Adhesion to polyethylene and polypropylene

D. M. Brewis
School of Chemistry, Leicester Polytechnic, Leicester LE1 9BH, UK
and D. Briggs
ICI Plastics Division, Welwyn Garden City, Hertfordshire AL7 1HD, UK
(*Received* 13 *August* 1980)

Adhesion to polyethylene and polypropylene is a complex subject requiring understanding of (a) the poor adhesive characteristics of these polymers; (b) the superior performance following certain pretreatments and (c) the nature of the changes brought about by these pretreatments and the mechanisms involved. This review discusses work on these topics and examines the impact of recent data resulting from the application of surface analytical techniques. The roles of 'weak boundary layers', surface energy and wettability and specific interactions are discussed in some detail.

INTRODUCTION

In terms of tonnage polyethylene (PE) is the most widely used synthetic polymer and polypropylene (PP) is one of the three other most widely used[1]. Many of the applications of these polymers require good adhesion, and problems arise in a number of different situations (*Table 1*). If good adhesion between a polyolefin and another material is required it is usually necessary to carry out a pretreatment. Surface treatments for low density polyethylene (LDPE) were introduced more than 30 years ago. A wide range of treatments has been examined since and some of these are given in *Table 2*.

Although the commercial treatments were introduced to improve the adhesion characteristics of LDPE, the treatments are also generally effective with high density polyethylene (HDPE) and PP. The most widely used pretreatments are corona discharge for films and flame treatment for thicker sections such as bottles. Chromic acid is used to treat complex shapes and also prior to metal coating of plastics. The other methods are not widely used.

Because of the commercial importance of polyethylene and polypropylene and the frequency of adhesion problems with these polymers, a large amount of adhesion research has been carried out on them. The object of this review is to summarize and assess this work.

Before describing the often conflicting results from investigations into this complex subject, the main controversies are summarized. There are two general areas of disagreement. The first is whether adhesion problems of PE and PP are due to weak boundary layers of 'inadequate wetting'. The second concerns which criteria for wetting are appropriate. Many of the controversies in the literature can be summarized in terms of the following often related questions:

(a) Is the poor adhesion obtained with PE and PP simply due to the presence of a weak boundary layer (WBL)? Conversely, if small molecules are present on substrate surfaces, need they necessarily lead to low adhesion levels?

(b) Is the primary function of a pretreatment to eliminate weak boundary layers? Is any chemical modification, e.g. oxidation, which occurs of secondary importance?

(c) Is the poor adhesion due to poor wetting resulting from the low surface energies of PE and PP?

(d) Which groups are introduced during pretreatments? What concentration of these groups are required to give good adhesion? Are specific interactions important?

(e) How can thermodynamic and kinetic aspects of wetting best be investigated? What degree of wetting is required for good adhesion?

(f) Do morphological changes brought about by pretreatments of PE and PP have an important effect on adhesion levels? Does mechanical keying play an important part in adhesion with these substrates? Is the crosslinking which occurs with some pretreatments coincidental to the introduction of polar groups as far as adhesion is concerned?

Table 1

Cases of adhesion problems with polyolefins

Adhesive bonding
Printing
Extrusion coatings e.g. polyethylene on aluminium
Coatings on polyolefins e.g. paints or barrier layers
Metallized polyolefins (vacuum or solution deposited)
Composites e.g. glass filled polypropylene
Heat sealing

Table 2

Surface pretreatments for polyolefins

Chlorine + u.v. radiation	– Visking Corporation USP 2502841
U.v. radiation	– W. Berry, R. A. Rose and C. R. Bruce, BP 723 631
Dichromate/sulphuric acid	– P. V. Horton, USP 2668 134
Hot chlorinated solvents	– J. J. Ziccarelli, ***Mod. Plast.***, 1962, **40**, 126
Flame treatment	– W. H. Kreidl, USP 2632921 M. F. Kritchever, USP 2648097
Corona discharge treatment	– A. Traver, USP 3018189
CASING	– R. H. Hansen and H. Schonhorn, *J. Poly. Sci.* B4, 1966, 203

0032-3861/81/010007-10$02.00

The following sections summarize the available data and this is assessed in the Discussion section in a way which attempts to provide answers to some of the above questions.

WEAK BOUNDARY LAYERS

Bikerman[2] suggested that adhesion problems associated with polyethylene are due to weak boundary layers. He suggested that molecules of low molecular weight, that are normally present in commercial polyethylenes separate from the melt and create a region of low strength on the surface.

Bikerman put forward various evidence in support of his theory. For example, he dissolved three commercial polyethylenes in toluene and then reprecipitated the high molecular weight polymer with acetone or butanone, leaving the small molecules in solution. He then used the reprecipitated polyethylenes as melt adhesives for steel and glass. Bikerman claimed much higher joint strengths with the reprecipitated polyethylenes than with the original polymers.

Bikerman and Marshall[3] found that adhesion levels were much lower if ~1% oleic acid was added to the purified polyethylenes. By adding a compound, such as ethyl palmitate, which is miscible with both polyethylene and oleic acid, high joint strengths were obtained by avoiding a weak boundary layer consisting of oleic acid.

The weak boundary theory received considerable support from other research work and some of this is outlined below. It is certainly easy to envisage various possible sources of weak boundary layers on polyolefin surfaces, namely:

(a) impurities arising during the polymerization process;
(b) the low molecular weight tail of a polymer;
(c) additives e.g. antioxidants and slip agents;
(d) external processing aids e.g. mould release agents;
(e) contamination after fabrication.

It is worth noting that the interpretation of Bikerman's evidence is complicated by his use of polyethylene as an adhesive and not as the substrate as discussed in the next section. However, Schonhorn and coworkers have put forward evidence in favour of the weak boundary concept which does use polyethylene as the substrate.

In 1966, Hansen and Schonhorn[4] reported work in which they bombarded polyethylene and certain other polymers with activated inert gases and found the adhesion of an epoxide adhesive to the polymers had greatly increased, although the critical surface tensions of the polymers were unchanged. Also, using *ATR*-infra-red analysis they were unable to detect any chemical changes in the surface. They therefore proposed that regions of low molecular weight on the surface were cross-linked to the long polymer chains thereby eliminating weak boundary layers. In fact, Hansen and Schonhorn suggested that surface treatments in general act primarily by eliminating weak boundary layers. Over the next four years Schonhorn and coworkers proposed further evidence in favour of the weak boundary concept.

For example, Schonhorn and Ryan[5] melted polyethylene against aluminium and then dissolved the aluminium with sodium hydroxide solution. They obtained high joint strengths by bonding the polyethylene with an epoxide adhesive. They could detect no polar groups by *ATR*-i.r. and attributed the increased adhesion to a highly crystalline surface region.

In some later work, Schonhorn and Ryan[6] exposed polyethylene to u.v. radiation. They found joint strengths with an epoxide adhesive much increased, but there was no evidence of oxidation using *ATR* and contact angle measurements. They concluded that cross-linking at the surface occurred thereby eliminating a weak boundary layer.

SURFACE ENERGY

Critical surface tension

To obtain good adhesion it is clearly necessary, but not necessarily sufficient, to obtain substantial contact between the wetting liquid and the substrate.

