

Effect of surface polarity on self-adhesion of polymers

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The work of detachment, W , of two attached polymers has been determined experimentally for systems consisting of unoxidized and chemically oxidized low density polyethylene (PE) film. The surface density of polar, mainly carbonyl, sites at the surfaces of oxidized polyethylene has been measured by adsorption of calcium ions. Independent measurements of the wettability of these surfaces by pure liquids allows the establishment of a relation between the thermodynamic free energy of adhesion, W_A , the polar contribution, γ_s^p , of the polymer to this energy and the surface density of polar sites. An attempt to correlate these parameters with the adhesion energy, W , has been made. The importance of the surface polarity on the possible mechanism of polymer self-adhesion is discussed.

INTRODUCTION

Adhesion generally signifies the sticking together of two materials A and B. Two different forms of adhesion are frequently found in the literature: the practical or apparent adhesion (more commonly termed adhesive strength or joint strength) which may be defined as the force required to detach two attached materials, and the thermodynamic adhesion or reversible work of adhesion.

In the case of self-adhesion, when the bond is achieved without any intermediate layer of adhesive, one can distinguish two main types of failure of adhesive joints: cohesive failure when the detachment takes place by a rupturing inside the mass of one of two adhering materials; and interfacial which may be located at the interface between two adhering materials.

For an ideal interfacial separation the thermodynamic adhesion may be calculated by the classic Dupré equation:

$$W_A = \gamma_A + \gamma_B - \gamma_{AB} \quad (1)$$

where γ_A and γ_B are the surface free energies of A and B, respectively, and γ_{AB} refers to the interfacial energy. When $\gamma_A = \gamma_B$, W_A is equal to $2\gamma_A$. This relation is always valid for two identical liquid materials. However, it is not necessarily verified for two solid surfaces¹.

The values for practical adhesion W or of the work of detachment are substantially larger than those which one calculates from equation (1)¹. The reason for this difference is the energy dissipation and inelastic deformation occurring during the breaking of the adhesive joint or detachment. Also, W_A refers to the perfect interface whereas in real situations the interface contains a large number of flaws. That is why the apparent energy of adhesion, W , is not a thermodynamically reversible quantity^{2,3}.

However, the apparent energy of adhesion W is necessarily related to the substrate adhesive interactions across the interface and depends, amongst other factors, on the chemical compositions of the surfaces in contact^{4,5}.

In the work presented here we have studied the effect of

the surface density of polar sites created during the chemical oxidation of polyethylene films on W_A and the effect of temperature on the work W , for a joint constituted by two polyethylene films either unoxidized or oxidized.

EXPERIMENTAL

Materials

Polyethylene. Low density polyethylene film, PE, known under the commercial name 'Visqueen' and produced by Cellophane was used for this work. Its thickness was 100 μm and its density was 0.929 g/cm^3 . It melts between 109° and 112°C. Circular samples of the film, 30 mm in diameter, were used for contact angle and adsorption measurements. For peeling experiments strips of film were cut. They were purified in carbon tetrachloride for 15 min and then extracted with boiling acetone for 5 h. This extraction time led to reproducible values of the contact angle with tridistilled water used as a reference liquid.

Liquids. Water was tridistilled from a permanganate solution using Pyrex apparatus. Its surface tension was equal to 72.8 ergs/cm^2 . Methylene iodide was a Rhône Poulenc AR grade product and was used as received. Its surface tension was equal to 50.8 ergs/cm^2 . ⁴⁵Ca calcium chloride was obtained from the Commissariat à l'Energie Nucléaire, France. Aqueous solutions of different concentrations of CaCl_2 with a specific activity 110 mCi/g were prepared for adsorption measurements.

Oxidizing mixtures were prepared from sulphuric acid (sp. grade 1.84 pure grade) and potassium chlorate (reagent grade).

Methods

Oxidation. Polyethylene films, either circular samples or strips, were immersed in oxidizing mixtures of different concentrations at room temperature. The duration of immersion was 2 min. The samples were then withdrawn, rinsed several times with distilled water and dried in a desiccator.

