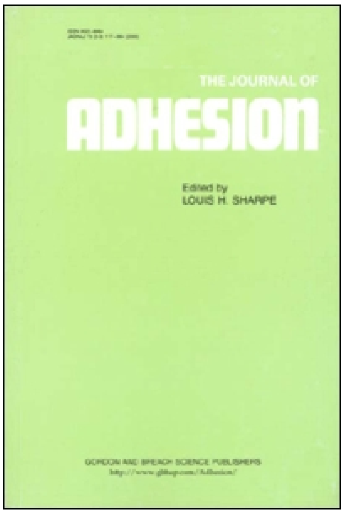

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Corona Versus Low Pressure Plasma Treatment: Effect on Surface Properties and Adhesion of Polymers

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Low density polyethylene (PE) and polyethylene terephthalate (PET) films were treated in air plasma of a low pressure (500 mTorr) large area microwave (2.45 GHz) discharge, or in a corona discharge at atmospheric pressure. The modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS) for their oxygen content [O] and surface chemical structure, which were related to the corresponding peel strength of PE/PE and PE/PET laminates. Although the oxygen concentration at the surface increased monotonically with the degree of treatment, the peel force reached a maximum and then sharply decreased. Regardless of the treatment type, the maximum peel force occurred for [O] values between 10–15 at.%. The highest peel force has been found to occur when the concentration of C—O (hydroxyl, ether, epoxy, . . .) groups is highest and that of O=C—O (carboxyl) groups is lowest, which corresponds to the situation when the effect of a weak boundary layer, due to low molecular weight materials, is minimal (low O=C—O concentration).

KEY WORDS adhesion; surface modification; low pressure plasma; corona discharge; polyethylene; polyethylene terephthalate; peel strength; peel force.

1. INTRODUCTION

Several techniques have been developed to modify polymer surfaces in attempts to improve adhesion, wettability, printability, dye-uptake, and other surface characteristics, without altering their volume properties. These include wet-chemical treatment and exposure to flames or corona discharges.[1-4] Besides the above mentioned more conventional approaches, low pressure nonequilibrium plasma offers an attractive way to control surface functionalities (nitrogenation, oxidation, fluorination etc.);[5-9] the same plasma reactors can also be used for etching or for deposition of films. Since the processes involved in various surface modification techniques are substantially different, their systematic comparison is difficult and so far absent from the literature.

The aim of the present work is to compare the effect of two types of plasma,

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namely that of a low pressure discharge and that of a corona discharge, on the surface chemical structure and adhesion of conventional polymers. In plasma treatment, the modification generally proceeds *via* activation, followed by chemical reactions. Energetic particles (electrons, ions, photons, free radicals) interact with the organic surface *via* processes which lead to multiple reactions: breakage of covalent chemical bonds, crosslinking, reaction of surface free radicals and, finally, incorporation of chemical groups originating from the plasma.

Plasma-surface interactions can affect surface properties which result in improved adhesion. Contaminants such as release agents and lubricants can be removed from the polymer surface; the surface can be microetched leading to an enhanced microroughness, and the surface energy is increased *via* the incorporation of polar groups. Liquid adhesives then wet more effectively and the contact area is increased. Ultraviolet radiation from the plasma can cause crosslinking, which can also inhibit the outward diffusion of mobile additives such as antioxidants and plasticizers from the polymer bulk. Finally, plasma treatment can provide the necessary chemical groups, which may eventually lead to covalent bonding between materials.

Adhesion of corona-treated polyolefins has been related to different mechanisms such as electrostatic attraction[10] or to the formation of keto groups on the PE chain.[11] These groups enolize and new hydrogen bonds are formed with carbonyl groups in the adjacent film when the two are heated together under pressure. Recently, joint strength has been interpreted in terms of a weak boundary layer due to low molecular weight (LMW) materials and the aging process has also been investigated.[12-14]

In our laboratory, we have been using low pressure, large area microwave discharges to modify the surface of commercial polymers for improved metal adhesion, printability and dyeability,[15-17] while the corona discharge has been used for the surface treatment of components in fiber-reinforced polymer composites.[18] In the present work, we quantitatively compare the effect of low pressure plasma and of the corona discharge in air on the overall oxygen uptake, the formation of different surface chemical moieties, and the adhesion of polymers, namely polyethylene and polyethylene terephthalate.

EXPERIMENTAL METHODOLOGY

Polymers were treated in two different experimental systems. Low pressure plasma modification was performed in a reactor which consists of a cylindrical, turbomolecularly pumped stainless steel vessel, equipped with a fused silica window (28 cm in diameter) through which microwave (2.45 GHz) power is applied from a periodic slow wave structure (for more details, see Refs. 15–17). The substrates were mounted on a substrate holder (facing the window, at a distance of 4 cm) allowing a uniform treatment of surfaces up to 18 cm in diameter. The plasma treatments were carried out at a pressure of 500 mTorr, using a flow rate of 50 sccm of air, and a total microwave power of 100 W. The level of treatment was controlled by varying the exposure time, t, of the sample to the discharge.