Zisman suggested that contact angles are a useful inverse measure of the degree of contact between a liquid and a solid. The interactions between liquids and high energy solids such as metal oxides will generally be sufficient to overcome the cohesive forces of the liquid and the contact angle will be zero if the viscosity is sufficiently low. Conversely many polar liquids form large contact angles with polyethylene and other non-polar polymers.

Zisman[7] and coworkers determined the contact angles between many pure liquids and low energy substrates including many polymers. They found that plots of the cosine of the contact angle, θ, *versus* the surface tension of the organic liquids, γ_L, gave a series of straight lines, depending on whether the liquids are non-polar, polar and non H bonding or H bonding.

The straight lines led Zisman to propose his idea of critical surface tension of wetting, γ_C, which is the intercept of the line $\cos\theta = 1$ with the extrapolated straight line plot of $\cos\theta$ vs γ_L. Thus a liquid with a lower surface tension than γ_C should spread on the substrate. The critical surface tension provides a convenient indication of the surface energies of polymers, although it does not actually measure this parameter.

The critical surface tensions of some important polymers are shown in *Table 3*.

These data show that the introduction of polarizable atoms or groups into the hydrocarbon chain increases γ_c; hence the introduction of such groups by surface treatments should lead to a similar result.

The importance of relative surface energies in adhesion received support from Levine *et al.*[8] who measured joint strengths for various polymers bonded with an epoxide adhesive. They found, with one or two exceptions, a good relationship between joint strengths and the polymer's critical surface tension.

Sharpe and Schonhorn[9] melted non-polar polymers such as PE ($\gamma_c = 31$ m Nm^{-1}) onto a cured epoxide* and obtained good adhesion. This contrasts with the more usual practical situation in which the epoxide is spread onto the PE; in the absence of a pretreatment adhesion is very poor. This supports the idea that the wetting liquid should have a lower γ_c than the substrate for good adhesion. However, Iyengor and Erickson[10] found that if solvent-based PE ($\gamma_c = 31$) is coated onto PET ($\gamma_c = 43$) and allowed to dry (at 130°–160°C) the adhesive strength is poor.

---

* The surface tension of the uncured adhesive was 32.9 mNm^{-1}

Table 3 Critical surface tensions of some important polymers

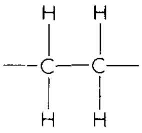
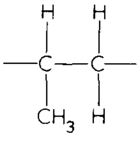
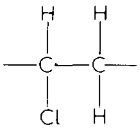
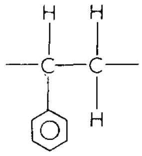
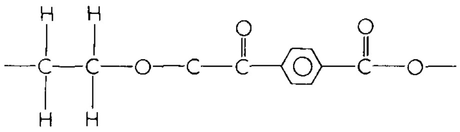
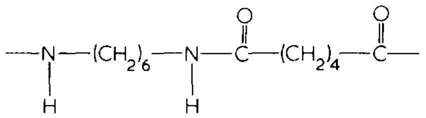
	Polymer	mNm^{-1}	Structural feature (compared with PE)
Polyethylene PE	 $-CH_2-CH_2-$	31	
Polypropylene PP	 $-CH_2-CH(CH_3)-$	31	Replace one H by CH_3
Poly(vinyl chloride) PVC	 $-CH_2-CHCl-$	39	Replace one H by Cl (highly polarisable atom)
Polystyrene PS		43	Replace one H by benzene ring (polarisable π electron cloud)
Poly(ethylene terephthalate) PET		43	Insertion of polar groups (ester, amide) into hydrocarbon chain
Poly(hexamethylene adipamide) Nylon 6,6	 $-NH-(CH_2)_6-NH-CO-(CH_2)_4-CO-$	46	

Table 4 Components of surface energies for various polymers

Polymer	γ_s^d	γ_s^p mNm^{-1}	γ_s	Ref
LDPE	32.0	1.1	33.1	12
Poly (vinyl fluoride)	31.3	5.4	36.7	12
PP	30.2	0.0	30.2	15
Flame treated PP	33.5	4.1	37.6	15
Poly(methylene oxide)	21.8	11.5	33.3	16
Poly(ethylene terephthalate)	37.8	3.5	41.3	12
Polytetrafluoroethylene	16.9	1.1	18.0	16
Polytetrafluoroethylene (etched)	36.1	14.5	50.6	16

Dispersion and polar components

Fowkes[11] introduced the idea of the additivity of intermolecular forces. Thus the surface energy of a solid, γ_s, consists of contributions from dispersion, γ_s^d, and polar, γ_s^p, forces. The geometrical mean of the dispersion force components $(\gamma_s^d\gamma_L^d)^{1/2}$ across an interface (where γ_L^d refers to the wetting liquid) is a measure of the interaction energy caused by dispersion forces. Owens and Wendt[12], and Kaelble and Uy[13] extended this concept to include polar interactions, and consider that dispersion and polar forces only interact across interfaces with their like. The contributions of dispersion and polar forces to the surface energies of some polymers are given in *Table 4*.

Kaelble[14] introduced the idea of a 'wettability envelope' for the surface of a polymer (*Figure 1*). The envelope is calculated from the contact angles of several liquids whose dispersion and polar contributions (γ_L^d, γ_L^p) to surface tension are known. If the values of γ_L^d and γ_L^p for an adhesive or printing ink fall within the wettability envelope spreading should occur.

These approaches, which assume that all types of molecular interaction can be represented in the same way as dispersion force interactions, i.e. $W_A^x = 2\sqrt{\gamma_1{}^x\gamma_2{}^x}$, have recently been criticised by Fowkes[17]. He argues that this assumption is incorrect for H bonding interactions and, because polar and H bonding interactions are usually taken together (W_A^p), it is therefore incorrect for 'polar interactions'.

Wetting and spreading

Huntsberger[18,19] has pointed out that the terms 'wetting' and 'spreading' have been used interchangeably. He argues that the term 'wetting' should be limited to the intermolecular contact achieved between a liquid and the substrate. Thus in *Figure 2a* the liquid has spread on the substrate as indicated by zero contact angle but the wetting is incomplete while in *Figure 2b* spreading and wetting are complete.

Furthermore, Huntsberger has shown, by considering free energy changes, that complete wetting can occur even if $\theta > 90°$.

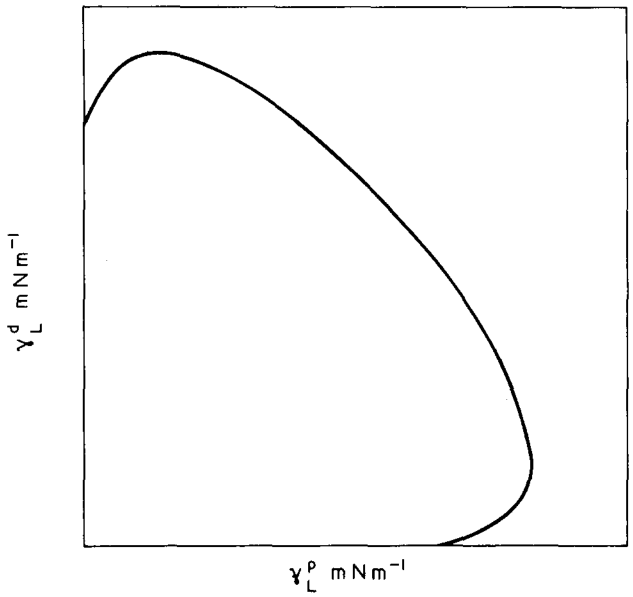


Figure 1 Typical form of wettability envelope

Cherry[20] and others have pointed out the importance of the kinetics of wetting. Clearly, the degree of wetting will be low if the viscosity of an adhesive is high or if the setting time is short, i.e. the system will be far from equilibrium.

