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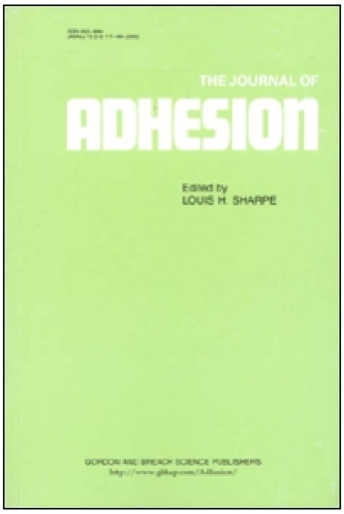

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Corona Discharge Treatment of Polyolefins*

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The effects of corona discharge treatment on polyethylene and polypropylene homopolymers have been studied. X-ray photoelectron spectroscopy was used to determine surface compositions which were related to surface free energy estimates from contact angle measurements. Changes in composition and surface free energy were measured as a function of treatment level. The work of adhesion was seen to increase with oxygen incorporation. The increase was not linear and this is attributed to an increase in the degree of sub-surface to near-surface oxidation at intense treatment levels. Aging of samples followed by XPS and contact angle measurement showed that surface wettability is reduced whereas a slight increase in surface oxygen was found. This phenomenon was attributed to the reorientation/migration of functional groups. Morphological examination by scanning electron microscopy indicated no surface roughening at any power level.

KEY WORDS corona discharge treatment; polyethylene; polypropylene; XPS; surface free energy; contact angles; reorientation; migration; SEM.

INTRODUCTION

Polyolefins have a low surface free energy and so it is normally necessary to pretreat their surface in some way in order to obtain satisfactory properties for adhesive bonding. There are several methods that can be used to increase the surface free energy of polyolefins; however, the ease and speed of corona discharge treatment has led to it being extensively used, particularly for the activation of polyolefin films. In corona discharge treatment the electrical discharge produced contains electrons, ions and radicals. Some of these impinge on the polymer surface and initiate free radical reaction sequences, which result in the introduction of functionality onto the surface. The majority of the functional groups incorporated contain oxygen[1–3] although nitrogen has also been reported.[4]

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In this study we report the results of corona discharge treatment of polyethylene and polypropylene homopolymers, respectively. The films were subjected to different intensities of surface treatment. The amount of oxygen introduced into the surface region was measured by X-ray photoelectron spectroscopy and related to the water wettability. The extent of oxidation at the two different polymer surfaces was compared and monitored over a period of three months. Variable angle XPS was used in conjunction with a simplified model of the treated surface to estimate the depth of the altered layer produced.

EXPERIMENTAL

The biaxially drawn films (thickness ~25 μm) used in this study consisted of coextruded polypropylene cores with melt coats (thickness ~5 μm) of polyethylene (PE, $\rho \sim 935$ kg m^{-3}) and polypropylene (PP, $\rho \sim 906$–908 kg m^{-3}). The polymers contained low levels of essential additives only, that is <0.1% w/w of calcium stearate, and <0.2% w/w of antioxidants/stabilisers. Discharge treatment was performed immediately after film manufacture by an in-line Sherman Treaters (GT 140) industrial corona discharge unit using an electrode gap of ~2 mm, electrode length of 1 m and film line-speed of 50 m min^{-1}, with untreated film being produced in exactly the same way except with no voltage being applied to the electrode system. Reels of treated and untreated films of at least 200 m length and of 1 m width were produced, from which representative samples were cut and stored in the form of "blankets" and stored under cool, dark and dry conditions for aging studies. Corona input powers of 0, 1, 2 and 3 kW were employed as representative of treatment levels above and below the usually-used commercial level of 2 kW. XPS analysis was performed 1 day after surface treatment.

XPS spectra were recorded on a VG ESCALAB spectrometer using an Al Kα X-ray source, a constant energy analyser pass energy, and take-off angles of 90° and 30° with respect to the sample surface. The spectra were charge referenced to the C_{1s} peak occurring at a binding energy of 284.6 eV, quantification being achieved, with a reproducibility of ±5% or better, by measurement of peak area after subtraction of a Shirley type background. Correction was made for photoelectron cross-section,[5] angular asymmetry parameter,[6] energy dependence of the inelastic mean free path[7] and the transmission of the energy analyser.[8] Care was taken to avoid beam damage by minimising exposure to X-rays. Spectra recorded for the untreated films showed them to be free from contaminants and no evidence for the presence of migratory additives was observed either before or after surface treatment.