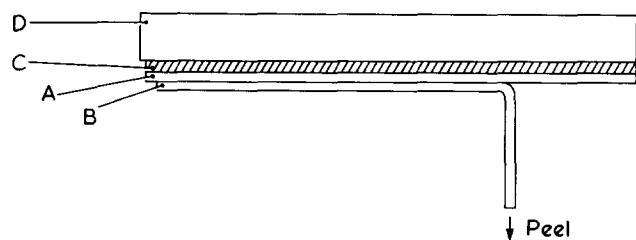


Figure 1 Diagram of peel test. A and B, adhesive joint; C, double scotch adhesive tape; D, rigid support

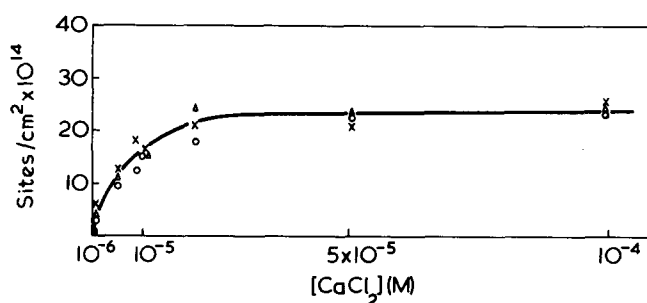


Figure 2 Isotherm of Ca^{2+} adsorption on oxidized PE film. Concentration of KClO_3 in the oxidizing mixture 4.76% w/w

cator under reduced pressure. The oxidation treatment, as shown by i.r. studies, creates polar sites, mainly carbonyls, in the thin superficial region of the polymer^{6,8}.

Adsorption measurements. A radio tracer technique was used to determine the surface density of polar sites created during oxidation of PE films. The details of this method have been described elsewhere^{5,9}.

Contact angle measurements. A drop-on-plate method and apparatus described below⁹ were used. The values of contact angle reported here are an average of at least six readings.

Formation of adhesive joints and measurement of separation work, W . The oxidized or unoxidized films were joined together in a mechanical press equipped with electrically heated plates and with a cooling system consisting of an external water circuit. The temperature, pressure and time of contact were adjustable. For this work the pressure was fixed at 4.4 kg/cm², which assured a uniform contact of two pressed films and a reproducibility of results to within $\pm 20\%$.

For our experiments we used two strips, the dimensions of which were 12.5 x 3.5 cm and 12 x 3 cm. The two strips of film joined under a determined temperature were cooled in the press to room temperature (23°–25°C).

The compressed sandwich was then fixed by means of a double scotch adhesive tape to the rigid support (Figure 1). The peel angle was 90° and the work of detachment per unit area of interface (the apparent energy of adhesion) was equal to the peel force, F , per unit width of the detaching layer ($W = P$)¹⁰. The rate of peel for different peel forces applied was measured by means of the horizontal cathetometer which is able to follow the advance of the point of separation of two strips. Measurements were also carried out by pulling apart the two joined strips using an Instron testing machine (peel rate 3 x 10³ mm/h; peel angle 180° and $W = 2P$).

RESULTS

Adsorption of calcium ions at the interface oxidized polyethylene/aqueous solution of CaCl_2

The isotherm of adsorption of Ca^{2+} ions at the surface of the oxidized PE film is shown in Figure 2. The concentration of KClO_3 in the oxidizing mixture was equal to 4.76% w/w. It may be noticed that adsorption increases with the increase of CaCl_2 concentration and that the plateau value corresponding to saturation of adsorption is obtained when the calcium concentration in solution is equal to 2.5×10^{-5} M. The variation of the surface density of polar sites as a function of the concentration of KClO_3 in the oxidizing mixtures is shown in Figure 3. The results plotted in this Figure correspond to measurements of calcium ion adsorption from a 5×10^{-5} M CaCl_2 solution. At this concentration saturation of adsorption is attained (Figure 2). It may be noted (Figure 3) that the plateau value is obtained when the concentration of KClO_3 in the oxidizing mixture is between 2 and 5%.

