Surface modification of poly(ethylene terephthalate) by electrical discharge treatment

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Poly(ethylene terephthalate) (PET) film has been discharge-treated under controlled conditions and the resulting surface modifications analysed via X.p.s. (ESCA), contact angle and surface energy measurements. Changes in surface properties have been followed as a function of ageing time. These measurements have been correlated with the adhesive properties of the treated surfaces using autoadhesion (treated–treated seals) as the probe. Discharge treatment introduces phenolic –OH and carboxylic acid –COOH groups into the surface resulting in increased wetting and much enhanced autoadhesion via hydrogen bonding of phenol groups to carbonyl groups. Much chain scission also occurs; the low molecular weight material is easily removed by washing and migrates into the film on ageing. The new functionalities in relatively immobile chains slowly reorientate and internally H-bond. The former process is largely responsible for the wettability change on aging, the latter for the loss of adhesive properties.

INTRODUCTION

An important contribution to the understanding of the role of electrical ('corona') discharge treatment in enhancing the adhesive properties of polymer surfaces was the work of Owens[1,2] on the autoadhesion of discharge treated low density polyethylene (LDPE) and poly(ethylene terephthalate) (PET). His conclusion was that the adhesive bond is formed through the interaction of carbonyl groups with weakly acidic protons (enol in the case of LDPE, phenol in the case of PET) via hydrogen bonds. His work also produced interesting data on the thermal activation of the process of joint formation and adherability loss and raised several questions about the mechanisms of these processes.

In the case of LDPE autoadhesion, Owen's hydrogen bonding theory was in conflict with the conclusions of Canadian workers who proposed[3] a theory based on electret formation. In a previous paper[4], we described the use of X-ray photoelectron spectroscopy (X.p.s.) or ESCA) to examine discharge-treated LDPE surfaces. This information proved crucial in deciding that the electret theory was invalid. Therefore, it seemed worthwhile to extend the study to PET surfaces, especially since Russian workers have recently proposed that electret charge on discharge-treated PET is responsible for the increased wettability[5].

The use of electrical discharge treatment to enhance the adhesive properties of PET film surfaces is not as widespread as is the case for polyethylene or polypropylene films. This may be due, in part, to the general impression that discharge-treated PET surfaces age unacceptably (i.e. the increased wetabbility produced deteriorates over a relatively short time). The time-dependence of PET autoadhesion was not considered by Owens, but this forms a major part of the present investigation. Discharge treatment was carried out with a specially constructed cell, and surfaces were characterized in terms of autoadhesion, X.p.s. and contact angle of two pure liquids.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate). The PET film used in these experiments was 36 μm thick ICI 'Melinex' O, an additive-free grade polymer biaxially orientated.

Liquids. Deionized water was distilled from a permanganate solution in an all-pyrex apparatus. The water used always had a surface tension greater than 72.0 mN m^{-1}. Formamide was 'Analar' grade material obtained from BDH Ltd, which had a surface tension of 58.2 mN m^{-1}.

Method of discharge treatment

A circular, parallel-plate, electrode cell similar to that described previously[4] was used. The only differences were (a) larger diameter electrodes and insulating glass plates (electrode diameter 150 mm) (b) no bell jar, since laboratory air discharges only were used and (c) an air-blower was placed such that the air between the glass plates was continuously renewed during the discharge (significant differences have been found between LDPE surfaces treated in this apparatus with, and without, an enforced air flow[6]). The plate separation was maintained at 2 mm and the electrical energy dissipated per cycle in the discharge was measured as described previously[4].

Measurement of autoadhesion

In order to test autoadhesion, a compressive heat seal was first formed between two sheets of the film in question

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Table 1 Minimum time required to form a 'good' seal (>200 g/25 mm) at various temperatures for surfaces discharge-treated at 620 mJ cm^{-2}

Sealing temperature °C	Minimum time to form seal (s)[a]
100	≃12[b]
110	4
120	2.5
130	1.5–2.0
135	<0.5