PHYSICAL CHANGES CAUSED BY PRETREATMENTS

It is important to have information on surface topography because this can affect the level of adhesion. Increased surface roughness can lead to increased adhesion through mechanical keying and a greater potential bonding area. Alternatively it may lead to reduced adhesion because a smaller area of bonding is achieved or because stress concentration occurs due to the presence of voids. The actual effect will depend on surface energies, the viscosity of the wetting liquid and the size and shape of the irregularities.

Although contact angle measurements can provide a guide to relative surface roughness, electron microscopy provides much more direct and detailed information on surface geometry and morphology.

The chromic acid treatment of polyolefins has been studied with electron microscopy by various workers. Shields[21] found that etching of PP at 20°C for 20 min resulted in hole diameters about 8 times those in the untreated film. He found etching at 80°C for 5 min resulted in further roughening. In contrast, Blais *et al.*[22] found very little roughening of PP at 70°C except for a sample which had been initially annealed to produce large spherulites. Before etching the polymer surface was featureless, but after etching the spherulitic regions were clearly defined. It is clear from this and other work that the thermal history and the grade of polyolefin have an important influence on the topography of a polymer after some pretreatments.

Blais *et al.*[22] found that chromic acid etching at 70°C resulted in much more severe roughening with HDPE and LDPE than with 'normal' PP.

Garnish[23], using *SEM*, showed that trichloroethylene vapour caused rapid and extensive roughening of a PP surface. He found that the adhesion of the PP to an epoxide adhesive increased approximately 6 fold for exposure times of up to about 10 s but thereafter there was a rapid decline in joint strength.

Some workers have detected surface roughening during discharge treatment although there is some disagreement over whether these morphological changes occur only in oxidative atmospheres or not[24,25]. In general these treatments are severe in comparison with commercial levels of treatment and the surface 'mounds' which appear are thought to arise from the agglomeration of low molecular weight degradation products.

However, Sweeting[26] has studied commercially discharge treated polyethylene film by *TEM* and found that good printability correlated with 'considerable, but not excessive', micropitting. He concluded that ink penetration into these craters led to mechanical keying on drying. Using the same technique Spell and Christensen[27] found that increased surface roughness accompanied increased chemical modification, eventually leading to an 'overtreatment' condition associated with poor ink adhesion.

CHEMICAL CHANGES CAUSED BY PRETREATMENTS

Chemical changes in LDPE brought about by air oxidation and photo-oxidation were detected in the early 1950's using transmission infra-red spectroscopy. For example, Rugg *et al.*[28] concluded that in thermal oxidation mainly keto groups resulted plus some aldehyde and acid groups. In photo-oxidised polyethylene, similar quantities of aldehyde, acid and keto groups resulted. They also detected changes in levels of unsaturation in both types of oxidation and with thermal oxidation postulated the formation of unstable hydroperoxide groups. Rossmann[29], using severe electrical pretreatments and after considerable experimental difficulty, found an increased concentration of keto groups in polyethylene.

Until recently, very little information has been published on chemical changes caused by commercial levels of pretreatment. One procedure[30,31] which is able to give information on the first 1000 Å of surface involves the surface abrasion of the polymer usually with potassium bromide, followed by transmission i.r. study of a disc pressed from the mixture. However, the method is tedious and much care is required in the interpretation of results as has been discussed by Willis and Zichy[32]. These workers reported a study of the corona-discharge treatment of polypropylene. Carbonyl, hydroxyl and nitrate ester groups, and nitrate ions were detected.

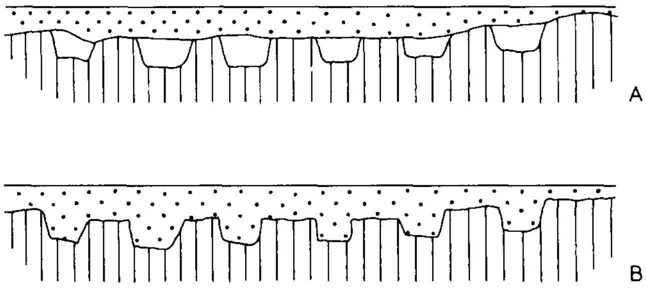


Figure 2 (A) Spreading has occurred but wetting is incomplete. (B) Spreading has occurred with complete wetting

Table 5 Surface composition and adhesion of etched polymers

Polymer	Etching conditions	C : S Atomic ratio	O : S Atomic ratio	% of C atoms with SO_3H groups	% O (not in SO_3H groups) to total C (% O : C)	Lap shear strength MN m^{-2}	Failure† type	Ols : 02s
LDPE	None	–	–	–	0.25	0.55	I	–
LDPE	Conc H_2SO_4 1 h at 70°C	36.8	3.2	2.7	0.6	3.3	I	11.6
LDPE	Acid B* 5s at 20°C	198	9.1	0.5	3.1	4.8	I + M	–
LDPE	Acid A* 1 min at 20°C	269	12.7	0.4	3.6	7.5	M	13.0
LDPE	Acid A 30 mins at 70°C	80.0	10.4	1.3	9.3	7.6	M	9.2
LDPE	Acid A 6 hrs at 70°C	47.1	9.5	2.1	13.9	9.5	M	9.9
LDPE	None	–	–	–	0.52	0.38	I	–
HDPE	Conc. H_2SO_4 1 h at 70°C	64.3	4.2	1.6	1.8	3.5	I	18.2
HDPE	Acid B 5s at 20°C	145	9.2	0.7	4.3	7.0	M	25.1
PP	None	–	–	–	0.25	0.28	I	–
PP	Conc H_2SO_4 1 h at 70°C	262	9.7	0.4	2.6	1.1	I	–
PP	Acid B 5s at 20°C	382	14.5	0.3	3.3	2.8	I	35.9
PP	Acid A 1 min of 20°C	283	16.2	0.4	4.6	4.7	I	22.7
PP	Acid A 6 hrs at 70°C	261	13.5	0.4	4.0	11.2	M	13.7

* Acid A 'normal' chromic–sulphuric acid ($K_2Cr_2O_7 : H_2O : H_2SO_4$ = 7 : 12 : 150 by weight)
Acid B as Acid A but 1/100th strength with respect to $K_2Cr_2O_7$
† Apparent interfacial failure
M, Material failure

ATR or *MIR* (multiple internal reflection) infra-red spectroscopy has provided information on the changes caused by the treatment of polyethylene with chromic acid. In this way, Blais *et al.*[22], on etching LDPE with chromic acid at 70°C, found –OH, and C=O groups. Using the same treatment Willis and Zichy[32] found these groups plus sulphate and alkyl sulphonate groups. By contrast, Rasmussen *et al.*[33] found that the surface functionality consisted mainly of carbonyl groups with approximately 60% of these as carboxylic acid and 40% as ketones or aldehydes; there was no evidence for –OH groups. Carlsson and Wiles[34], using *ATR*, detected various chemical changes after the electrical ('corona') discharge treatment of PP in oxygen or nitrogen. However, the treatment conditions used were much more severe than those used commercially.