Corona treatment was performed in a system also described in more detail elsewhere.[18,19] It consists of a high voltage, silica-covered electrode, and a grounded rotating aluminium cylinder, 8 cm in diameter. High a.c. voltage (3.5 kHz, 10–15 kV) was applied to the quartz electrode. The film substrates, 6 cm in width, were mounted onto the grounded electrode. The exposure time of samples to the corona discharge and the corona current level were used to control the degree of treatment. The experiments were performed in laboratory air at 50% relative humidity.

Polymeric materials (25 μm thick films) studied in this work were polyethylene terephthalate (PET; DuPont "Mylar") and linear low density polyethylene (PE; Dow Chemical Canada Inc.); the latter, specially prepared for this investigation, was nominally free of additives. The surface chemical structure was determined in a VG-ESCALAB 3MKII surface analytical instrument by X-ray photoelectron spectroscopy (XPS), using Mg-K_α radiation. The pressure in the analytical system was below 5×10^{-9} Torr, and the take-off angle was 45°, unless otherwise specified in the text. The measured XPS spectra were not smoothed prior to deconvolution. The inelastic background was subtracted using Shirley's method.[20] A curve-fitting SURFSOFT program has been used, which allows a variation of parameters such as the Gaussian/Lorentzian ratio (60%/40% used here), the full width at half maximum (FWHM), and the peak positions. The curve-fitting quality was evaluated by the chi-square convergence.

The sample surfaces were not cleaned prior to plasma treatment, since even very pure solvents (*e.g.* methanol or water) are known to leave traces of oxygen.[9] No oxygen has been detected on the as-received PE, and the FWHM value of its high resolution C(1s) peak was 1.35 eV. On the surface of PET, the [O]/[C] ratio was found to be 0.35; compared with the stoichiometric value of 0.40, this suggests the presence of some hydrocarbon contamination from the atmosphere.

Laminates of untreated and treated films were prepared using a Carver Laboratory press at 40°C and 33 MPa for 20 seconds. The peel force was measured in a T-peel test using an IMASS SP-103B Slip/Peel Tester. The experimental conditions were as follows: peel rate 12 in/min, sample width 1 in.

3. RESULTS AND DISCUSSION

3.1. Effect of Oxygen Concentration on Peel Force

In this work we have attempted to treat the polymers using comparable conditions of energy density during treatment in both the low pressure and the corona discharges. Treatment efficiency can therefore be correlated with the parameter "degree of treatment," W, defined as the nominal electrical energy delivered per unit area of the treated sample surface. Since both treatment systems can be approximated by a parallel electrode configuration, we use $W = (P \cdot t)/A$, where P is the nominal power dissipated in the plasma, and A is the sample area exposed to the discharge.

Figure 1, a plot of [O] *versus* W, shows that experimental points for corona at different current levels and for low pressure plasma follow the same trend. Therefore, the oxidation efficiency in both treatment systems can be considered comparable, even if some uncertainty in the exact plasma volume were to be taken into account.