Wettability of oxidized PE films by pure liquids

The wettability measurements were performed with two pure liquids: water and methylene iodide. The advancing contact angles for oxidized polyethylenes are presented in Table 1. In Figure 4 we present the variation of the thermodynamic work of adhesion W_A , calculated by the Young-Dupré equation: $W_A = \gamma_1 (1 + \cos \theta)$ and plotted as a function of the surface density of polar sites. The contact angles for oxidized PE films (oxidizing mixture containing 4.76% of KClO_3) measured after the strips had been peeled apart gave an average value of 76°. The value of the contact angle on separated unoxidized films was 94°.

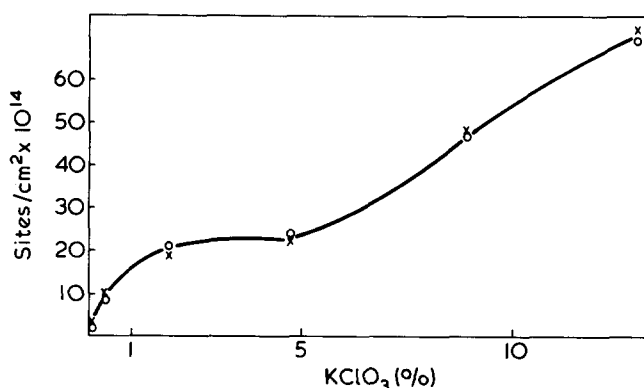


Figure 3 Surface density of polar groups versus KClO_3 concentration in the oxidizing mixture $[\text{Ca}] = 2.5 \times 10^{-5}$ M

Table 1 Contact angles (θ) and thermodynamic adhesion free energies (W_A) for different degrees of oxidation of PE films

Degree of oxidation of PE (%)	$\theta_{\text{H}_2\text{O}}$ (degrees)	$W_A(\text{H}_2\text{O})$ (ergs/cm ²)	$\theta_{\text{CH}_2\text{I}_2}$ (degrees)	$W_A(\text{CH}_2\text{I}_2)$ (ergs/cm ²)
0	94	67.7	47	85.4
0.37	80	81.6	44	87.3
1.98	74	92.9	42	88.6
4.76	73	94.1	41	89.1
9.09	70	97.7	40	89.7
13.03	70	97.7	40	87.7

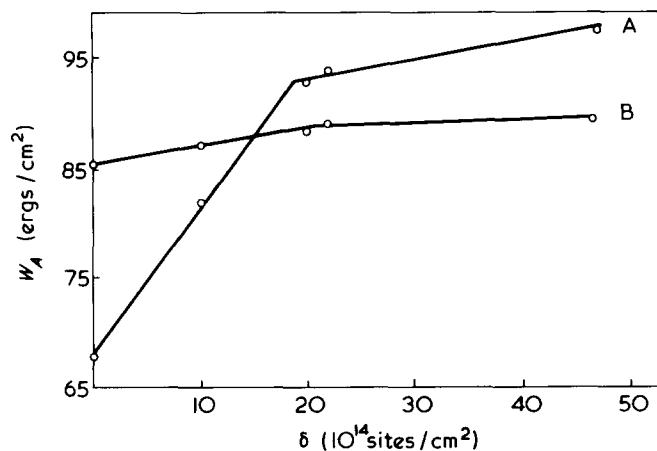


Figure 4 Thermodynamic free energy of adhesion W_A versus density of polar groups. A, H_2O ; B, CH_2I_2

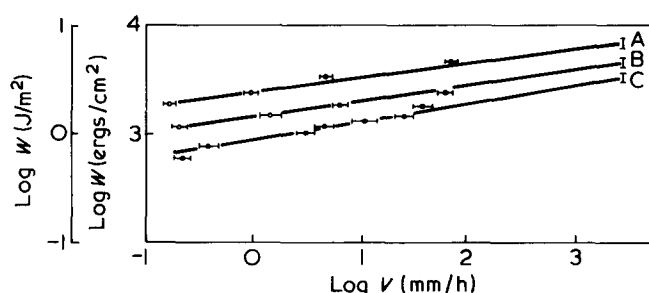


Figure 5 Adhesion energy W as a function of the rate of detachment. A, 4.76%; B, 0.37%; C, unoxidized