Discharge treatment under commercially realistic conditions has been studied by Carley and Kitze[35]. They used diphenyldipicryl hydrazyl (DPPH) reactions (with colorimetry) to probe treated polyethylene surfaces. The concentrations of radicals produced by the decomposition of unstable species was determined by reaction with DPPH. The observed reaction kinetics were consistent with the breakdown of ozonides (RO_3R^1) and peroxides (RO_2R^1). The concentration of these groups, calculated from the kinetic data, correlated with the wettability and peel strengths of surfaces treated under a variety of conditions.

More direct information of surface chemical changes has recently been obtained using X-ray photoelectron spectroscopy[36] (X.p.s. or e.s.c.a.), a technique which analyses the surface to ≈50 Å in depth. The results from a systematic re-examination of pretreatments for PE and PP by Briggs and coworkers are summarized below.

Chromic acid etching

Initial studies[37] allowed the identification of C–OH, C=O, –O–C=O and –SO_3H groups on the surface of etched LDPE and PP. The role of sulphonation was then studied[38] by etching with concentrated sulphuric acid and etching extended to very mild conditions. The X.p.s. data and associated joint strengths are collected in *Table 5*. For each polymer there is clearly a correlation between the degree of oxidation (i.e. number of carbon–oxygen functions, type unspecified) and adhesion. There is no such correlation for the number of sulphonate groups. The 01s:02s peak intensity ratio can be used as a guide to the depth of modification within the top ~100 Å, the sampling depth of the more energetic 02s electron. The ratio decreases as the depth of oxidation increases, reaching a limiting value of ~10 when the top 100 Å of polymer is uniformly oxidised. Clearly for mild treatments

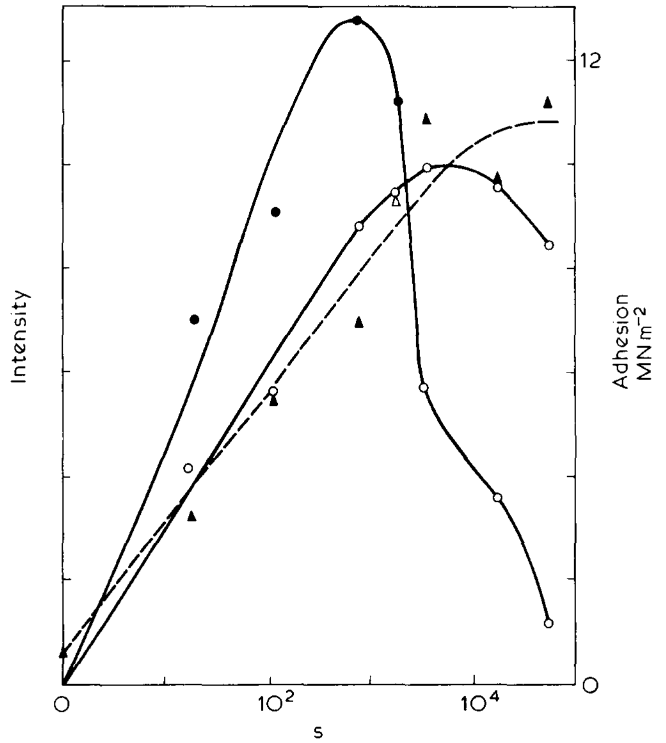


Figure 3 CrO_3–H_2O etching of LDPE as a function of time at 25°C. ●, Cr2p 3/2 peak intensity (10^3 counts s^{-1} *FSD*); ○, O1s peak intensity (10^4 counts s^{-1} *FSD*); ▲, lap shear strength of adhesive joint with epoxide (ref 38)

the modification depth is <100 Å. It has also been shown[37] that the surface oxidation of PP rapidly reaches an equilibrium with a low modification depth whereas with LDPE oxidation continues to increase both in degree and in depth (see also *Table 5*). This observation explains the previous results of Blais[22]. Compared with LDPE, PP can only be oxidised to a low level before chain scission results in material loss into solution, although the equilibrium surface oxidation level is high enough to give good adhesion. The modification depth at equilibrium is too low to cause changes to the *ATR* spectra of PP, but can become great enough for changes to be observed in the case of LDPE.

A detailed study has also been made[38] of the CrO_3–water etching of LDPE (in conjunction with *ATR*). The course of oxidation on the molecular and depth scales was closely monitored and compared with joint strength results (*Figures 3* and *4*), again revealing the correlation of adhesion with oxidation level. The variation in the residual Cr concentration can be fitted into a mechanistic scheme in which Cr is bound to the surface in an intermediate complex, and this is also consistent with the changes in the number and type of oxygen function. It is interesting to note that this etchant is used for the pretreatment of polypropylene mouldings prior to metallization and that Ghorashi[39] has shown the importance of residual surface Cr in achieving good adhesion between polymer and deposited metal. *Figure 3* clearly reveals the sharp optimum in the Cr concentration and a tentative explanation for the effect on adhesion has been put forward[38].

Melting LDPE against aluminium

In an exact repeat[40] of experiments performed by Schonhorn and Ryan[5], LDPE and HDPE were melted against aluminium and the metal then dissolved away using NaOH. X.p.s. showed oxidation to have taken place at the polymer–metal (oxide) interface. Increasing the melting temperature increased the level of oxidation and also increased the joint strengths in subsequent adhesion measurements. Thus, the formation of a relatively thick *trans*-crystalline region at the polymer surface brought about by this process is accompanied by oxidation on a depth scale below that accessible to *ATR* analysis. X.p.s. therefore confirms early suggestions, from less direct evidence[41,42], that oxidation of polyethylene during melting onto metals has an important effect on subsequent adhesion.

Thermal oxidation of LDPE and lamination to aluminium

The oxidation of LDPE which occurs on its extrusion at high temperature is not confined to the surface since it can easily be detected by *ATR*. Measurement of total >C=O concentration by this technique established a correlation between oxidation level and adhesion of LDPE to aluminium in laminates[32]. It is known that LDPE resins containing high levels of antioxidant can be difficult to laminate to Al and an ozone pretreatment procedure has been developed which overcomes this problem (*Figure 5*). X.p.s. studies[43] of LDPE surfaces laminated to Al under a variety of conditions (variation of extrusion temperature, antioxidant level in resin, application of ozone pretreatment) established a good correlation between surface oxidation and the level of adhesion*.