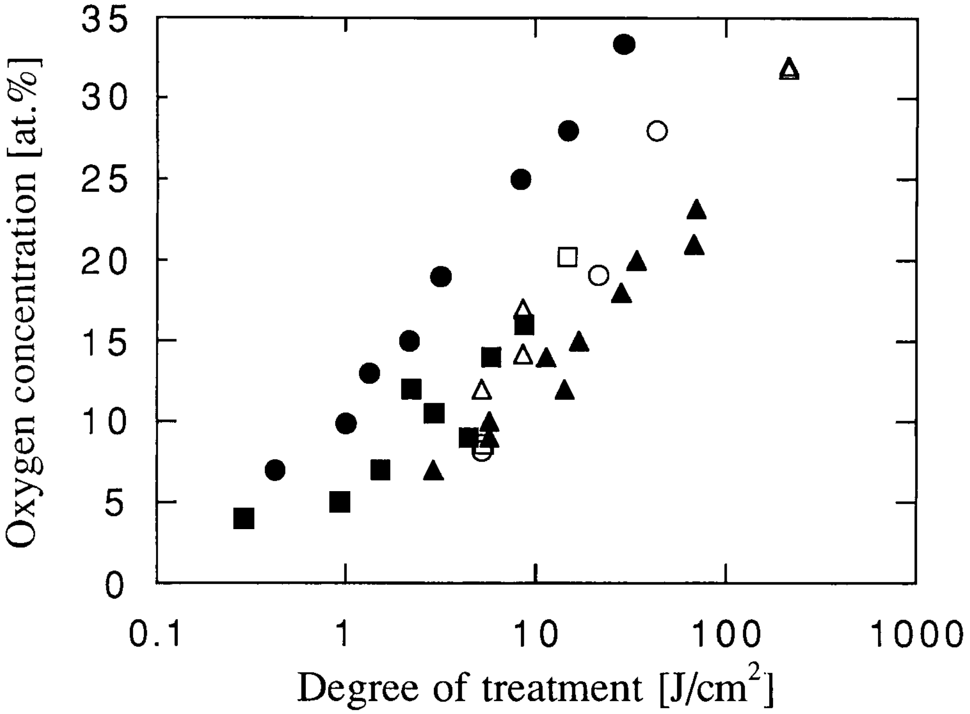


FIGURE 1 Oxygen concentration on PE surfaces as a function of degree of treatment, W, by low pressure plasma (▲) and by corona discharge in air at different discharge currents (■ 3 mA, ● 5 mA, △ 10 mA, □ 15 mA, ○ 20 mA).

We now examine the effect of treatment time, t, at different power levels, on the peel force. The peel force of the plasma-modified PET/PE laminate, plotted as a function of t, displays a clear maximum (see Fig. 2a); compared with the monotonic increase in [O] values (Fig. 2b), this behaviour indicates an enhancement of adhesion at lower [O] values, but that higher surface oxidation (*i.e.* excessive plasma exposure) is counterproductive. The PE/PE laminates behave in a similar manner (see Fig. 3): while [O] values increase monotonically with treatment time (Fig. 3b), the peel force exhibits a sharp maximum (Fig. 3a), the position of which depends on the power density during treatment. Clearly, the treatment time required to achieve maximum peel force decreases with increasing power density, P/A.

Reduced peel strength following long exposure is well known for corona treated films[11] but not for modifications by low pressure plasma.[5] The reason that this is observed in the present experiments is presumably that the polymeric substrates are directly exposed to the microwave plasma, which is substantially more efficient in producing reactive species than plasma excited at lower frequencies (*e.g.* radio-frequency, 13.56 MHz) or in a "downstream" flow-type reactor.[5,6] In the case of corona, the drop in peel force following longer treatment times has been associated with excessive amounts of LMW oxidized materials,[13] which are known to form a weak boundary layer at the polymer-polymer interface.

