5×10^4 carbon atom cm^{-2} in the LDPE surface). In the case of cross-linking *via* alcoholic —OH twice as many groups are involved.

It is interesting to note that whilst the enhanced autoadhesive bonds resulting from discharge treatment are immediately disrupted by the presence of water[7,13] the use of TAA as a cross-linking agent gives some hydrolytic stability, as might be anticipated. In the presence of water peel strengths of the order of 60–100 g/25 mm are retained throughout the peel test.

Chromic acid treatment

Chromic acid treatments are used extensively for improving adhesion to irregular shaped objects, such as mouldings which require decoration. The metallisation of automobile components fabricated from polypropylene or ABS (acrylonitrile-butadiene-styrene copolymer) is an important example. Recently Ghorashi[18] found that in the case of CrO_3/water etching of polypropylene, residual Cr had an important effect on the adhesion of the metal layer deposited by the electroless process (Figure 4). As part of a wider

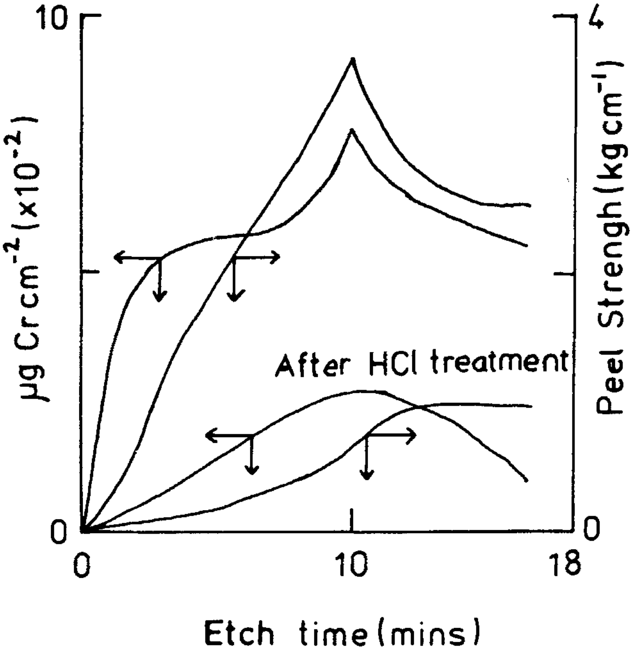


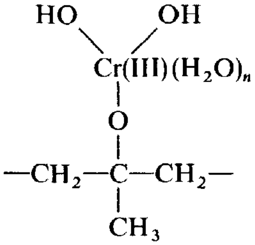
FIGURE 4 Effect of residual Cr on metal adhesion to injection moulded etched polypropylene (after Ghorashi, Ref. 18).

study of chromic acid treatments XPS was used to shed some light onto this effect.[9]

It is worth noting at this point that previous reflection —IR studies of chromic acid etching of polyolefins had failed to detect oxidation of polypropylene (PP) but had detected the oxidation of LDPE (after treatment times rather longer than used commercially). XPS has shown[3,9] that this is due to the very different relative rates of chain scission and total oxidation. For PP the ratio is high, material is lost into solution quite rapidly and the "equilibrium" thickness of the oxidised surface layer is not sufficient for IR detection (sampling depth typically 1 μm). For LDPE oxidation occurs in depth with less material loss. In the work discussed here the etching of LDPE by CrO_3-water was studied[9] in order that corresponding IR data could be obtained.

Figure 5 shows the variation in O1s and $Cr2p_{3/2}$ peak intensities as a function of etching time at 25°C. Although not pertinent to this discussion the figure also shows the increase in adhesion to an epoxide adhesive (*not* affected by residual Cr). Note the very pronounced maximum in the surface Cr

The final stable state is Cr(III). Some of this could be present on the surface as an intermediate complex such as



Further oxidation must result in chain cleavage and leads to the eventual production of carboxylic acids (with loss of Cr), but the mechanisms for these reactions are not well understood. The maximum surface concentration of Cr is not inconsistent with the concentration of branch points in LDPE. Furthermore, the acid hydrolysis which is required to remove this bound Cr would be explained by the reaction

$$\mathrm{C{-}O{-}Cr(III)} \xrightarrow{\mathrm{H_3O^+}} \mathrm{C{-}OH + HO{-}Cr(III)}$$

In electroless metal plating (*e.g.*, of copper or nickel) the etched surface is first sensitised with $SnCl_2$ and activated with $PdCl_2$:

$$\mathrm{Sn(II)(sorbed) + Pd(II) \rightarrow Sn(IV) + Pd(O)}$$

the Pd sites then nucleate growth of the metal film. If the Cr (III) present on the surface catalyses either or both of these steps:

$$\mathrm{2Cr(III) + Sn(II) \rightarrow 2Cr(II) + Sn(IV)}$$

$$\mathrm{Pd(II) + 2Cr(II) \rightarrow Pd(O) + 2Cr(III)}$$

then the Pd sites will be formed over the whole of the porous surface (internal and external) in a way which might not otherwise occur. This would result in improved "wetting" of polymer by metal and good mechanical keying. Although this is a tentative explanation it does account for the experimental observations, especially why the time of chromic acid etching can be so critical to the metal adhesion achieved.

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