[a] Jaws pressure = 25 psi

[b] Two consecutive periods of 6 s (the maximum contact time for the sealing machine)

using a Sentinel Heat Sealer (Model No 12 AS). The sealing temperature, jaw pressure and contact time were all variable. Strips 25 mm wide were cut from the sealed samples after cooling, and peeled (90°) at a rate of 305 mm min^{-1} on an automatic peel-strength testing machine. Samples displaying a significant degree of autoadhesion commonly tore rather than peeled, giving a wide range of 'apparent' peel-strength readings. Moreover, the seal behaviour was very sensitive to the sealing conditions, i.e. a gradual increase in contact time or temperature tended to produce a step change in seal behaviour from a peel of very low strength to a tearing seal. For the purpose of this work, the actual seal strength is not important, as will be made clear below. A 'good' seal was taken to be one which gave a value of >200 g/25 mm (peel or tear).

X-Ray photoelectron spectroscopy (X.p.s.)

An AEI ES200B spectrometer was used which employs an Mg Kα source (1253.6 eV) operated at up to 450 W. Samples were attached to the probe tip with double-sided sellotape and trimmed to overlap the tip slightly (7 mm x 20 mm) without touching the area to be examined. The working pressure was $<10^{-7}$ Torr. The spectrometer was calibrated such that the Cls peaks from LDPE excited by MgKα and AlKα (an *in situ* impurity line due to electron bombardment of the gun window) were separated by 233.0 eV. All peaks are referred arbitrarily to the Cls maximum from PET at 285.0 eV to correct for surface charging. Be's are considered accurate to ± 0.2 eV. The analyser was operated in the fixed retarding ratio (FRR) mode.

Measurement of contact angles

Constant volume droplets of 0.5 μl were delivered from the tip of a 5 μl syringe onto the film sample. A polaroid photograph of the droplet was taken 30 s after deposition. We have previously suggested that this interval was sufficient for the droplet to attain an equilibrium contact angle (θ), yet short enough for negligible evaporation loss. Assuming the sessile drop to be a spherical cap, θ was determined from the base diameter (d) of the droplet and drop height (h) using the relation $\tan\theta/2 = 2h/d$. Each contact angle quoted is the mean of at least three measurements, with a maximum error in θ of $\pm 2°$.

RESULTS

Autoadhesion measurements

Most samples were discharge-treated for 40 s at mains frequency (50 Hz) with an applied peak voltage of 15.9 kV, which corresponds to a total energy input into the discharge of 620 mJ cm^{-2}. These conditions were chosen on the basis of preliminary spectroscopic and contact angle data (see below). As described above, it proved difficult to produce a curve of peel strength against heat-sealing temperature, because of the tendency of 'good' seals to tear. Instead, the thermal activation of autoadhesion was followed by finding the minimum contact time needed to produce a good seal at a given temperature and fixed jaw pressure. These results are shown in the *Table*. It was also shown that the influence of pressure (once adequate for achieving good contact between the film surfaces) was slight. Most test seals were made for 2 s at 25 psi (1.7×10^5 Pa) and, with the discharge treatment conditions described, good seals were formed at 130°C. Such seals failed immediately when brought into contact with a drop of water, but this effect was reversed if the film surfaces were allowed to dry undisturbed. Treated surfaces could be washed in distilled water and, provided drying was rigorous, this did not result in a loss of autoadhesive characteristics. Treated surfaces did fail to autoadhere if heated to 150°C for 3 min before heat sealing. Treated surfaces did seal to untreated surfaces; in fact, the autoadhesive characteristics were better than for treated–treated seals, since good seals could be formed at temperatures as low as 105°C with 2 s contact time. However, if the treatment conditions were made less severe, this situation changed. Treating for 10 s at 8.9 kV (energy input = 12 mJ cm^{-2}), whilst still giving good seals between treated surfaces at 130°, gave no seal between treated and untreated surfaces even at 160°.

We also examined the ageing behaviour of surfaces treated for 40 s at 15.9 kV. Several samples were treated and stored in a way which prevented pick-up of dust. The sealing behaviour was measured immediately, and subsequently at regular intervals over a period of weeks. The trend is shown in *Figure* 1. Surfaces which would no longer seal well at 130°C could be made to seal by increasing the temperature. It was found that the longer the time between treating and sealing, the higher the minimum temperature (Tm) necessary to give good seals, *viz.* Tm ≃130, 140, 145, 150°C after 0, 17, 31, 45 days respectively.