Advancing contact angles were measured using a Krüss G40 goniometer. Values quoted are averages from the measurement of the contact angle of at least six drops, with the standard deviation not exceeding 2° in most cases. The liquids used were triply-distilled water, dimethylsulphoxide (Romil Chemicals, 99.9%), ethane-1,2-diol (Aldrich, 99+%), dimethylformamide (Aldrich, 99.9%) and diiodomethane (Aldrich, 99%). The surface tensions of these liquids were checked using a Du Nouy ring, with the experimental values agreeing well with those found in the literature. Surface free energies were calculated using the procedures described by Owens and Wendt.[9] Reduction in the surface tension of contact angle liquids caused by the dissolution of small molecules at the surface can give misleading values for surface energies. The surface tensions of the liquids used were measured while in contact with a treated polymer surface. No evidence for a decrease in surface tension was found in this instance. At a magnification of ×20,000 SEM analysis did not detect any significant increase in roughness of the surface as a result of treatment.

RESULTS

Figures 1 and 2 show the effect of different treatment levels on the oxidation behaviour and water contact angle of PP and PE surfaces, respectively. Under the conditions employed, the oxygen content of the surface increases with treatment level and a corresponding decrease is observed in the water contact angle. Maximum surface free energies of 36.4 mJ m^{-2} and 40.9 mJ m^{-2} were obtained for PP and PE, respectively, in contrast to 31.9 mJ m^{-2} and 31.6 mJ m^{-2} for the respective untreated homopolymers. As expected, the increases in surface free energy are due to higher polar components (γ_s^p) on the treated surfaces, with the dispersion components (γ_s^d) remaining largely unaltered. More oxygen is detected on PE than PP.

Attempts were made to identify the depth of oxidation in each case using two model oxygen depth profiles. The first assumes that a uniform oxidized layer exists in which the concentration of oxygen atoms is constant as shown schematically in Figure 3(a). Values of 5–7 nm were obtained for both PP and PE from this step type model. The second model assumes that the oxygen concentration decreases exponentially as a function of depth into the treated polymer surface, as shown schematically in Figure 3(b). This model is perhaps more realistic. The results obtained suggest that the oxygen concentration decreases to half its value at the surface at a distance of 3–5 nm into the polymer. For both model types, the calculated values were obtained from variable take-off angle XPS measurements, taking into account the relative sensitivity factors as described in the experimental section and assuming inelastic mean free paths (IMFP, λ) of 40Å and 35.7Å for C_{1s} and O_{1s} photoelectrons, respectively. It appears that both PE and PP are oxidized to a similar depth although, in view of the assumptions made, absolute values for depth of oxidation must be regarded as approximate. For comparable levels of treatment a higher oxygen content was always obtained for the PE sample. Since the depth of oxidation is similar for both polymers, this may be attributed to a greater degree of oxidation within the modified surface layer on the PE sample.

Figure 4 shows the relationship between oxygen concentration as measured by XPS and the work of adhesion between the water and the two polymers. The work of adhesion (W_{sl}) was calculated from contact angle measurements (θ) using,

$$W_{sl} = \gamma(1 + \cos\theta) + \pi_e$$

where γ is the surface tension of water and π_e is the equilibrium spreading pressure of the liquid upon the solid surface. Surface adsorption of liquid vapour acts to reduce the free energy of the surface; however, for low surface energy solids vapour adsorption is negligible and, therefore, the spreading pressure may safely be

