Chemical basis of adhesion to electrical discharge treated polyethylene

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In a previous paper[1] we showed that enhanced autoadhesion resulting from electrical ('corona') discharge treatment of low density polyethylene (LDPE) was due to the interaction of oxygen functions, probably through hydrogen bonds as suggested by Owens[2]. X-ray photoelectron spectroscopy (X.p.s. or e.s.c.a.), the technique used for surface analysis of films, could not distinguish clearly all the groups present and we indicated that derivatization techniques would be investigated. Recently, work along these lines in connection with the printability of discharge treated LDPE has been reported[3] and since some of the conclusions from this work differ from our own we present here a summary of our results.

Discharge treatment of LDPE was carried out in air using parallel-plate electrode cells[4] similar in principle to that described previously[1]. In these experiments an air blower was used to replenish the air in the electrode gap continuously, in order to simulate more closely the film movement in continuous plant treatment.

Details of the derivatization techniques will be described elsewhere; for the purposes of this communication it is sufficient to note that carbonyl groups (keto or aldehydo) were converted into pentafluoro-phenylhydrazones and carboxylic acid groups to the sodium salt. The former reaction occurs rapidly (seconds) in an alcoholic medium. The latter reaction using 1N NaOH (in water) is slow (hours) and rinsing requires great care (see below); we used Na_3PO_4 solutions at pH 11 as recommended by Ramussen *et al.*[5]. Quantification (relative) was carried out via F1s: C1s and Na1s: C1s peak intensity ratios, respectively.

Autoadhesion studies were carried out on additive free 'Alkathene' 33 as described previously[1]. Printability studies used 'Alkathene' 77/11* an additive containing grade which was extracted with ether for 1 h at room temperature prior to use. Printability was assessed using the 'Scotch tape' test[6] and a commercial nitrocellulose-based ink.

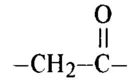
By use of specific chemical reagents and their effect on the ability of treated surfaces to autoadhere Owens deduced that the adhesive bond was between carbonyl and its enol tautomer across the interface[2]. Extending this principle and using X.p.s. to follow the reactions *directly* showed that –COOH groups (blocked/analysed via conversion to –COO$^-$Na$^+$) are present but do not take part in the autoadhesion mechanism. –C = O groups (keto/aldehydo; blocked/analysed via conversion to hydrazones) are present and are essential for autoadhesion. Br_2 (either in H_2O or CCl_4) prevents autoadhesion and is taken up without affecting the oxygen groups or the ability of the surface subsequently to react with phenylhydrazine. A phenyl hydrazine treated surface is slowly reoxidized and brominated by Br/H_2O. These observations prove that keto–enol tautomerization can occur. The results in the Table show that provided one surface contains enol (or potential enol) groups and the other contains carbonyl groups, then autoadhesion is not lost; thus brominated surfaces still adhere to discharge-treated surfaces because carbonyl groups remain in the former even though enolization is impossible At first sight the non-zero result for DT–PH is unexpected since one surface (PH) has neither carbonyl nor enol groups. However, an H– bond between enol groups in the DT surface and the –C=N–nitrog of the hydrazone in the PH surface can be formed. The result indicate the importance of H bonding through enolic –OH.

Table 1 Seal strength (g/25 mm) between surfaces discharge treated (*DT*) and then reacted with eiether Br_2/CCl_4 (Br) or phenylhydrazine/alcohol (PH). Seals were made at 85°C for 2 secs at 15 p.s.i.

	DT	Br	PH
DT	104	60	53
Br	60	0	0
PH	53	0	5

By discharge-treating LDPE for a range of times under fixed conditions of applied voltage and frequency, samples with printabilities over the range 0–100% ink adhesion were produced. X.p.s. analysis showed a monotonic increase in the population of –C=O (keto/aldehydo) and –COOH groups up to a plateau (corresponding to saturation of the polymer layer derivatized) which fortuitously occurs at the same time as perfect ink adhesion. Samples treated for a time slightly in excess of that required to give 100% ink adhesion were reacted with NaOH, Br_2/CCl_4 and phenyldrazine as before and then printed. Ink adhesion was destroyed by the last two reagents (without a significant change in wettability) and reduced slightly by NaOH treatment, but was unaffected by exposure to the solvents alone. Therefore adhesion to the ink is through enolic –OH groups in the discharge treated surface.

The difficulties inherent in work of this kind are illustrated by the comparison of our data with those of Spell and Christenson[3]. They assessed the effects of discharge treatmen in terms of changes in unsaturation, by following the uptake of bromine from Br_2 vapour (claimed not to attack other functionalities) and the number of –COOH groups, by following Na$^+$ uptake from dilute NaOH. Br_2 vapour must substitute the hydrogens in



$$-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-$$

since we find that exposing treated surfaces to this reagent leads to loss of autoadhesion, hence their Br uptake data does not just reflect increasing unsaturation. In fact we have previously given evidence that discharge treatment removes unsaturation . Their technique of rinsing NaOH-treated samples in distilled water gives rise to rapid reversal of –COO$^-$Na$^+$ to –COOH during the time required to remove sorbed NaOH[5]. X.p.s. confirms this and also shows that sorbed Na$^+$ is not removed by short exposures to water from samples with low wettability (a function of discharge treat-

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* 'Alkathene' polyethylenes are made by Imperial Chemical Industries Limited

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ment), hence their –COOH assessment is subject to several uncertainties.