At the highest temperatures used in these experiments, 160°C, no seal could be formed between untreated film surfaces.

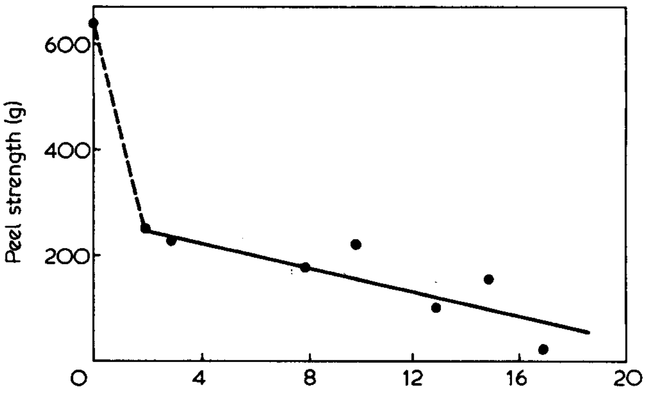

Figure 1 Seal strength (g/25 mm) for seals formed between discharge-treated surfaces (130°, 2 s at 25 psi) as a function of elapsed time between treating and sealing (ageing time)

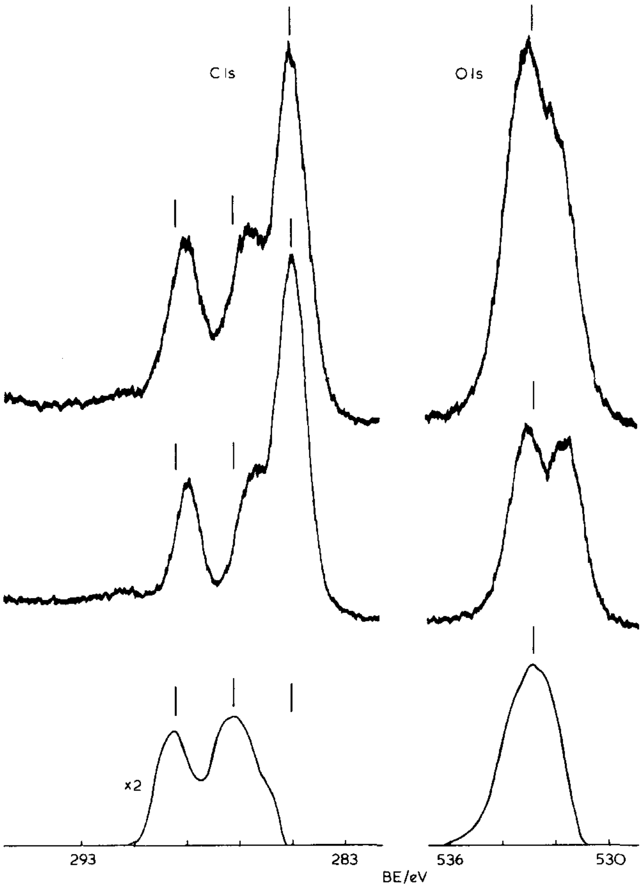

Figure 2 X.p.s. of the PET surface before (lower trace) and after (upper trace) discharge treatment (620 mJcm^{-2}). Subtracting these spectra gives the difference spectra

X.p.s. measurements

Spectra of the PET surface before and after treatment are shown in *Figure* 2. Subtracting these gives the difference spectra. This comparison was facilitated by running the two sets of spectra in such a way that the main Cls peak had the same intensity in both cases (normalization by adjustment of the X-ray power). Clearly, the surface has been oxidized since the average O:C ratio in the surface has significantly increased. It is also clear from *Figure* 2 that the oxygen-containing functions introduced differ from those originally present. A very weak Nls peak was also observed after treatment.