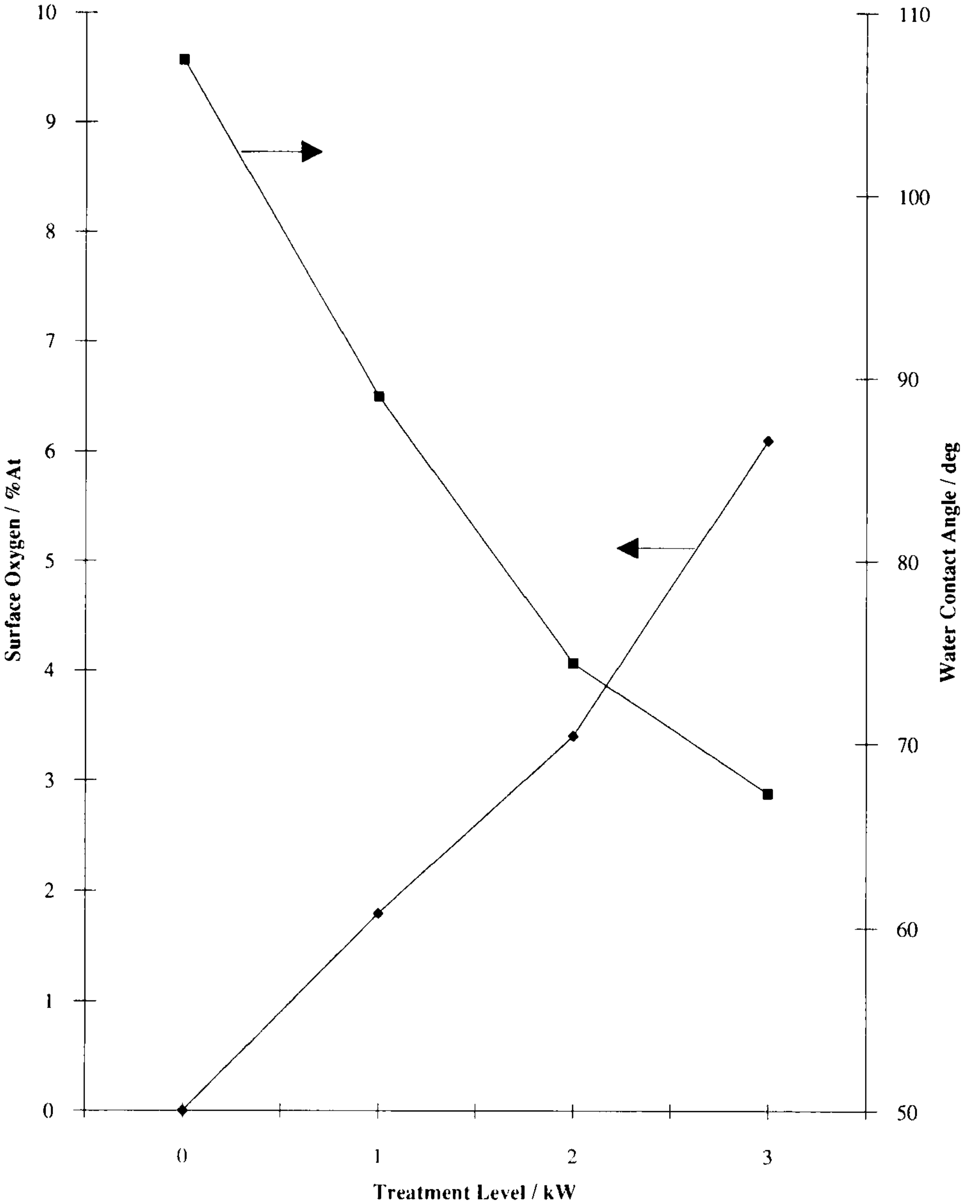

FIGURE 1 Surface oxygen concentration *versus* treatment power for polypropylene.