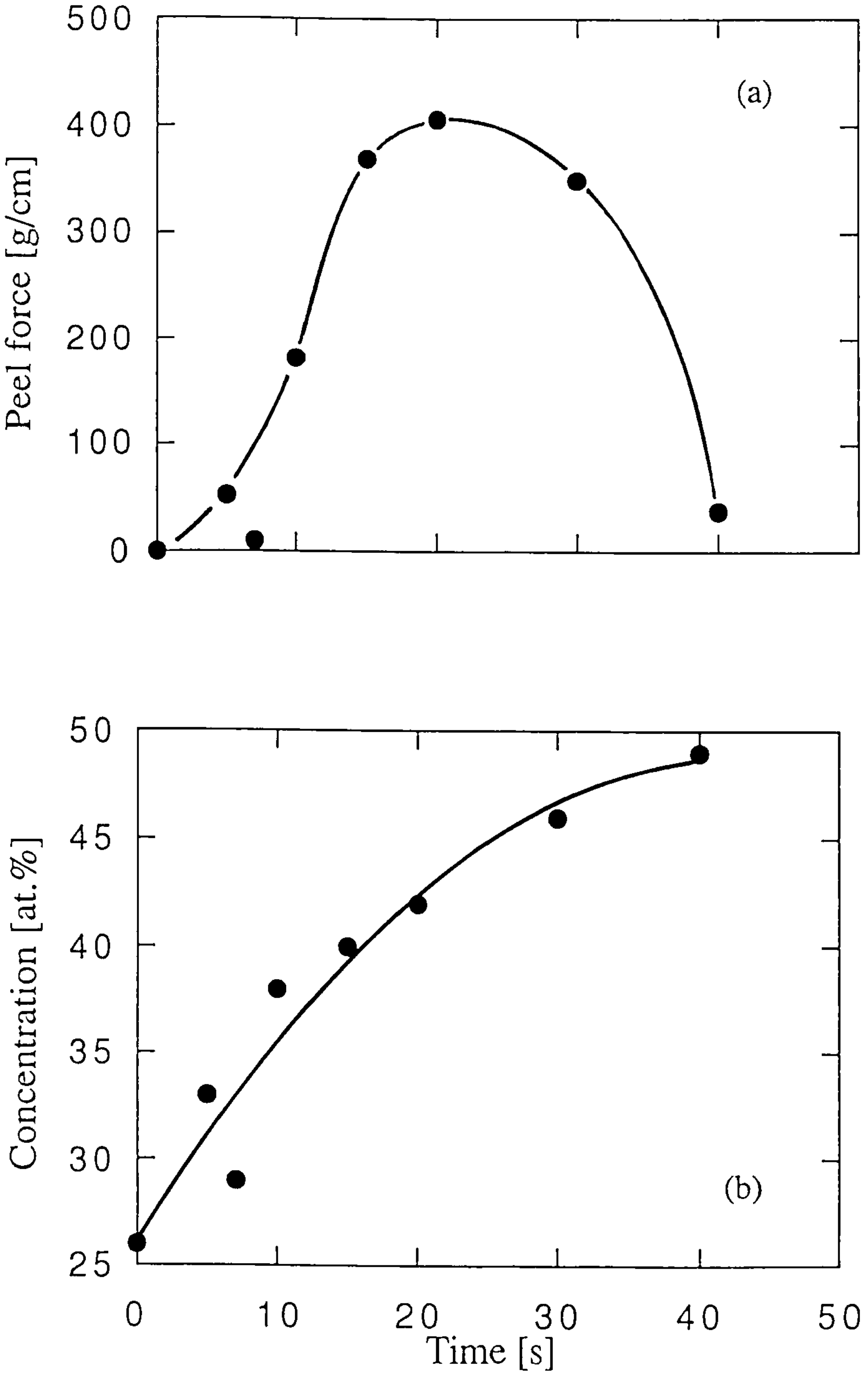


FIGURE 2 Peel force of PE/PET laminates (a) and oxygen concentration on the PET surface (b) as a function of treatment time in low pressure air plasma. Power density of 0.6 W/cm^2.

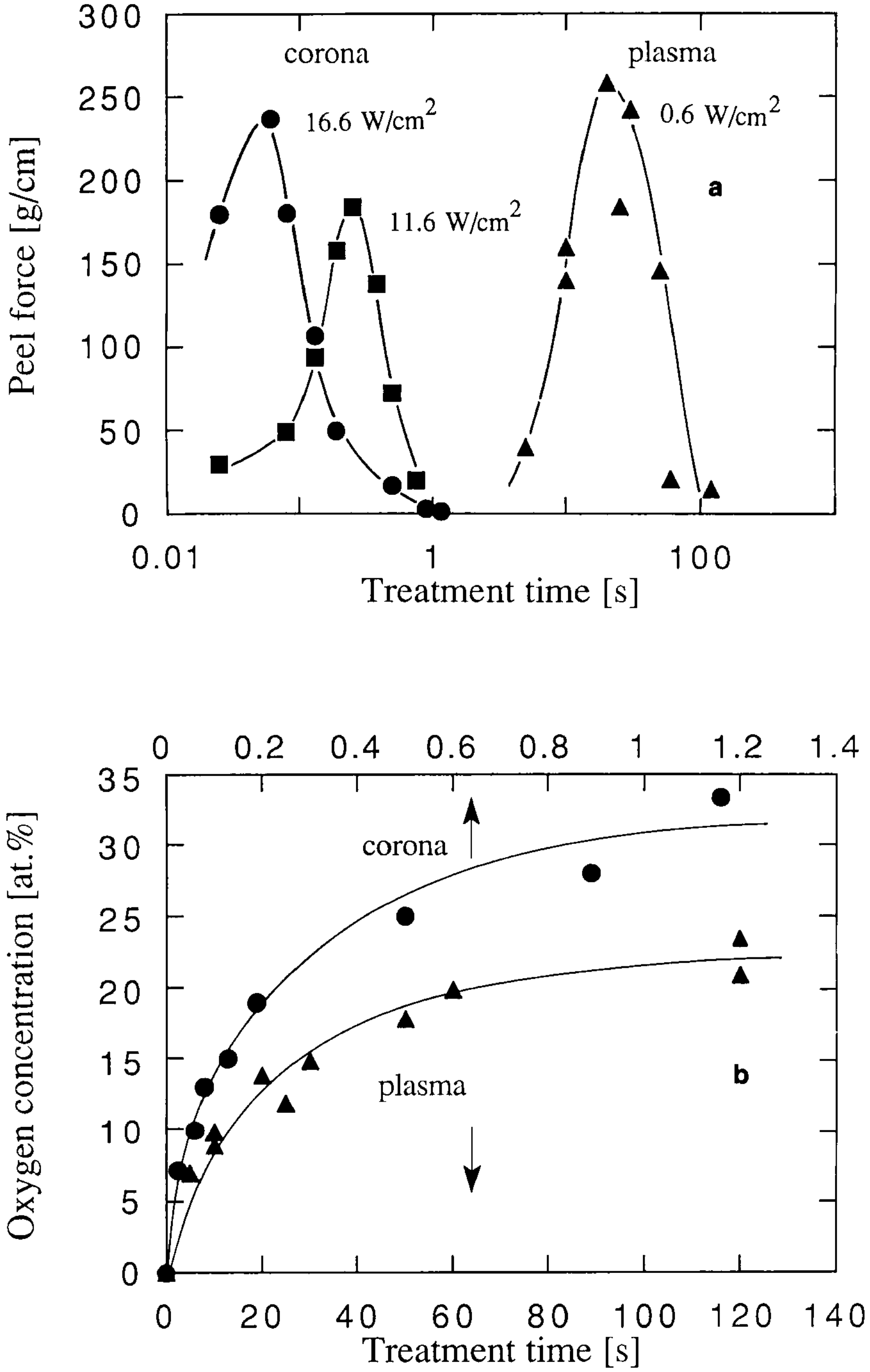
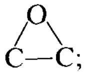