Separation work, W , of oxidized and unoxidized PE films

In Figure 5 are shown the plots of adhesion free energy W vs. rate of detachment for the systems oxidized PE—oxidized PE and unoxidized PE—unoxidized PE. We notice that straight lines with slopes which do not differ much from each other may be drawn through the experimental data.

It is also noteworthy (Table 2) that the adhesion energy W increases with the degree of oxidation up to the maximum value of 6.3 J/m^2 and that for the asymmetric system oxidized PE—unoxidized PE, the measured adhesion is equal to that of two unoxidized films.

Figure 6 shows the variation of the detachment work W , measured at the constant rate of detachment ($3 \times 10^3 \text{ mm/h}$), as a function of the temperature of formation of the joints in the press. It can be seen that the work of detachment of the oxidized PE films is enhanced for temperatures between 60° – 75°C and then decreases for temperatures above 80°C .

Experiments were also performed in order to study the effect of contact duration in the press on the attachment strength of two oxidized films. The results shown in Figure 7 indicate that this strength is constant for the range of contact times 3 min–336 h.

DISCUSSION

Determination of the surface density of polar sites, δ

If we compare the curve of the adsorption of calcium ions (Figure 3) with that of the thermodynamic free energy of adhesion for oxidized PE films (Figure 4), we can

see that the rapid increase of W_A corresponds to the creation of $(20 \pm 2) \times 10^{14}$ sites/ cm^2 . This increase is situated in the concentration range 2–5% KClO_3 in the oxidizing mixture.

Figure 5 also shows that if δ is greater than this value, W_A does not change further. This would indicate that for concentrations between 2 and 5% of KClO_3 in the oxidizing mixture, oxidation of polyethylene films reaches saturation.

Indeed, it is known, from the previous studies of solid–solid¹¹ and liquid–solid adhesion^{12–15} that the orientation of polar groups contributing to the total energy of adhesion is a very important factor. When the polar groups change their orientation from perpendicular to parallel to the surface or when they turn over inside the bulk, a decrease of adhesion is observed. The same effect is observed with a porous surface. In this case a great number of polar groups may have an orientation which is not either perpendicular to the surface or external, but still may adsorb Ca ions. This case corresponds to samples treated with a mixture containing high amounts of KClO_3 , where a rapid increase of adsorption of calcium ions is observed; the wettability of the treated surfaces, which depends mainly on the superficial polar groups is constant.

Table 2 Surface densities of polar sites (δ) and apparent energies of adhesion (W) for unoxidized and oxidized polyethylene films

	δ (sites/ $\text{cm}^2 \times 10^{-14}$)	W (J/m^2)
Unoxidized—unoxidized	0—0	3.30
Unoxidized—oxidized (4.76%)	0—22.5	3.30
Oxidized—oxidized	10—10	4.30
Oxidized—oxidized	20—20	5.90
Oxidized—oxidized	22.5—22.5	6.30
Oxidized—oxidized	47—47	6.30
Oxidized—oxidized	47—22.5	6.10