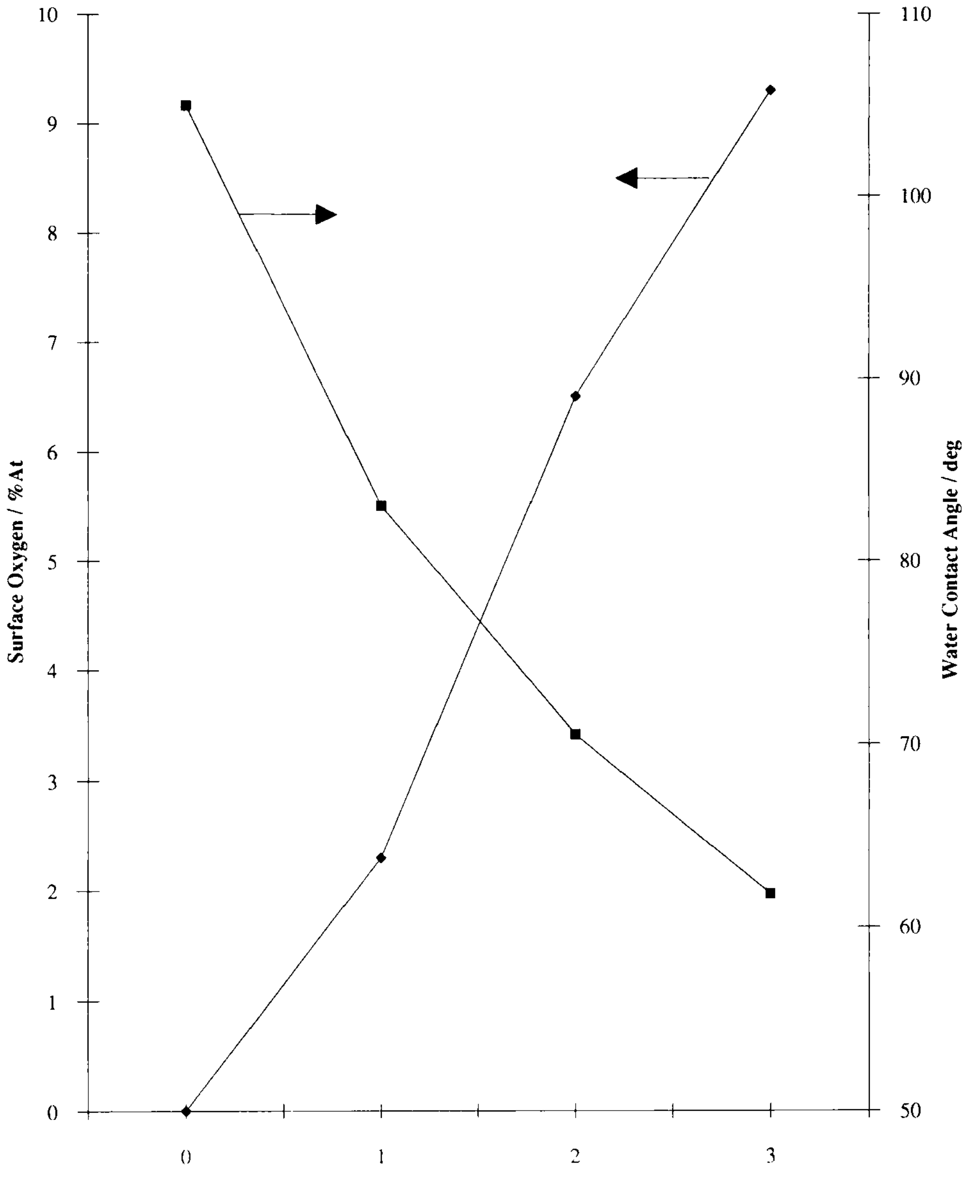

FIGURE 2 Surface oxygen concentration *versus* treatment power for polyethylene.