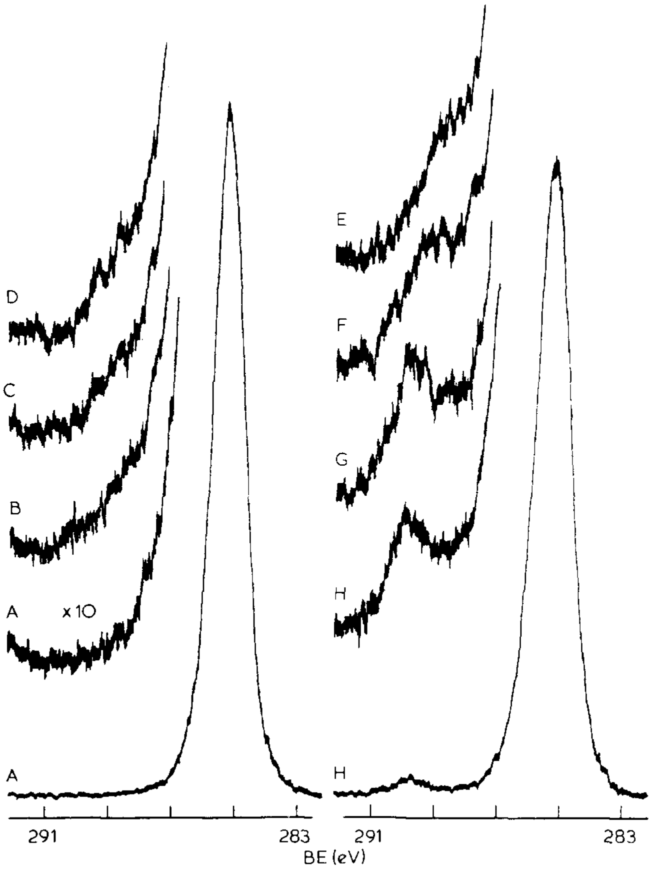


Figure 4 High resolution C1s spectrum for LDPE etched with CrO_3–H_2O at 25°C for the following times: (A) 0s, (B) 20s, (C) 40s, (D) 2 min, (E) 10 min, (F) 1 h, (G) 5 h, (H) 16 h. Count rate = 3×10^3 counts s^{-1} *FSD* (ref 38)

---

* It is important to note that in these studies the Al surface is smooth compared with the anodised surfaces used by Packham *et al.*[44] in their studies of mechanical keying between Al and melted PE.

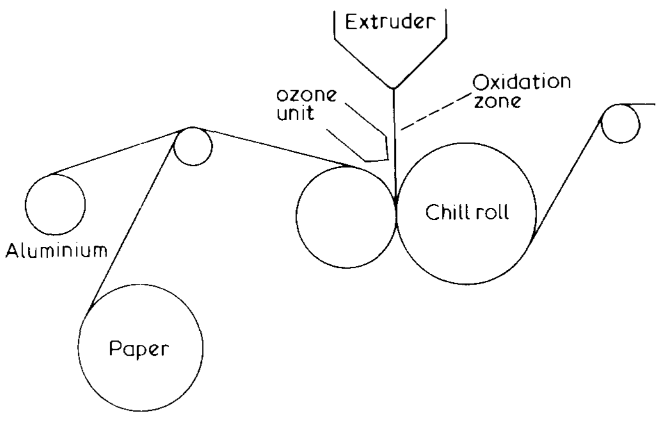


Figure 5 Schematic diagram of process for lamination of aluminium with polyethylene

Surface oxidation could be completely inhibited by a high enough level of antioxidant, but the ozone pretreatment reversed this and restored adhesion. X.p.s. also detected a significant concentration of nitrogen-containing species and showed that the overall surface chemistry was unaltered when the ozone shower was used. It was therefore concluded that the effect of ozone is to react with surface antioxidant, thereby nullifying its suppressive effect on surface oxidation, rather than to bring about oxidation by a different mechanism.

This work showed that the prevention of oxidation by antioxidants gave low (or zero) strength laminates. Russian workers have also shown[45] that PE–Al laminates prepared under vacuum had lower strengths than those prepared in air over a wide temperature range.

Flame treatment

A preliminary X.p.s. study of flame treated LDPE showed[46] that under normal conditions very high levels of oxidation occur, comparable to that achieved by severe chromic acid treatment. However the oxidation is confined to a thin layer of the polymer surface, estimated to be between 40 and 90 Å. Variation of the air:gas ratio led to marked surface chemistry changes, particularly in the ratio of oxygen and nitrogen containing groups. Antioxidant did not reduce the degree of oxidation or the level of adhesion to an epoxide adhesive.

Electrical ('corona') discharge treatment

Initially X.p.s. was used[47] to study the surface of LDPE subjected to discharge treatment in air and inert gases in order to repeat the auto-adhesion experiments of Stradal and Goring[48]. *Figure 6* shows that at an arbitrary value of peel strength (say 100 g/25 mm) the degree of oxidation is approximately the same for air, N_2 and Ar discharges. Moreover, at this point the total energy dissipated in the discharge is also the same; since the discharge characteristics of these gases vary widely, different power/exposure time combinations had to be employed. This confirms the findings of Stradal and Goring. However, discharge treatment in H_2 did not enhance autoadhesion and X.p.s. did not detect surface oxidation. It was therefore concluded that electret formation[48] cannot be responsible for the autoadhesion enhancement effect, whereas the theory based on the incorporation of oxygen functions put forward by Owens[49] was more likely. The detailed X.p-spectra from air-discharge treated surfaces, although indicating the probable presence of C–OH, $>C=O$ and –CO–O– groups (*Figure 7*) are not definitive enough to prove that specific hydrogen bonding (enol–carbonyl) is responsible for autoadhesion as claimed by Owens.

This work was therefore followed up[50] by experiments in which air-discharge treated surfaces were derivatized in such a way that particular oxygen functions would be detected unambiguously and quantitatively estimated by X.p.s., e.g. conversion of $-COOH$ to $-COO^-Na^+$ (detect Na) or $>C=O$ (keto/aldehyde) to $>C=N-N(H)C_6F_5$ (pentafluorophenylhydrazone, detect F).

These reagents, of course, successfully 'block' specific functions (the fact used by Owens[49] to indirectly establish the importance of enolic–OH in autoadhesion). The combination of X.p.s. data and autoadhesion results from these derivatized surfaces directly confirmed the 'Owens' theory. Similar experiments were also carried out[50] on discharge treated surfaces prior to printing with a nitrocellulose ink. Ink adhesion was destroyed by reagents which 'blocked' enolisable carbonyls, but not by reagents which block -COOH. However, it should be noted that the derivatization reactions did not significantly alter the wettability (surface energy) of the discharge treated surfaces.

Spell and Christenson[27] have also described X.p.s. techniques for the study of discharge treated polyethylene. Although there is some disagreement[50] over the detailed interpretation of the data, the results also show a strong correlation between surface chemistry and printability.

Concentration of functional groups

The concentration of polar groups on surfaces which have good adhesive characteristics is clearly important. Rasmussen *et al.*[33] assayed the density of carboxylic acid groups on chromic acid oxidised LDPE using fluorimet-

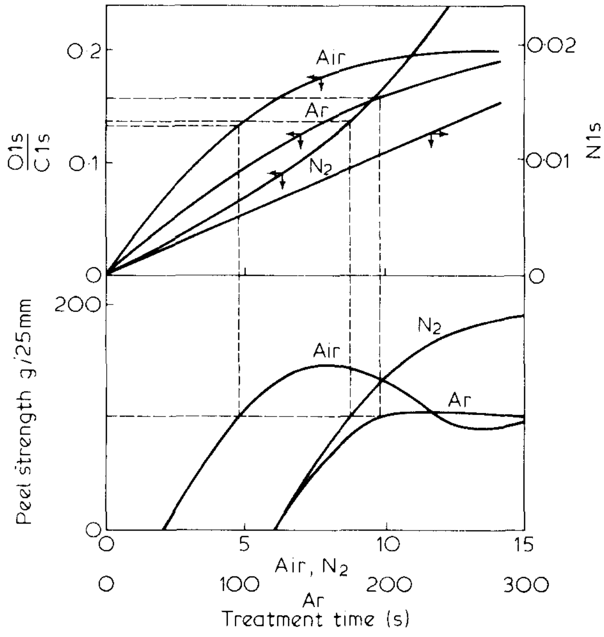


Figure 6 Comparison of autoadhesion (peel strength) and surface composition (from X.p.s. data) for LDPE discharge treated in air, nitrogen and argon. Heat seals were made at 75°C and 15 psi with 2s contact time. The O1s : C1s intensity ratio is a qualitative measure of surface oxidation level. N1s : C1s ratios refer only to surfaces treated in nitrogen. Note the similar surface oxidation level for samples giving peel strengths of 100 gm/25 mm, — — — —, (broken lines)