The ageing of treated PET surfaces was also followed spectroscopically to parallel the autoadhesion measurements described above. Using the same normalization procedure gives the family of spectra shown in *Figure* 3. Comparison of these spectra with those of *Figure* 2 shows that the surface composition gradually reverts to that of the untreated film. Heating discharge-treated film to 150°C for 3 min, or washing with distilled water also reversed the spectral changes (*Figure* 3*a*). The behaviour of the weak Nls peak during these stages is quite complex. Immediately after discharge treatment, the peak is very broad and, clearly, has two equal components with binding energies (BE's) of ca 400 and 401.5 eV. After ageing for 24 h, there is a relative change in their intensities and the peak maximum is at 401.4 eV whilst, after 23 days, the relative intensity of this higher BE peak has increased further. There is no marked change in overall intensity of the Nls peak to compare with that of the Ols peak during this time. After washing with distilled

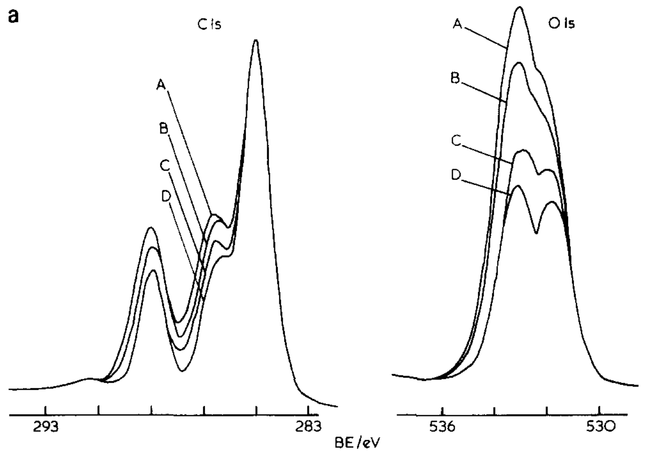

Figure 3(a) Changes in X.p.s. of discharge-treated PET (620 mJcm^{-2}) as a function of ageing time: (*a*) zero; (*b*) one day; (*c*) 23 days. Spectra (*c*) are virtually identical to those produced by washing the treated surface. Spectra (*d*) are for untreated film