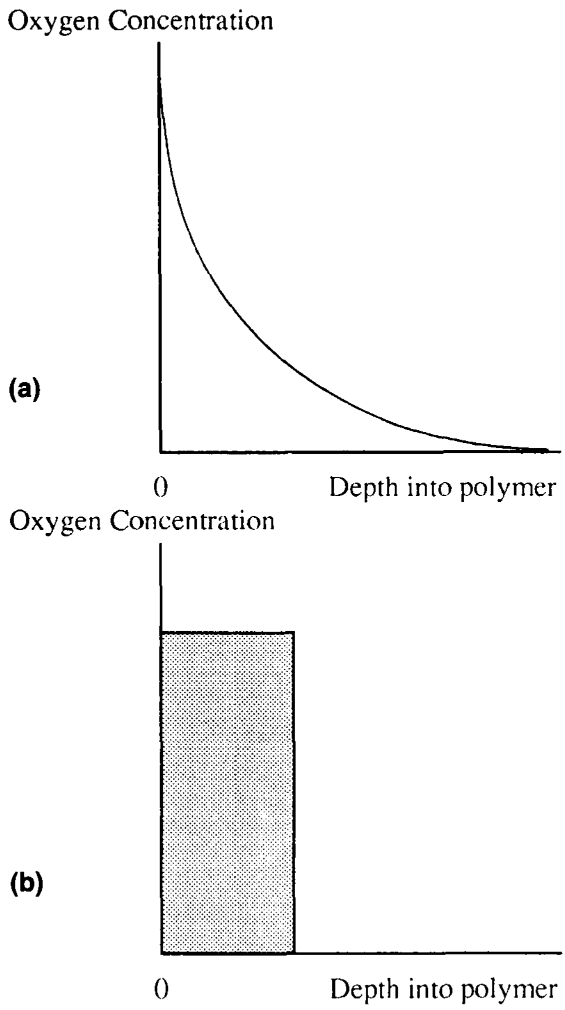

FIGURE 3 Schematic diagrams for (a) step model for oxygen concentration, (b) exponential decay model for oxygen concentration.

neglected.[10,11] The relationship between W_{sl} and oxygen concentration is not linear and both polymers show the same behaviour with regard to the effect of oxidation on the work of adhesion. The rate of increase in W_{sl} with oxygen concentration is high initially but reduces as the surfaces become more oxidized. Work of adhesion is determined principally by the interaction between a liquid and the outermost atomic layer of the polymer. This measurement is, therefore, more surface specific than XPS which samples to a depth of several nanometres. The lack of correspondence between W_{sl} and XPS measurements may be due to a greater degree of sub-surface oxidation following intense corona treatment. Similar conclusions were drawn from studies of flame-modified surfaces. At intense flame treatment the heat

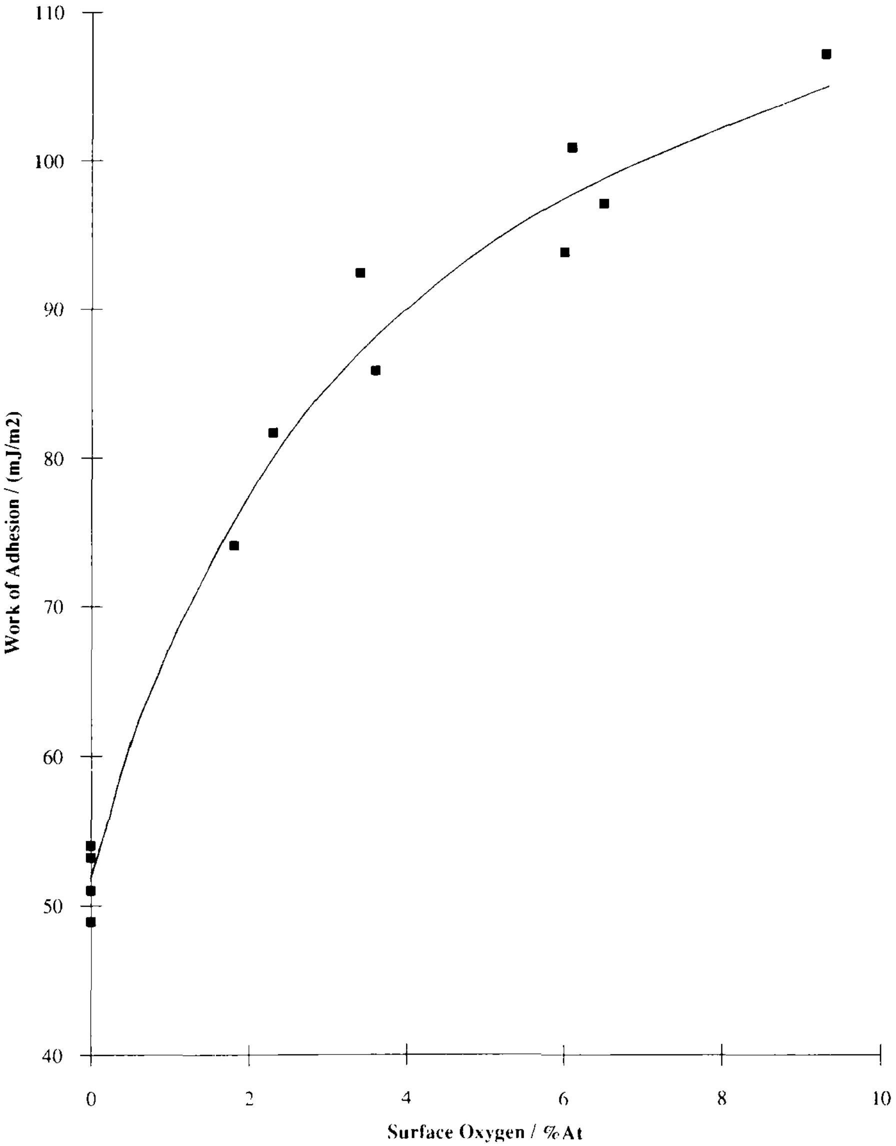

FIGURE 4 The work of adhesion with water of corona-treated samples *versus* surface oxygen concentration.