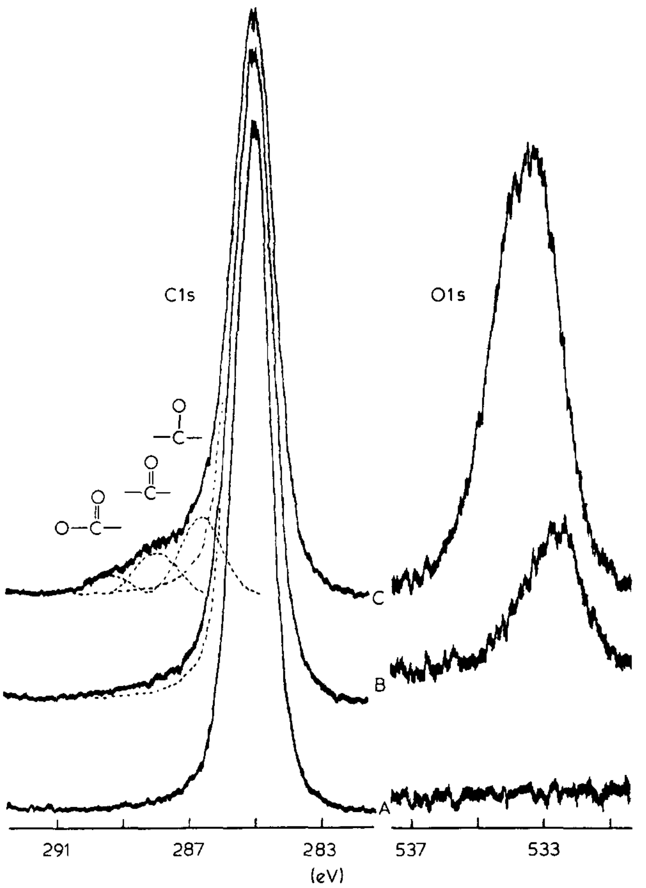


Figure 7 High resolution C1s and O1s spectra for LDPE (A) untreated (B) and (C) discharge treated in air (13.7 kV peak voltage) for 8s and 30s respectively. Count rates are 3 x 10^3 counts s^{-1} *FSD* (C1s) and 10^3 counts S^{-1} (O1s). Lack of specificity in the high binding energy C1s peaks is indicated by the following:— —$\rangle$C—O could be alcohol, enol, ether, alkyl ester, peroxide, hydroperoxide, etc $\rangle$C=O could be ketone or aldehyde, —CO—O could be carboxylic acid or ester, or peracid

ric techniques. These yielded a value of ~2 × 10^{15} groups cm^{-2}. These workers had difficulty in explaining why this figure is more than twice the maximum packing density for stearic acid units in a monolayer (5 × 10^{14} molecules cm^{-2}). It is clear from *ATR* and X.p.s. data[38] that oxidation is not confined to a monolayer, as required for their calculation. Thus, the number of surface -COOH groups is lower by a large but unknown factor.

X.p.s. data[38] from CrO_3–H_2O etched LDPE at the point where adhesion to an epoxide adhesive has just reached its plateau value shows the O:C atomic ratio within the sampling depth (~50 Å) to be ~4%. Since most of the oxygen containing groups are carboxyl (acid or ester) then only ~2% of the surface carbon atoms are oxidised assuming the concentration profile in oxygen is not steep within the first 50 Å of the polymer.

From the studies of discharge treated LDPE surfaces[50] X.p.s. showed that the attainment of excellent ink adhesion again corresponded to an O:C atomic ratio of ~4%[51]. However, from the derivatization results it can be estimated[51] that the ink adhesion is due to only ≃0.4% of the surface carbon atoms being convertedinto potential enolic-OH groups. This represents a concentration of 2 × 10^{12} groups cm^{-2} (assuming 5 × 10^{14} carbon atoms cm^{-2} in LDPE film).

SELF-ADHESION

Although self-adhesion is a somewhat specialised aspect of adhesion to polyethylene and polypropylene it is a subject which goes beyond the mere heat-sealing of these polymer films. The self-adhesion (or autoadhesion) of polyethylene has been much studied and has given rise to controversy in its own right. It has been known for many years that 'corona' discharge treatment of LDPE can enhance autoadhesion (i.e. effective seals can be formed at lower temperatures than normal). Discharge treatment in reactive atmospheres (air, oxygen) and inert atmospheres (nitrogen, noble gases) are both effective. This fact, together with careful correlation of the degree of autoadhesion enhancement with the power consumed in the discharge, led Canadian workers to conclude[48] that electret formation leads to the observed effects. However, recent X.p.s. studies[47,50] have confirmed an alternative theory based on H bonding interactions as described above.

The degree of discharge treatment required to bring about this effect is low by comparison with treatment levels applied commercially where the usual aim is to optimize the wettability required for any further conversion (printing, lamination etc.). Under these circumstances it is usually observed[52] that heat sealing of discharge treated surfaces is more difficult (i.e. higher temperatures required to achieve a given peel strength) than for untreated surfaces (see below). This may be due to the creation of low molecular weight material via oxidative degradation which hinders interdiffusion or entanglement of the hydrocarbon polymer chains. Alternatively, the lower heat seal strength at a given temperature may be due to the reduced chain mobility caused by oxidation. It must also be emphasised that studies of the discharge treatment induced enhancement of autoadhesion have been exclusively concerned with additive free grades of polymer film whereas commercial films usually contain additives (other than a low level of antioxidant to prevent degradation during extrusion or to reduce ageing effects) such as slip, antiblock and antistatic agents. In many cases the presence of these additives requires high levels of discharge treatment to be employed in order to achieve adequate adhesion, e.g. for printing or lamination[53].

DISCUSSION

The subject of adhesion to polyolefins, even without additives, is clearly complex as indicated by the questions raised in the introduction. The main controversies centre on the importance of surface energies, weak boundary layers, surface topography and specific interactions.

It is not disputed that to achieve satisfactory adhesion to a polyolefin surface, it is usually necessary to pretreat the plastic. It is also clear that the pretreatments used commercially cause substantial oxidations of the surfaces. However, Hansen and Schonhorn[4] have argued that the main function of surface treatments is to eliminate weak boundary layers and that any oxidation is of secondary importance. It is certainly true that some pretreatments, e.g. CASING[4], cause crosslinking and in principle, any small molecules on a surface may be incorporated into the network. Also with an etching treatment, such as chromic acid, small molecules could be washed away from the

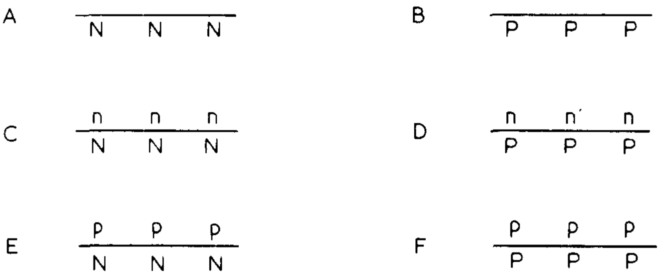


Figure 8 Simplified cases of low molecular weight species on polyolefin surfaces where N and P refer to non-polar and polar high molecular weight (strong) material, and n and p the corresponding low molecular weight (weak) material

surface. One key question is, therefore, whether it is necessary to introduce chemical functionality into a polyolefin surface to achieve good adhesion.