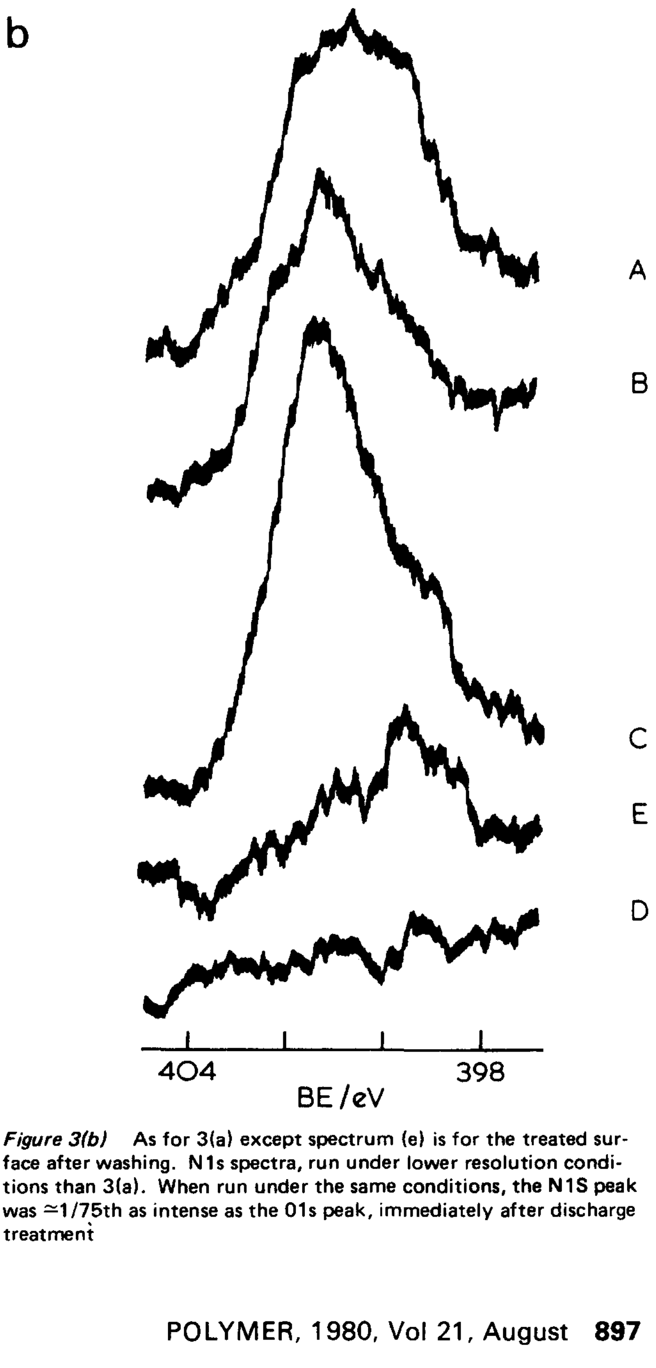

Figure 3(b) As for 3(a) except spectrum (e) is for the treated surface after washing. N1s spectra, run under lower resolution conditions than 3(a). When run under the same conditions, the N1S peak was ≃1/75th as intense as the 01s peak, immediately after discharge treatment

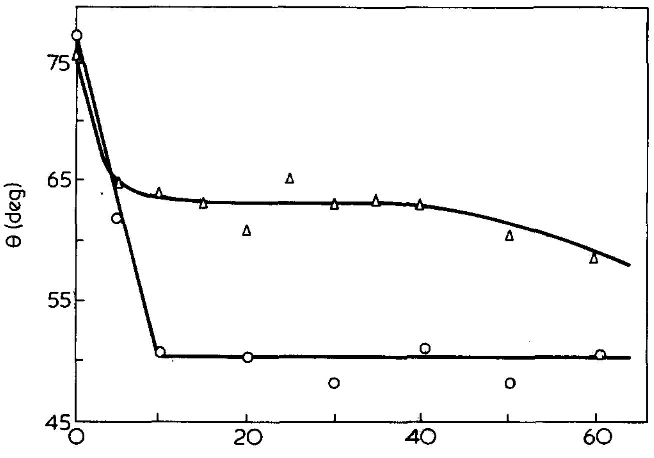

Figure 4 Variation of water contact angle on PET with discharge treatment time (s) and the effect of washing the treated surface ○ unwashed film, △ washed film

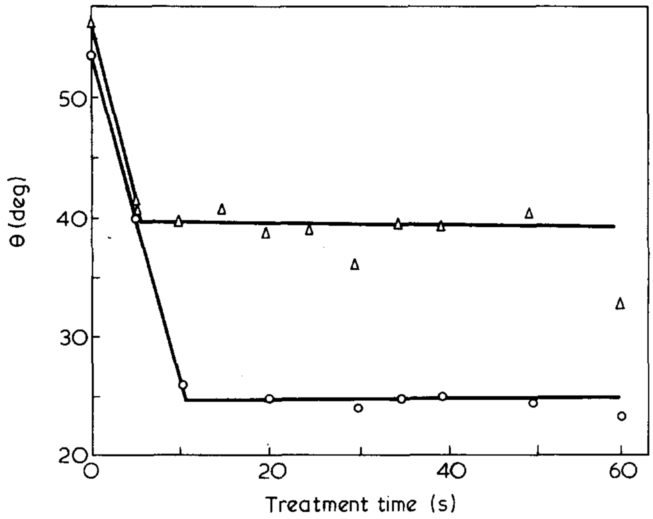

Figure 5 Variation of formamide contact angle on PET with discharge treatment time (s) and the effect of washing the treated surface ○ unwashed film, △, washed film

water, there is a drastic loss of intensity and the peak maximum is then at 399.4 eV (*Figure 3b*).

Contact angle measurements

Equilibrium contact angles for water and formamide drops against treatment time for discharge-treated PET surfaces are shown in *Figures* 4 and 5. The applied voltage was maintained at 15.9 kV during discharge treatment. Measurements were made immediately after treatment, and for both liquids, the contact angle decreased rapidly with treatment time and remained essentially constant after 10 s treatment.

Samples of discharge-treated PET were thoroughly washed with distilled water whcih was previously ultrafiltered using a 'Millipore' filter of 0.22 μm pore size to remove dust, and were dried in a vacuum dessicator over P_2O_5. Contact angle measurements made 24 h after washing are shown in *Figures* 4 and 5. The effect of washing discharge-treated film is to raise the contact angle of both water and formamide drops by $\simeq 15°$, suggesting the removal of a polar surface layer by water.