transfer to the surface increases the mobility of functional groups and a decrease in W_{sl} is observed as they migrate away from the surface.[12]

The observation of a greater degree of oxidation for PE is in agreement with previous work.[13] The difference could be explained by the production of volatile, low molecular weight, oxidized fragments during corona discharge as PP is thought to be more prone to chain scission due to the radical stabilising effect of the pendant

TABLE I
The effect of ether washing on surface oxygen concentration and work of adhesion with water

Melt coat	Treatment level/kW	[O] initial/%At	W_{sl} initial /mJ m^{-2}	[O] washed/%At	W_{sl} washed /mJ m^{-2}
PE	0	0	54	—	—
PE	1	2.3	81.7	2.9	84.3
PE	2	6.5	97.1	4.9	86.9
PE	3	9.3	107.2	5	88.4
PP	0	0	51	—	—
PP	1	1.8	74.1	1.6	53.7
PP	2	3.4	92.4	1.4	57.3
PP	3	6.1	100.9	2.4	63.5

methyl group.[14] In order to check for the presence of low molecular weight oxidized material at the surface, samples were washed in diethyl ether and reanalysed, results of which are shown in Table I. Both PP and PE samples showed a reduction in measured oxygen concentration as a result of diethyl ether washing. The reduction in surface oxygen was more severe in the case of PP, with up to a 60% decrease compared with about 45% for PE. Corresponding decreases were observed for the work of adhesion with water; Figure 5 shows the effect of ether washing on the work of adhesion of the surfaces with water. This indicates more low molecular weight oxidised material was formed at higher treatment levels, this observation being consistent with a mechanism involving the production of free radicals at the polymer surface which would be expected to be more numerous at higher input powers. In addition, it appears that less low molecular weight oxidised material is formed at the PE surface than at the PP surface, again suggesting that PE is more stable than PP to free radical degradation. The reduction in measured surface oxygen is attributed principally to the removal of low molecular weight oxidized material, although reorientation/migration of functional groups into the polymers during solvent extraction could contribute to the effect. The presence of low molecular weight material could form a weak boundary layer and adversely affect adhesion, although this will depend upon the quantity of the low molecular weight material and its compatibility with the adhesive or printing ink used.

The results from aging of the sample surfaces are summarised in Table II. A recent study has reported no change in oxygen concentration and wettability over the period of 30 days.[15] In the work reported here changes were detected, but over a longer time scale. The work of adhesion between polymer and water is observed to decrease, while the oxygen concentrations for both PP and PE surfaces increase slightly with aging.

The decrease in work of adhesion without a corresponding reduction in oxygen concentration was unexpected but may be explained by the reorientation/migration of oxygen-containing groups[16] in the modified surface layer. Movement of groups away from the near surface would reduce the surface free energy of the polymers and have a large effect on work of adhesion. Additives in the polymer migrating to the surface could also contribute to the reduction in surface free energy. Since XPS