It can be calculated, that provided wetting is complete, dispersion forces are more than sufficient to account for the highest adhesion levels that have been observed in direct tension[54]. Also, Huntsberger[18,19] has argued that at thermodynamic equilibrium, wetting will normally be complete. However, on a sub-microscopic level real surfaces may be highly irregular and the degree of wetting (using Huntsberger's concept) may be far from complete. This will certainly be true if the viscosity of the 'wetting substance' is high and the 'setting time' is low. It is unknown what degree of wetting is required to give satisfactory adhesion. The overall interaction between the polyolefin surface and the 'wetting liquid' will depend on the degree of contact achieved and the magnitude of the intermolecular forces involved (dispersion, H bonding, etc.).

The commercial pretreatments for polyolefins certainly will increase the surface energies of polyolefins. This may lead to a substantially higher degree of wetting. Also the intermolecular forces will be stronger and stress concentrations due to voids will be reduced. Although *ATR*–i.r. has failed to detect any chemical changes with several different treatments of polyolefins, X.p.s. has detected substantial surface oxidation in all the cases examined. In the CASING process using inert gases Hansen and Schonhorn claimed no oxidation occurred although this has been disputed by Sowell *et al.*[55], and by Malpass and Bright[56].

It could, therefore, be argued that the increase in surface energy, resulting from the introduction of polar functions, is sufficient to improve adhesion. However, there is evidence to the contrary. When Schonhorn and Hansen[57] used the CASING process with fluorine, a decrease in critical surface tension of LDPE occurred, although adhesion increased and this was taken as evidence in favour of the weak boundary layer concept. Briggs and Kendall[50] have shown that the printability of discharge treated polyethylene can be destroyed by chemically blocking enoliseable carbonyl functions without altering the surface energy. This latter result is firm evidence for importance of specific interactions in adhesion, in this case H bonding. Likewise, it is possible to explain the result of Schonhorn and Hansen: as the PE surface is progressively fluorinated, the H bonding capability of the remaining C–H bonds is very much increased. The 'polar' component of the surface energy of poly(vinyl fluoride) is, for example, higher than that of a typical flame treated PP surface (see *Table 4*).

We suggest that the balance of evidence favours the following general view. Perfect wetting of a polyolefin surface would lead to high levels of adhesion even if only dispersion forces were involved. Therefore, wetting with untreated polyolefins must be inadequate and surface pretreatments result in chemical modifications which either increase the degree of wetting or lead to interactions stronger than dispersion forces. Usually, both occur because oxidation is involved giving rise to polar functions, some of which are capable of participating in relatively strong specific H bonding interactions. Much more work is required to identify the role of strong interactions, but the importance of such interactions has now been demonstrated directly[50] (discharge treated PE–'nitrocellulose-based' ink) and is indicated by the adhesion levels between partially fluorinated hydrocarbons and epoxide adhesives[8,57]. Exceptions to this generalization are likely to be cases where surface topography is all important, e.g. the large increase in adhesion resulting from trichlorethylene vapour treatment of PP[23] is probably due to mechanical keying. We believe that for commercial pretreatments of polyolefins, surface topography, is of secondary importance. Large increases in adhesion can be obtained with a mild chromic acid treatment of LDPE without any noticeable changes in topography.

Weak boundary layers may be important in isolated cases but much evidence has been presented against the idea that weak boundary layers are the main reason for adhesion problems involving polyolefins. However, it is important to understand the role of low molecular weight species on polyolefin surfaces. In the context of this paper we can distinguish six possible cases simplified in *Figure 8*: where N and P refer to non-polar and polar high molecular weight (strong) material, n and p the corresponding low molecular weight (weak) material. Case A represents the view of those who believe the poor adhesion of polyolefins is due to a lack of functional groups. The other cases can be associated with practical situations, e.g.

(B) chromic acid etched and washed PE.

(D) chromic acid etched PE contaminated with hydrocarbon oil or grease.

(D) untreated PE with a high level of slip agent.

(F) discharge treated PE with antistatic or slip agent.

Case C represents the weak boundary explanation for lack of adhesion to polyolefins. Briggs *et al.*[37] have followed the chromic acid etching of LDPE (Alkathene 47, $MFI = 2.0$) under very mild conditions and did not observe the expected discontinuity in either oxidation level or adhesion (to an epoxide) at low etching time. No evidence of transfer of hydrocarbon to an epoxide from an untreated surface of this LDPE was observed. Case E is well known to LDPE convertors. Migration of polar additives required for surface properties such as low-friction or low static charging cause problems in discharge treating for printing or lamination.

Case D has been studied by Brewis[58]. The chromic acid etching of HDPE increased the bond strength with an epoxide from 18.3 to 176.1 kg cm^{-2} (lap shear). Spreading a layer of petroleum jelly ($\sim 2 \times 10^4$ Å thick) over the etched surface only reduced the bond strength to 126.8 kg cm^{-2}, indicating the importance of displacement mechanisms.

Case F is relevant to several situations. It is well known that printing discharge treated LDPE of PP film containing some additives (particularly slip and antistatic) becomes more difficult as the film ages due to additive bloom. Briggs *et al.*[38] have shown that very small quantities of a silicon containing contaminant (probably silicic acid or a silicone) have a large effect on the adhesion of epoxide to a chromic acid etched PE surface. Overtreatment of polyolefin film surfaces by discharge treatment (and also probably flame and chromic acid[59] treatments) causes low molecular weight oxidised material to be produced via degradation. This may or may not affect subsequent adhesion problems. Some ink systems are tolerant to high levels of this material, presumably because it can be solvated and incorporated into the dried ink layer. However, lamination or heat sealing operations are likely to be hindered.

The existence of small molecules on polyolefin surfaces is probably common. However, low molecular weight material on the surface will not behave as a weak boundary layer if the interaction between substrate and adhesive (etc) is sufficiently strong to cause displacement or if an incorporation mechanism exists. Subtle effects can operate here as demonstrated by the quite different effects of additives with similar chemical compositions. It is also important to remember that a potential weak boundary layer can be created by a pretreatment (e.g. discharge treatment).

CONCLUSION

In the past there has been a tendency for adhesion problems with polyolefins to be ascribed to one particular property (e.g. weak boundary layers, low surface energy) with concomitant efforts to explain successful pretreatments in terms of changing this property. A more useful approach is to consider each adhesion situation on its own merits having regard to the effects of chemical composition of the surface (in terms of type and density of functional groups) on surface energy-wettability and strength of interaction with the adherend. It is also necessary to ascertain the importance of additives and other species of low molecular weight; the possibility that the wetting liquid can displace or dissolve these small molecules should be considered. In certain cases surface roughness will also be an important parameter.