The results of our work give direct confirmation to Owens' hypothesis[2] that enolic –OH is involved in the enhanced autoadhesive bonding of discharge treated polyethylene. The fact that it is also crucial to the mechanism of ink adhesion to such a surface seems to indicate the more general importance of this functional group in adhesion.

Acknowledgement

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Craze-proof bromostyrene–crosslinked polyester

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A novel phenomenon regarding craze resistance of bromostyrene*–crosslinked polyesters has been discovered while performing a group of studies on flame retardancy and other physical properties of these resins[1–4]. In these studies an alkyd resin composed of equal proportions of propylene glycol and of phthalic and furaric acids was crosslinked by a series of styrene/bromostyrene monomer mixtures. The total amount of crosslinking monomer amounted to 0.0048 moles per 1 g alkyd, resulting in a ratio of 2 moles of styrene/bromostyrene to 1 mole of alkyd double bonds. Six resin compositions were tested, in which the mole fraction of the bromostyrene of the total monomer amount was 0, 0.2, 0.4, 0.6, 0.8 and 1.0.

The assessment of the weathering stability of the resins included exposures of thin polyester plates to boiling water for different treatment periods. It was noted that whereas crazes were formed readily on the surface of the pure styrene-crosslinked polyesters, the tendency of craze formation decreased gradually as the bromostyrene proportion increased, and disappeared completely in the pure bromostyrene-crosslinked polyester. *Figure 1* presents a series of such plates after 12 h of water–boil treatment, and the gradual disappearance of crazing is clear. When the water–boil treatment laster for a longer period of time the crazes – where formed initially – resulted in disintegration of the polyester plates. In bromine containing plates, where craze formation was inhibited, round swells developed gra·

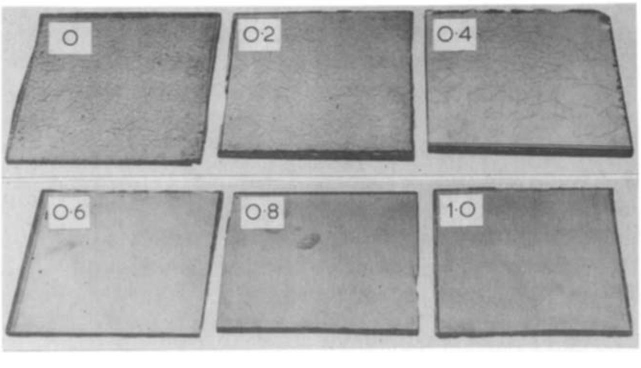

Figure 1 Polyester plates exposed to boiling water for 12 h. The numbers denote mole fraction of bromostyrene of total monomer

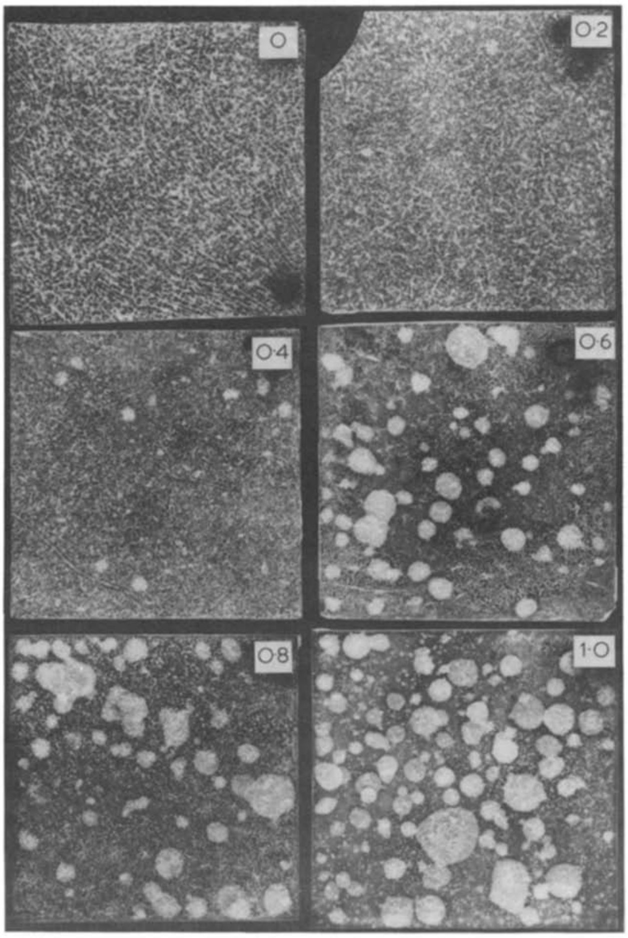

Figure 2 Polyester plates exposed to boiling water for 66 h photographed against a black background. The numbers denote mole fraction of bromostyrene of total monomer

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