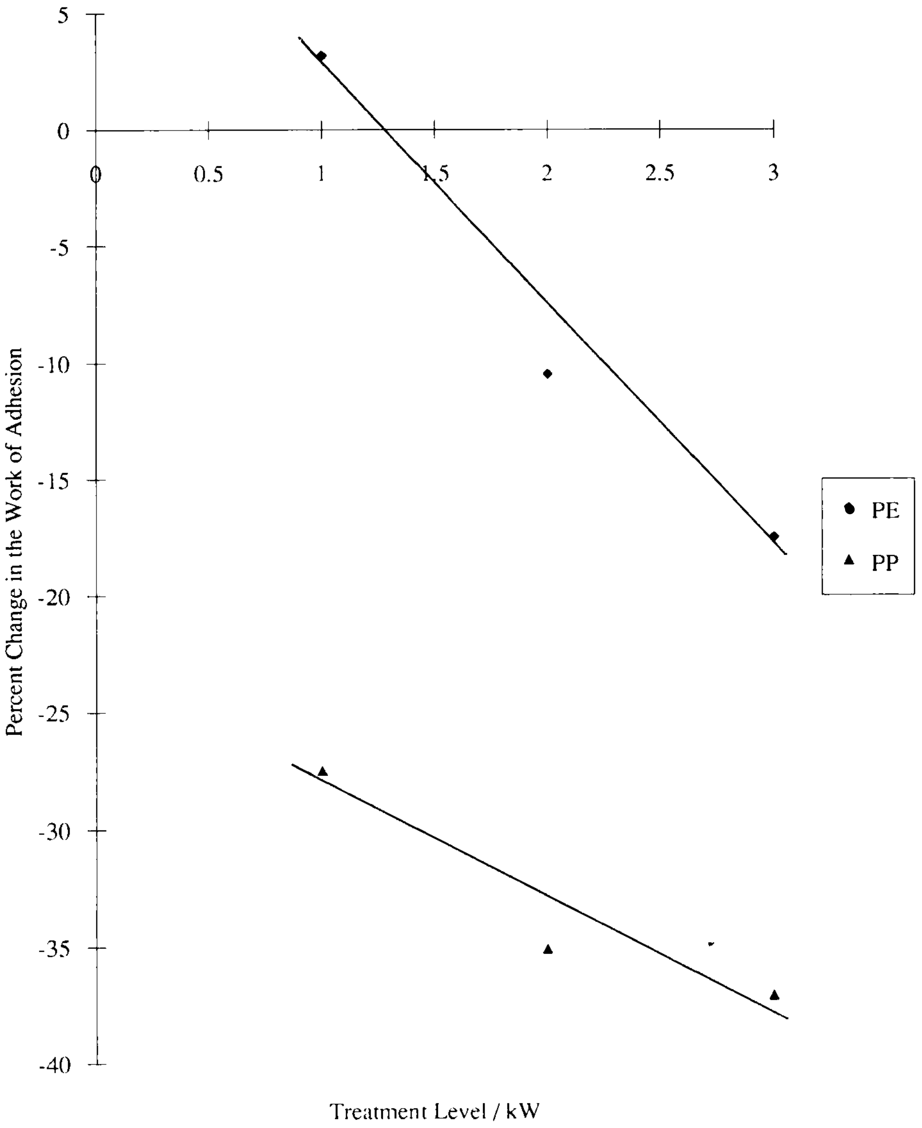

FIGURE 5 Percentage change in the work of adhesion of ether-washed polyethylene and polypropylene with water.

measurements have a sampling depth of several nanometres, they would be less affected by functional group migration in the very-near-surface region. The enhanced oxygen concentration on aging is thought to be due to an increased sub-surface concentration of oxygen functional groups produced by reorientation/migration in the modified region.[17] Work is in progress to determine the mechanism by which wettability is reduced in more detail using angle-resolved XPS and model profiles and to characterise further the surface chemistry of the materials.

TABLE II
The effect of sample aging on oxygen concentration and work of adhesion for samples treated at 2 kW input power

	Polyethylene		**Polypropylene**	
Time/days	**[O]/%At**	**W_{sl}/mJ m^{-2}**	**[O]/%At**	**W_{sl}/mJ m^{-2}**
2	6.5	97.1	3.4	74.1
31	8.5	—	3.8	—
87	8.8	86.1	5.4	83.4
130	6.5	88.4	5.0	83.9

CONCLUSIONS

The effect of corona discharge treatment on the surface of PP and PE has been studied. XPS showed the presence of more oxygen at the treated surface of PE than PP, resulting in the PE samples having a higher surface free energy and greater water wettability. Angle-resolved XPS suggests that the thickness of the modified layer produced by corona discharge is similar for the two polymers. Values of 5–7 nm were obtained using simplified models for the treated surface. The presence of low molecular weight material at the surface was confirmed by washing in diethyl ether. Changes in water wettability on aging are attributed to migration/reorientation of functional groups within the modified surface region.

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