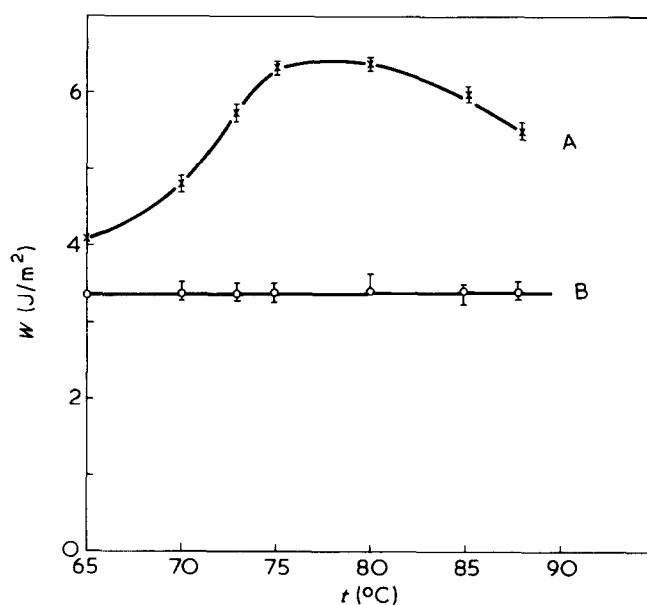


Figure 6 Adhesion energy W versus temperature. Rate of detachment $3 \times 10^3 \text{ mm/h}$. Oxidized polyethylene (concentration of KClO_3 in the oxidizing mixture 4.76% w/w). A, Oxidized; B, unoxidized

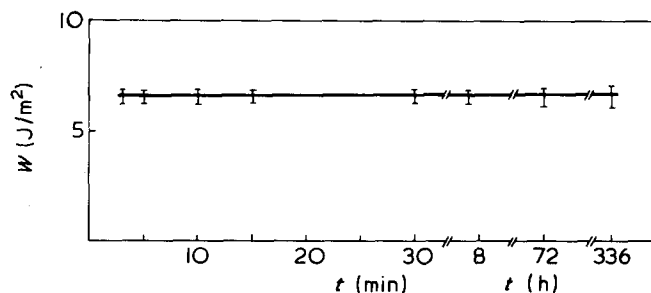


Figure 7 Adhesion energy W versus duration of contact. Adhesive joint of two oxidized PE films (oxidation 4.76% of KClO_3)

Determination of the thermodynamic surface energy of the oxidized PE as a function of its polarity

It has been proposed¹⁵ that the free energy of adhesion may be represented as a sum of two types of interactions operating independently across the solid-liquid interface:

$$W_A = W_A^d + W_A^p \quad (2)$$

where the superscripts d and p stand for the dispersion forces and for all the polar forces, respectively.

Fowkes¹⁶ has also shown that if only van der Waals dispersion forces contribute to the interaction between two liquids or between the liquid and a solid W_A^d can be accurately predicted by the following geometric mean:

$$W_A^d = 2(\gamma_s^d \gamma_l^d)^{1/2} \quad (3)$$

where γ_s^d and γ_l^d are respectively the surface free energies of a solid and a liquid.

Equation (2), initially established for the systems where the only forces operating at the interface are dispersion forces has been extended by Dahlquist¹⁷ and Wu¹⁸ for systems where the polar interactions are present.

$$W_A = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (4)$$

Equation (4) contains two unknown terms γ_s^d and γ_s^p .

To solve this equation and to calculate γ_s^p of the oxidized polyethylene we use the experimental values for W_A obtained with two liquids: water and methylene iodide (Figure 4) and the value for γ_l^d and γ_l^p from the results of Owens and Wendt¹⁹: water: $\gamma_l^d = 72.8$; $\gamma_l^p = 21.8$; $\gamma_l^p = 51.0$ ergs/cm²; methylene iodide: $\gamma_l^d = 50.8$; $\gamma_l^p = 49.5$; $\gamma_l^p = 1.3$ ergs/cm².

Thus we have:

$$W_{A1} = 2(\gamma_s^d \gamma_{l1}^d)^{1/2} + 2(\gamma_s^p \gamma_{l1}^p)^{1/2} \quad (5)$$

$$W_{A2} = 2(\gamma_s^d \gamma_{l2}^d)^{1/2} + 2(\gamma_s^p \gamma_{l2}^p)^{1/2} \quad (6)$$

The calculated values of γ_s^p are plotted versus the surface density of polar sites in Figure 8. This Figure shows that the polar force contribution to the surface free energy of oxidized polyethylene reaches its maximum value of 7.2 ergs/cm² i.e. 0.0072 J/m². Using equations (5) and (6) we have previously demonstrated²⁰ that the γ_s^d practically does not change with an increase of δ .