FIGURE 3 Peel force of PE/PE laminates (a) and oxygen concentration on PE surfaces (b) as a function of treatment time in low pressure air plasma and in corona in air discharge at different power densities.

Comparing the results presented in Figures 2 and 3, one may conclude that the maximum peel strength of the laminate occurs at a certain "optimum" surface concentration of oxygen, as shown in Figure 4. Regardless of the treatment type (corona or low pressure plasma), the maximum peel strength is attained at comparable [O] values, namely between 10 and 15 at.%. It is interesting to note that the absolute values of the peel force are also almost identical in both types of treatment, which suggests that the adhesion force of the present laminates is controlled by the same mechanism. In the following, this effect is correlated with the surface chemical structure of the PE/PE laminates.

3.2 Effect of the Surface Chemical Structure on the Peel Force

The surface chemical structure has been studied by high-resolution XPS measurements using peak assignments from the literature.[21] After treating the polymer in air discharges, the surface was, of course, found to contain carbon and oxygen, but only a negligible (<1 at.%) amount of nitrogen. The original narrow C(1s) peak for untreated PE (1.35 eV FWHM) broadens after treatment and four different peaks can be distinguished in the spectra (see Fig. 5): C1 (285 eV): hydrocarbons (C—H, C—C); C2 (286.5 eV): C—O groups such as hydroxyl (C—OH), ether (C—O—C) or epoxy  $\overset{O}{\mathrm{C{-}C}}$; C3 (288.1 eV): carbonyl (C=O) or double ether

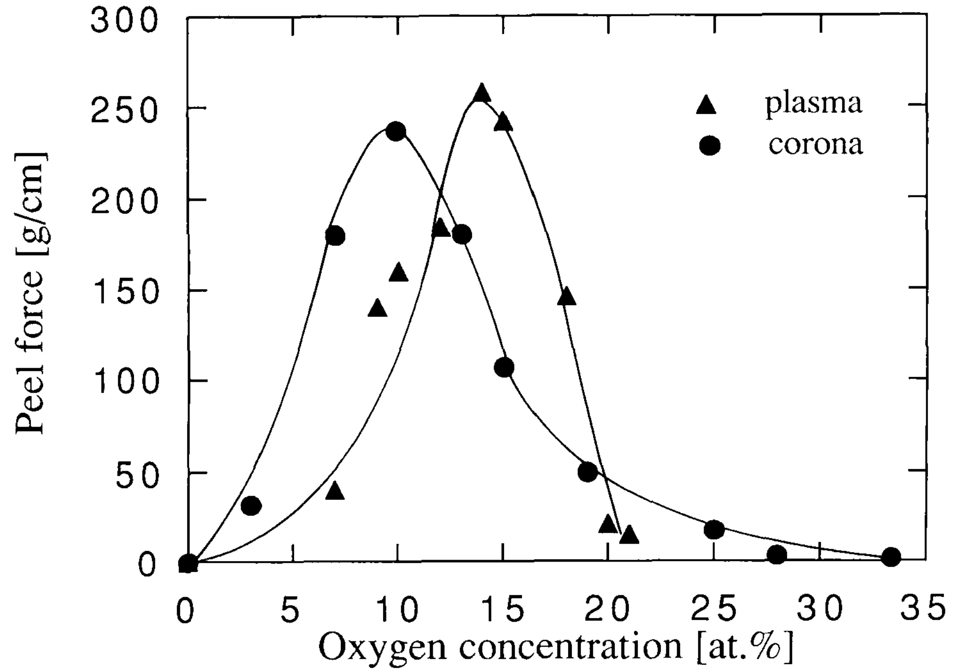


FIGURE 4 Peel force of PE/PE laminates as a function of oxygen concentration following low pressure plasma and corona discharge treatment.