The contact angle of water and formamide on a PET surface treated for 40s and 15.9 kV varies with time as shown in *Figure* 6. The contact angles increase rapidly over the first three days, followed by a slower increase until a plateau is reached. The limiting values of contact angle appear to be given by the values obtained for a washed sample.

CALCULATION OF THE POLAR AND DISPERSION FORCE CONTRIBUTIONS TO THE SURFACE FREE ENERGY OF PET FILM

The work of adhesion (W_A) of a liquid to a solid surface is given by the combined Young–Dupre equation

$$W_A = \gamma_L(1+\cos\theta) \qquad (1)$$

where γ_L is the surface tension of the liquid and θ is the contact angle of the liquid on the surface. The expression in the equation (1) is an approximation in that it assumes zero spreading pressure of the liquid on the solid, which is generally only true for low energy surfaces[7].

Fowkes[7] demonstrated that low energy surfaces where only London dispersion forces were operating, the work of adhesion could be related to the surface free energies of the solid (γ_s^d) and liquid (γ_l^d) by a geometric mean approximation. An extension of this work[8] also included polar interactions of the solid and liquid, assuming that a geometric mean approximation was also appropriate for polar forces

$$W_A = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^p \gamma_l^p)^{1/2} \qquad (2)$$

where superscripts d and p relate to dispersion force and polar contributions respectively. By working with low energy surfaces, Fowkes obtained values of γ_l^p and γ_l^d for a number of pure liquids. Hence, by combining equations (1) and (2), the contributions to the surface free energy of a solid can be obtained by measuring the contact angle of just two pure liquids. A number of workers have used this technique to characterize polymer film surfaces, particularly polyethylene, using water/methylene iodide[9,10] or water/formamide[11] as the liquid pair.

In this work, water and formamide were used, taking the data of Fowkes as follows:

For water — $\gamma_l^p = 51.0$ mNm^{-1}, $\gamma_l^d = 21.8$ mNm^{-1};

For formamide — $\gamma_l^p = 18.7$ mNm^{-1}, $\gamma_l^d = 39.5$ mNm^{-1}

The total surface free energy (γ_s) of the PET is then given by

$$\gamma_s = \gamma_s^p + \gamma_s^d \qquad (3)$$

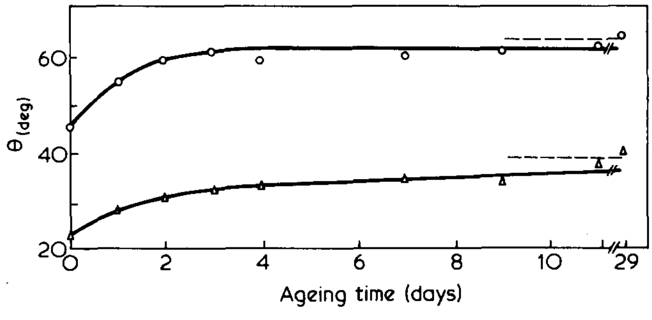

Figure 6 Variation of water and formamide contact angle on discharge-treated PET (620 mJcm^{-2}) with ageing time ○ water, △ formamide, — — — washed film

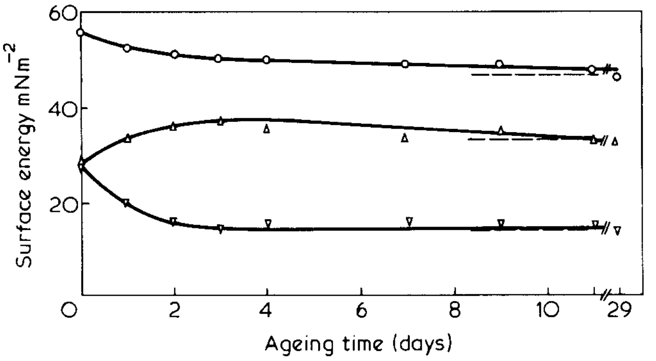

Figure 7 Variation of contributions to the surface energy of discharge-treated PET (620 mJcm^{-2}) with ageing time △ = $\gamma_s{}^d$, △ = $\gamma_s{}^p$, ○ = $\gamma_s{}^T$, — — — washed film

It has been shown[12] that using just one liquid pair does not give absolute values for the surface free energy of the solid or its components. Two reasonably polar liquids such as water and formamide tend to emphasize the polar nature of the surface. However, this method is particularly appropriate here in comparing contributions to the surface free energy on ageing a discharge-treated film (*Figure* 7).