Adhesion of polyethylene films

The curves in Figure 5 show the variation of the work of detachment, W , with the rate of detachment and they seem to indicate that the failure or detachment has a viscoelastic

component. The small forces required to obtain the separation of the joints, which when applied to the polyethylene films themselves do not involve any deformation, suggest that the locus of joint failure is in the interfacial region. Indeed the comparison of the measured work of detachment, W , which for the lowest rates of detachment varies between 600 and 1700 ergs/cm², with that deduced from the contact angle measurements ($W_A = 65.5$ ergs/cm²) shows that the observed failures could not be defined as a purely interfacial failure¹. Also the contact angle value obtained with water at the surfaces of the peeled oxidized polyethylene films (76°) is essentially different from that of the unoxidized surfaces after separation (94°). This seems to exclude the possibility of 100% cohesive failure which would lead to the creation of two unoxidized surfaces after separation.

On the other hand the measured works of detachment, W , are necessarily related to the interfacial chemical bonds across the interface. These energies increase with the surface polarity, e.g. with the degree of oxidation of polyethylene films, and they attain the maximum value of 6.3 J/m² for the surface density of $(20 \pm 2) \times 10^{14}$ sites/cm². The importance of the surface polarity in the adhesion of polymers has already been shown by other authors²¹⁻²³. However the quantitative determination of the surface density of the polar sites has never been defined in these studies.

It has been proposed^{2,3} that the apparent adhesion W or work of detachment may be represented as a product of two terms: the thermodynamic free energy of adhesion, W_A , and a numerical term H associated with the energy dissipation in the process of inelastic deformation of the adhering polymers during their separation.

Two equations may be written for the curves in Figure 5:

$$W_1 = 2\gamma_s H_1 \quad (7)$$

for the self-adhesion or attachment of unoxidized PE films, where the thermodynamic free energy of adhesion, W_A , is essentially due to the dispersion contribution equal to $2\gamma_s$ and:

$$W_2 = 2(\gamma_s^d + \gamma_s^p) H_2 \quad (8)$$

for the self-adhesion or attachment of oxidized PE films where additionally polar interactions are present at the interface.

If we take the value previously obtained of 32.75 ergs/cm² for γ_s^d polyethylene²⁴ then for the lowest rate of separation (0.15 mm/h) we obtain from equation (7): for unoxidized polyethylene 650 ergs/cm² = 65.5 ergs/cm² $\times H_1$, $H_1 = 9.6$; and for oxidized polyethylene (oxidation with

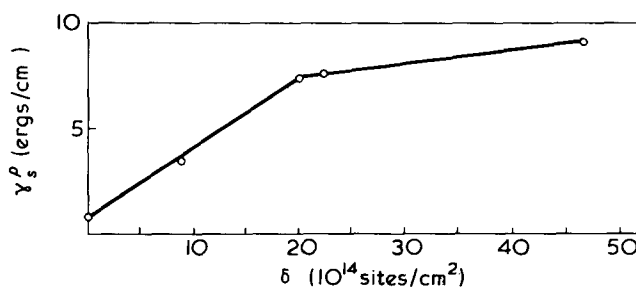


Figure 8 γ_s^p versus density of polar groups

4.76% of KClO_3 in the mixture) using $\gamma_s^p = 7.2 \text{ ergs/cm}^2$ (from Figure 8) and equation (8), $1700 \text{ ergs/cm}^2 = 80 \text{ ergs/cm}^2 \times H_2$, $H_2 = 21.3$.