ACKNOWLEDGEMENT

The authors wish to thank Dr D. G. Rance for critically reading the manuscript and making many helpful suggestions.

REFERENCES

1 *European Plastics News*, January 1980, 10
2 Bikermann, J. J. *Adhesives Age* 1959, **2** **(2)**, 23
3 Bikerman, J. J. and Marshall, D. W. *J. Appl. Poly. Sci.* 1963, **7**, 1031
4 Hansen, R. H. and Schonhorn, H. *J. Poly. Sci.* 1966, **B4**, 203
5 Schonhorn, H. and Ryan, F. W. *J. Poly. Sci. A2* 1968, **6**, 231
6 Schonhorn, H. and Ryan, F. W. *J. Appl. Poly. Sci.* 1974, **18**, 235
7 Zisman, W. A. *Ind. Eng. Chem.* 1963, **55** **(10)**, 19
8 Levine, M., Ilkka, G. A. and Weiss P. *J. Poly. Sci. B2* 1964, 915
9 Sharpe, L. H. and Schonhorn, H. *Adv. Chem. Ser.* 1964, **43**, 189
10 Iyengor, Y. and Erickson, D. E. *J. Appl. Poly. Sci.* 1967, **11**, 2311
11 Fowkes, F. M. *J. Phys. Chem.* 1963, **67**, 2538
12 Owens, D. K. and Wendt, R. C. *J. Appl. Poly. Sci.* 1969, **13**, 1741
13 Kaelble, D. H. and Uy, K. C. *J. Adhesion* 1970, **2**, 50
14 Cirlin, E. H. and Kaelble, D. H. *J. Poly. Sci. Polym. Phys. Edn.* 1973, **11**, 785
15 Owens, D. K. *J. Appl. Poly. Sci.* 1970, **14**, 1725
16 Kaelble, D. H. and Cirlin, E. H. *J. Poly. Sci. A2* 1971, **9**, 363
17 Fowkes, M. F. and Mostafa, M. A. *Ind. Eng. Chem. Prod. Res. Dev.* 1978, **17**, 3
18 Huntsberger, J. R. *Adhesives Age* 1978, 23
19 Huntsberger, J. R. in 'Treatise on Adhesion and Adhesives', Vol. 1. Ch. 4 Ed. R. L. Patrick, Marcel Dekker Inc., New York, 1967
20 Cherry, B. W. and Muddarris, E. S. *J. Adhesion* 1970, **2**, 42
21 Shields, J. *Sira Report* 1972, R500
22 Blais, P., Carlsson, D. J., Csullog, G. W. and Wiles, D. M. *J. Coll. Int. Sci.* 1974, **47** **(3)**, 636
23 Garnish, E. W. and Haskins, C. G. in 'Aspects of Adhesion — 5', Ed. D. J. Alner, University of London Press, London, 1969, p. 259
24 Blais, P., Carlsson, D. J. and Wiles, D. M. *J. Appl. Poly. Sci.* 1971, **15**, 129
25 Kim, C. Y. and Goring, D. A. I. *J. Appl. Poly. Sci.* 1971, **15**, 1357
26 Sweeting O. J. 'The Science and Technology of Polymer Films', Vol. 2, Wiley, New Yor, 1971, p. 188
27 Spell, H. L. and Christenson, C. P. *Tappi* 1979, **62** **(6)**, 77
28 Rugg, F. M., Smith, J. J. and Bacon, R. C. *J. Poly. Sci.* 1954, **13**, 535
29 Rossmann, K. *J. Poly. Sci.* 1956, **19**, 141
30 Johnson, W. T. M. *Official Digest of the Oil and Colour Chemists' Association* 1960, **32**, 1067
31 Johnson, W. T. M. *Official Digest of the Oil and Colour Chemists' Association* 1961, **33**, 1489
32 Willis, H. A. and Zichy, V. J. I. in 'Polymer Surfaces', Eds. D. T. Clark and W. J. Feast, Wiley, New York, 1978, Chapter 15
33 Rasmussen, J. R., Stedronsky, E. R. and Whitesides, G. M. *JACS* 1977, **99** **(14)**, 4736
34 Carlsson, D. J. and Wiles, D. M. *Can J. Chem.* 1970, **43**, 2397
35 Carley, J. F. and Kitze, P. T. Paper presented at the 37th Society of Plastic Engineers Ann. Tech. Conf. New Orleans, May 1979, p. 728 (*Poly. Eng. Sci.* 1980, **20**, 330)
36 'Handbook of X-ray and Ultravoilet Photoelectron Spectroscopy', Ed. D. Briggs, Heyden, London, 1977
37 Briggs, D., Brewis, D. M. and Konieczko, M. B. *J. Mat. Sci.* 1976, **11**, 1270
38 Briggs, D., Brewis, D. M., Comyn, J., Dahm, R. H., Green, M. A. and Konieczko, M. B. *Surf. Interface Anal.* 1980, **2** (3), 107
39 Ghorashi, H. M. *Plating and Surface Finishing* April 1977, 42
40 Briggs, D., Brewis, D. M. and Konieczko, M. B. *J. Mat. Sci.* 1977, **12**, 429
41 Bright, K. and Malpass, B. W. *Eur. Polym. J.* 1968, **4**, 431
42 Sykes, J. M. and Hoar, T. P. *J. Poly. Sci. Al.* 1969, **7**, 1385
43 Briggs, D., Brewis, D. M. and Konieczko, M. B. *Eur. Poly. J.* 1978, **14**, 1
44 Packham, D. E., Bright, K. and Malpass, B. W. *J. Appl. Poly. Sci.* 1974, **18**, 3237
45 Egorenkov, N. I. and Tishkov, N. I. *Mekh. Polim.* 1977, **(5)**, 933
46 Briggs, D., Brewis, D. M. and Konieczko, M. B. *J. Mat. Sci.* 1979, **14**, 1344
47 Blythe, A. R., Briggs, D., Kendall, C. R., Rance, D. G. and Zichy, V. J. I. *Polymer* 1978, **19**, 1273
48 Stradal, M. and Goring, D. A. I. *Can. J. Chem. Eng.* 1975, **53**, 427
49 Owens, D. K. *J. Appl. Poly. Sci.* 1975, **19**, 265
50 Briggs, D. and Kendall, C. R. *Polymer* 1979, **20**, 1053
51 Briggs, D., unpublished results
52 Sharples, L. K. *Plastics and Polymers* April, 1969, 135
53 Gregory, B. H. and Carrol, R. J. USI Europe NV report 'Preparation of Polyethylene Film for Adhesive Lamination'
54 Tabor, D. *Ann. Repts. for Chem. Ind. Prog. Appl. Chem.* 1951, **36**, 621
55 Sowell, R. R., DeLollis, N. J., Gregory, H. J. and Montoya, O. *J. Adhesion* 1972, **4**, 15
56 Malpass, B. W. and Bright, K. in 'Aspects of Adhesion – 5', Ed. D. J. Alner, University of London Press, London, 1969, p. 214
57 Schonhorn, H. and Hansen, R. H. *J. Appl. Poly. Sci.* 1968, **12**, 1231
58 Brewis, D. M. *J. Mat. Sci.* 1968, **3**, 262
59 Yamakawa, S. and Yamamoto, F. *J. Appl. Poly. Sci.* 1980, **25**, 40