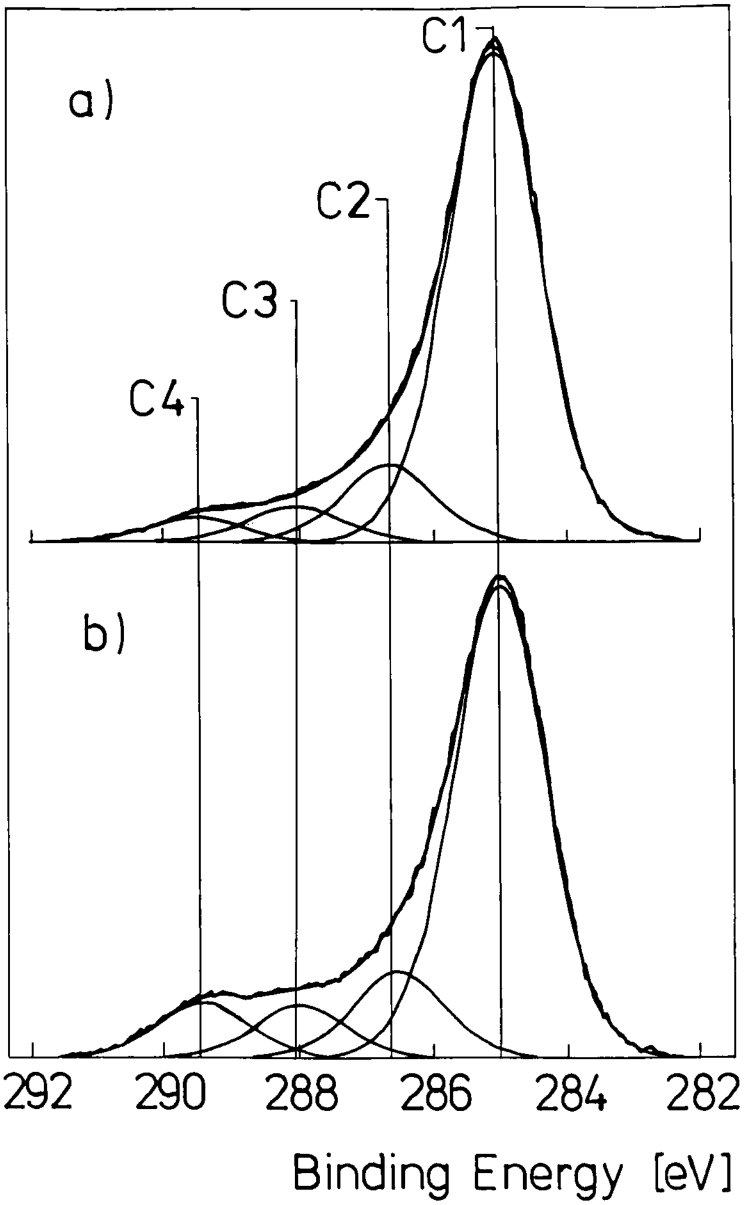


FIGURE 5 C(1s) XPS spectra of PE treated in: a) low pressure plasma, P/A = 0.6 W/cm^2, t = 60s, [O] = 23 at.%, and b) corona discharges, P/A = 16 W/cm^2, t = 0.5s, [O] = 25 at.%.

(O—C—O); and C4 (289.3): carboxyl (O=C—OH) or ester (O=C—O—C). It follows from Figure 5 that even at comparable [O] values (23 to 25 at.%), the corona treated surface exhibits a higher concentration of carboxyl groups. The concentration of oxygen derived from high-resolution XPS spectra agrees to within 2% with the corresponding [O] values calculated from the survey scans. The different chemical groups have also been found to be uniformly distributed throughout the XPS sampling depth (~80 Å), since no spectral variations have been observed for different take-off angles between 20 and 90 degrees, as in our previous work on surface nitrogenation.[16]

Using the above-mentioned assignments, the evolution of individual chemical moieties has been determined as a function of treatment time and the results are shown in Figure 6. The relative concentration of C2 groups decreases rapidly with t; on the other hand, the concentration of C4 groups rises monotonically, while the relative concentration of carbonyl (C3) groups decreases only slowly.

During exposure to plasma, the first reaction step involves the attack of the polymeric chain, for which UV radiation and ion bombardment are thought to be the major causes.[5,7,9] This leads to the formation of reactive surface sites, for example free radicals.

In the second step, these surface radicals can react with one another, resulting in the creation of crosslinks, or they can react with species from the gas phase. Based on our data shown in Figure 6, the following sequence of events may be deduced: At short exposure times, the oxygen mainly gives rise to the formation of C2 groups, and it can contribute to crosslinking. Some of the oxygen replaces hydrogen and carbonyl groups are formed, the relative concentration of which does not change with time. On the other hand, prolonged treatment leads to higher relative concentrations of carboxyl groups, which we surmise to be incorporated in low-molecular-weight (LMW) material. In fact, we (and others) have found that rinsing the plasma treated surface with distilled water leads to a substantial decrease of the C4 peak in the C(1s) spectra, which tends to support the interpretation just suggested.