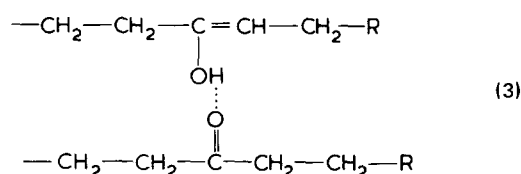
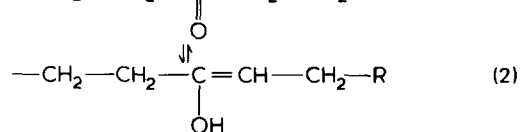
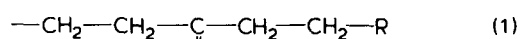
The relatively small difference of numerical terms H_1 and H_2 , which, for a given rate of separation, can vary within several orders of magnitude depending on the viscoelastic properties of the system², shows that the superficial oxidation modifies only very slightly the viscoelastic properties of the interfacial region where the failure takes place.

The effect of temperature on the formation of the adhesive joints represented in Figure 6 indicates that the self-adhesion of oxidized polyethylene films increases in the temperature range $65^\circ - 75^\circ \text{C}$. Similar results have been obtained by Owens¹¹ for the autohesion of corona-treated polyethylene and poly(ethylene terephthalate) films. Owens has attributed the increase of W with temperature to the apparent activation energy necessary for joint formation. However when the temperature in the press is higher than 80°C one can observe a decrease of the adhesion energy W of the system. This is presumably due to the decrease of the surface polarity of oxidized PE films; the effect which we have already analysed in our previous work on the influence of temperature on the solid-liquid adhesion of oxidized polyethylene is observed. As the mobility of superficial chains of the polyethylene increases, polar groups may re-orient towards the bulk of the polymer, and thus decrease W .

It is difficult to determine the mechanism of the self-adhesion of oxidized polyethylene films. Nevertheless, two hypotheses may be put forward: the interpenetration by diffusion of polymer chains during heating in the press and the formation of hydrogen bonds between two oxidized polyethylene films.

If the first hypothesis were predominant we would expect the contact time to be an important influence upon the adhesion energy, W . However, the results shown in Figure 7 do not indicate any increase of W in the range of contact time studied. The diffusion of polymer chains may, of course, occur immediately after the two polyethylene films are brought into contact, as has been demonstrated for the low density polyisobutylenes²⁵ and recently for butyl rubber²⁶. Even if the possibility of chain diffusion for our system could not be totally excluded, it seems that the formation of hydrogen bonds between two oxidized surfaces is much more likely.

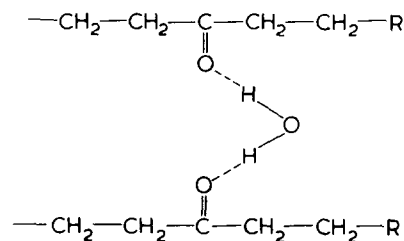
The formation of hydrogen bonds may be a result of tautomerization according to a series of the following transformations:



Here the carbonyl group at the surface of the oxidized polyethylene may undergo the tautomerization of the ketone to the enol form (steps 1,2). The enolic form which

exhibits an acidic character may form a bond with a carbonyl group of an adjacent surface (step 3). This mechanism proposed by Owens¹¹ for the self-adhesion of corona-treated polymer film may also be applied to our system.

Another possibility of H-bond formation may be realized by a crosslinked chemisorbed water molecule:



The following arguments may be given in favour of the H-bond hypothesis.

(a) The increase of the adhesion energy, W , up to saturation of the surface in polar carbonyl groups (Table 2) and the decrease of W above the temperature of the beginning of the melting transition would imply that the phenomenon of the self-adhesion of oxidized polyethylene films is governed substantially by superficial interactions.

(b) The energy of adhesion, W , of unoxidized and oxidized films has the same value as that of two unoxidized surfaces (Table 2). This seems to indicate that adhesion is enhanced only by the presence of carbonyl groups on both surfaces of polyethylene film in contact.

The work of detachment (peeling force) at a given temperature and speed, of two polyethylene films increases when polar groups are created on the surfaces of the two attached films. When the attachment is carried out at a given pressure and temperature, this work increases with the surface density of the polar groups and attains a saturation value when the surface capacity for the polar groups is attained.

However, the capacity and work of attachment display a maximum at a given temperature close to, but lower than that of the beginning of polyethylene melting.

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