After treatment of PET film at 15.9 kV for 40s, the calculated values of γ_s^p and γ_s^d are found to be equal, but γ_s^p decreases rapidly with time, accompanied by a corresponding increase in γ_s^d. The total surface free energy given by equation (3) decreases with time, and all surface energies eventually approach values obtained for a film which had been washed after discharge treatment under the same conditions.

The increase in contact angle of water and formamide on washing a discharge-treated film together with the decrease in surface free energy, particularly the decrease in γ_s^d, shows that there is a loss of polar species from the surface which is capable of hydrogen-bonding.

It is notable that the contact angle measurements, which are characteristically sensitive to the topmost surface layer, show no differences between the discharge-treated film after washing or ageing. This is in contrast with other techniques, e.g., seal strength measurements. A treated PET surface after washing or ageing still has a higher surface free energy than untreated film; the value of γ_s^p remains $\simeq 100\%$ higher than that of an untreated surface. This suggests that not all the oxidized species are of sufficiently low molecular weight to be removed by washing.

DISCUSSION

The surface chemical changes which take place during electrical discharge treatment of PET have not previously been the subject of direct study. However, Owens[2], by exposing treated surfaces to specific chemical reagents and noting their effects on subsequent autoadhesion measurements, did make deductions about the groups resulting from discharge treatment. He also examined chromatographically the material obtained by base extraction of treated film. The only new substituent group detected was phenolic –OH. Owens postulated that autoadhesion of treated surfaces results from hydrogen bonding between these groups and the ester carbonyl present in the original polymer.

The X.p.s. difference spectrum shows the appearance of at least two new species, chemically shifted by 2.2 eV and 4.2 eV respectively from the peak due to the aromatic carbons. There is also the suggestion of a less intense peak with chemical shift 1.2 eV. The first of these peaks would be consistent when phenolic –OH. The second is close to the original ester carbonyl group, and could, therefore, be a free carboxylic acid end-group –COOH. The third is very close to the original peak due to $-CH_2-O-$ and could be $-CH_2-OH$[4]. Justification for these assignments comes from studies of the model compounds *p*-hydroxybenzoic acid and its methyl ester. Relative to the principal C/S peak, the C–OH peak had a chemical shift of 2.0 ± 0.2 et, whilst the O=C–O peak had a chemical shift of 4.0 et (ester) and 4.2 et (acid). Slightly higher BE's for acid carboxyl compared with ester carboxyl have also been noted by Clark and Dilks[17]. The Ols BE for –OH (phenol) was consistent with the major component of the Ols difference spectrum. All these groups can be formed by a free-radical oxidation process, such as occurs during photodegradation. The similarity of discharge treatment to u.v. irradiation has been noted by Owens*. In the former, however, radicals can be formed by the interaction of ions, metastables (neutral molecules and atoms) and electrons with the polymer besides photons. The two Nls peaks are probably due to $-NH_2$ ($\simeq$400 eV) and $-CONH_2$ (401.5 kV)[13]. Because of the low population of these groups in comparison with the oxygen functions, it is unlikely they play an important role in surface interactions.

The spectroscopic data are, therefore, consistent with Owens' observations. X.p.s. also shows that the majority of the new chemical groups introduced into the polymer are in relatively low molecular weight chains since the spectra of water-washed and aged surfaces have almost reverted to those of an untreated surface. It is assumed that in washing this material is taken into solutions. We believe that, during ageing, this material migrates into the bulk of the film. The best evidence for this is that the contact angle and surface energy data, which refer to the uppermost surface layer, tend towards values identical to those for washed films more rapidly than do the corresponding x.p.-spectra which sample $\simeq$50A into the film (*Figures* 3 and 6).