The above-mentioned reaction scheme is also compatible with the relation between the peel force and the relative concentration of contributing chemical groups, as shown in Figure 7. For both low pressure plasma (Fig. 7a) and corona (Fig. 7b) treated surfaces, the maximum peel force occurs when the relative concentration of C2 groups is highest and that of carboxyl (C4) groups is lowest. The C2 groups are surmised to be indicative of crosslinking, hence of mechanical stabilization of the surface. Formation of C—O—C linkages, associated with the enhanced peel force, can also point to the creation of covalent bonds between the two polymers, but this interpretation must be confirmed by further experiments. On the other hand, a higher concentration of carboxyls relates to the scission of the polymeric chain. This bears witness to the formation of LMW species contributing to the weak boundary layer. It has been shown above that corona treated PE samples exhibit a systematically higher concentration of carboxyl groups than their low pressure plasma treated counterparts (see Figs. 5–7). This may explain why the maximum peel force occurs at a slightly lower [O] value for corona than for the low pressure plasma treated surface.

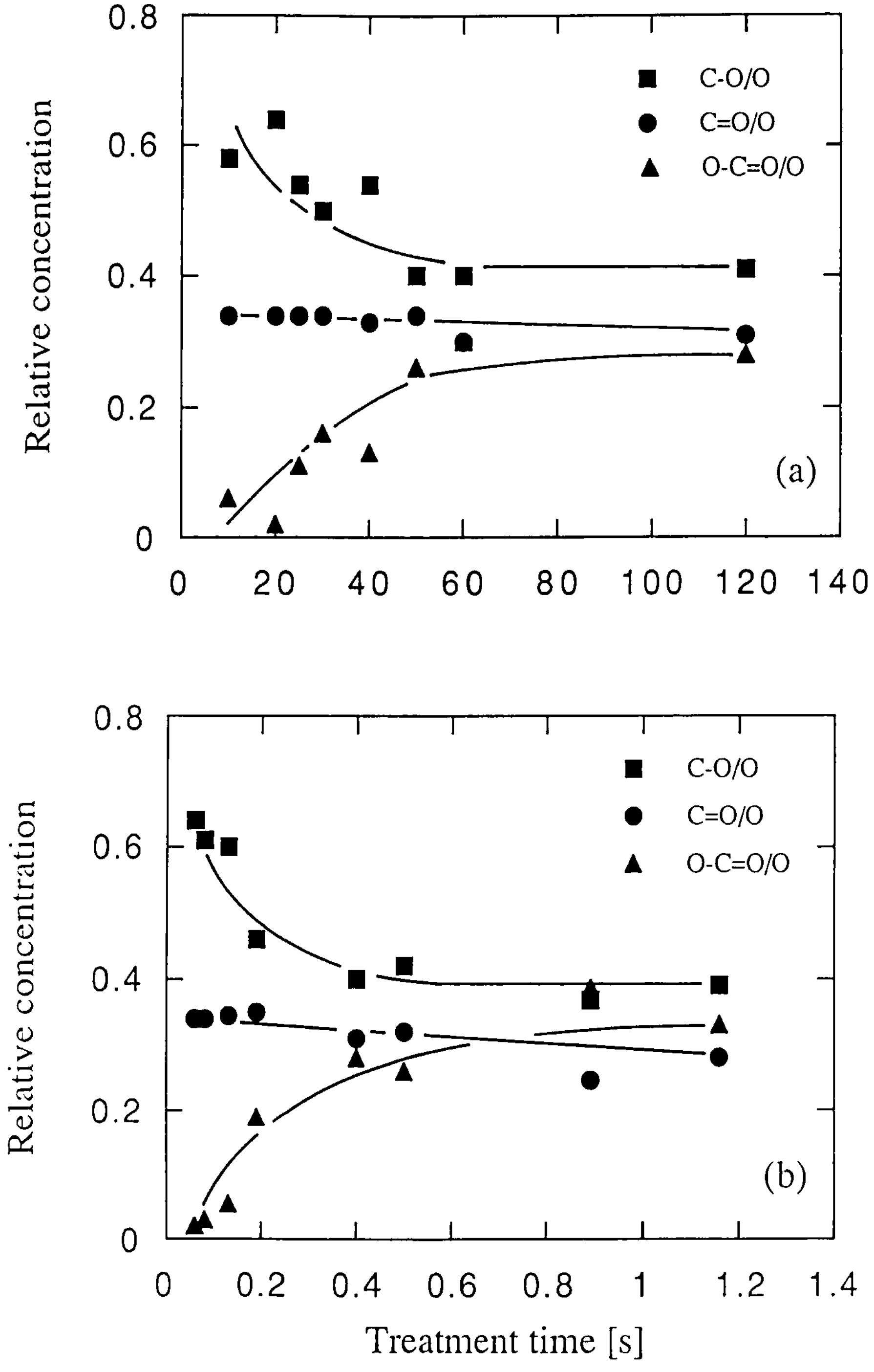


FIGURE 6 Relative concentration of oxygen-containing groups on PE surfaces as a function of treatment time in (a) low pressure plasma and (b) corona discharge.