It is clear from both contact angle and spectroscopic measurements on washed film that a significant population of the new polar groups introduced by discharge treatment are in polymer chains attached quite firmly to the film. These groups give rise to a pronounced enhancement in autoadhesion. What is less clear is the role of the oxidized low molecular weight material and whether its migration into the film is the only change which occurs during ageing. At first sight, it is tempting to associate the loss of autoadhesion with the migration of this material into the film, especially since, as ageing continues, progressively higher temperatures are necessary to achieve autoadhesion. However, this cannot be true because washed (freshly treated) film with a lower polarity than aged film exhibits better autoadhesion (lower Tm). Also the X.p.-spectra of treated surfaces that have been heated to 150°C (and which do not then autoadhere) are similar to those of the washed surface (strong autoadhesion). This suggests that the same groups can be predisposed either to participate in autoadhesive interactions or not, i.e. mole-

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* The similarity has also been noted by MIR-i.r., particularly in the marked increase in –COOH end-group concentration[16].

cular orientation effects are important. We propose, therefore, the following explanation of the above observations. Discharge treatment results in the introduction of new polar groups, particularly phenolic –OH and –COOH into the PET film surface, and also causes chain scission*. The low molecular weight products are easily removed by water washing, but they also migrate into the film on standing (ageing), resulting in a lowering of the initial polarity. Also during ageing, the less mobile chains slowly reorientate so that the phenolic –OH groups internally hydrogen bond resulting in a lowering of autoadhesion potential. Ageing effects are accelerated at higher temperatures.

Owens[2] did not obtain enhanced autoadhesion between treated and non-treated surfaces unless the latter were first hydrolysed with KOH solution. He postulated that the ester carbonyls in the untreated surface (to which phenolic –OH hydrogen bond) were unfavourably oriented and that hydrolysis produced favourably oriented carboxyl end-groups which could hydrogen bond instead. Our results show that treated to untreated seals can be made if the degree of treatment is high enough. Therefore, there must be a sufficient number of accessible (favourably oriented) ester carbonyl groups available in untreated surfaces to allow seals to be made, but the concentration of phenolic –OH must be high enough in the other surface to allow the required number of hydrogen bonds to be formed. In his experiments, Owens[2] obviously did not reach this level. (An alternative possibility is that some of the low *MW* fragments from the treated surface act as plasticizers when in contact with the non-treated surface.) Our spectroscopic data indicate that –COOH end-groups are also formed during discharge treatment, and these could take part in the hydrogen bonding between treated surfaces. Owens invoked their involvement in hydrolysed PET surfaces autoadhering to treated surfaces but not in the case of treated–treated seals. In his analytical procedure, base extraction necessarily introduced carboxyl groups into the analysed fragments, thereby masking their occurrence simply from the discharge treatment.

Surface thermodynamics requires that, where possible, rearrangement of molecules in the surface occurs such that the surface which is presented to air has the minimum free energy. In this respect, oxidized surfaces of polyethylene and PET are similar. Baszkin and Ter-Minassian-Saraga[14] have suggested that for chemically oxidized polyethylene, molecular reorientation occurs on heating the film resulting in polar groups being directed into the surface. This suggestion is also supported in the case of discharge-treated LDPE[4] which is heated to 80°C. Under these conditions, loss of autoadhesion occurs, but without a reduction of O functions in the surface as determined by X.p.s.

However, PET is a more polar polymer than polyethylene, so that low molecular weight species on the PET surface readily migrate into the polymer and rapidly disappear from X.p.s. sampling depth. At the same time, high molecular weight polymer chains slowly change their orientation, resulting in further loss of polar groups from the surface. This is aided possibly by a plasticizing effect of the low molecular weight material. The polymer chain mobility at the surface is sufficiently high in the case of PET to allow the surace to reach a minimum free energy configuration at room temperature. This is clearly not true in the case of polyethylene. Treatment of PET and LDPE by electrical discharge has in common the creation of hydrogen bonding groups which can give rise to autoadhesion[2], and to adhesion to inks etc.[15].

The overall similarity in behaviour would seem to suggest that, as in the case of LDPE[4], explanations of wettability increases for discharge-treated PET in terms of electret formation are invalid.

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* Assuming a Norrish type II mechanism is responsible.