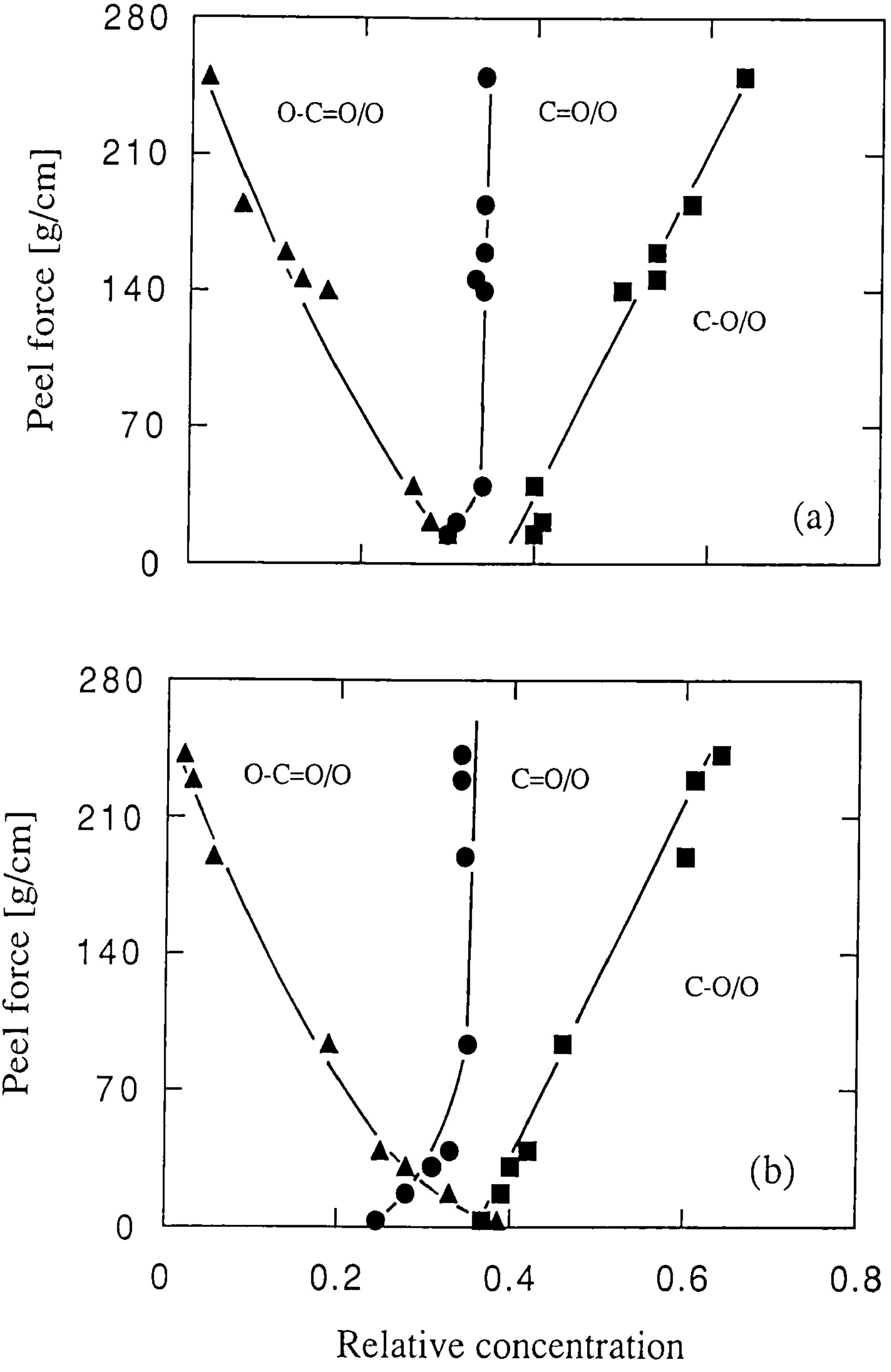


FIGURE 7 Peel force of PE/PE laminates *versus* relative concentration of contributing oxygen-containing groups from (a) low pressure plasma and in (b) corona discharge.

4. CONCLUSIONS

Surface chemical structure and adhesion have been studied for PE/PE and PE/PET laminates, following treatment in a low pressure microwave plasma, or in a corona discharge, both in air. At a comparable degree of treatment, the peel force exhibits a pronounced maximum between 10 and 15 at.% of oxygen, independent of the treatment type. Comparing the relative concentrations of various chemical groups with the peel force, we have found that maximum adhesion occurs when the concentration of such groups as hydroxyl, ether or epoxy is highest, and that of carboxylic acid groups is lowest. The highest peel force appears to occur when the effect of a weak boundary layer due to the low-molecular-weight materials is minimal.

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