THE EFFECT OF SURFACE COMPOSITION ON THE BOND STRENGTH OF CORONA AND LOW PRESSURE PLASMA TREATED POLYETHYLENE

A. Holländer(1), G. Czeremuszkin(2)+, J. E. Klemberg-Sapieha, and M. R. Wertheimer
Department of Engineering Physics, École Polytechnique, Box 6079, Station "A", Montréal, Quebec H3C 1A7, Canada
+Department of Chemical Engineering

ABSTRACT

Plasma- and corona-oxidized linear low density polyethylene was investigated with chemical derivatization and X-ray photoelectron spectroscopy, and the results were correlated to autoadhesive peel strength measurements. Strong evidence was found that acid-base interactions are largely responsible for the adhesion. The adsorption of water on the oxidized surfaces can drastically reduce the adhesion, and it may be responsible for the observed maximum in peel strength with increasing concentration of chemically bound oxygen on the sample surface.

INTRODUCTION

Most polymers have poor bonding properties as a result of their low surface energy, but surface oxidation resulting from the exposure to corona or to a low pressure plasma can greatly improve the bond strength with another surface. In the course of such treatments, a wide variety of functional groups can form on or near the polymer surface, and they all display different chemical properties. Much of the adhesive force, especially for the case of topographically "smooth" surfaces, results from chemical interactions, which can range from acid-base interactions to covalent bonding /1/. X-ray photoelectron spectroscopic (XPS) analysis of plasma-oxidized linear low density polyethylene (LLDPE) has shown that the autoadhesive peel strength depends on the chemical composition of the surface /2/. However, XPS alone is incapable of distinguishing functional groups, and of answering the question as to the role of particular functional groups in the interfacial interaction . The combination of XPS with chemical derivatization (CD) reactions can, on the other hand, help to provide this type of information: In general, CD permits a certain functional group to be transformed into another which can more readily be identified and characterized. A CD reaction designed for the use with XPS usually introduces a new element (e.g. fluorine, nitrogen) into the surface, that is, one

---

(1) permanent address: Fraunhofer-Einrichtung für Angewandte Polymerforschung (IAP), Teltow, Germany
(2) permanent address: Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Lodz, Poland

which was not there before. CD reactions suitable for carbonyl (C=O) /3/, carboxyl (COOH) /4/, hydroxyl (OH) /4,5/, hydroperoxide /3,6/, and epoxide /3/ groups have been reported in the literature. In the present work we report derivatization experiments for C=O, COOH, and OH groups, which are known to be the main constituents of PE surfaces which have been oxidized by low-pressure plasma or by corona. At the same time, these particular CD reactions have been used to block a functional group in adhesion experiments designed to elucidate the relative contribution of this particular group to the interfacial interaction.

EXPERIMENTAL

LLDPE films (Dow Chemical Canada, Inc.) were treated with a low-pressure oxygen plasma (2.45 GHz, 50 sccm, 0.5 Torr, 100 W) and with AC corona (40 W/cm^2, 3.5 kHz, air of 50 % relative humidity), using discharge systems described elsewhere /7/. The degree of the treatment was controlled by the duration of the exposure to the discharges.

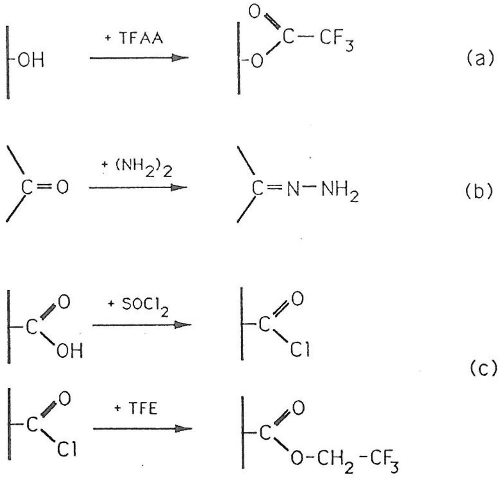

Figure 1: Derivatization reactions for hydroxyl (a), carbonyl (b), and carboxyl (c) groups (TFAA - trifluoroacetic anhydride; TFE - trifluoroethanol)

The derivatization reactions for particular functional groups of interest here (see Fig. 1) were carried out in the gas phase at the vapor pressure of the derivatizing agent. The samples were exposed to the agent for 10 minutes, following which excess adsorbed agent molecules were removed by evacuation.

The XPS investigations of the plasma- and corona-treated samples, before and after derivatization, were performed using a VG-ESCALAB 3 Mk II surface-analytical instrument. In preparation for the autoadhesion tests, the 25 μm PE film samples were pressed together with a load of 30 MPa at 40°C for 20 s. The peel force was measured in a T-peel test configuration using a IMASS model SP-103B-3M45 slip/peel tester; the delamination speed was 152 mm/min.

Adsorption experiments of chloroform and pyridine were carried out at ambient temperature, just before sample preparation for the peel testing; the purpose was to test the validity of acid-base theories of interfacial bond strength.

RESULTS AND DISCUSSION

A recent investigation in these laboratories, using the same LLDPE films /2/, revealed that the autoadhesive peel strength reaches a sharp maximum at a very precise degree of oxidation of the PE surface (10 < [O] < 15 at%) for both corona- and plasma-oxidized samples. XPS measurements showed that for both treatment types the peel strength increases with the concentration of carbon atoms which are singly bonded to oxygen, but decreases with increasing concentration of highly oxidized carbon.

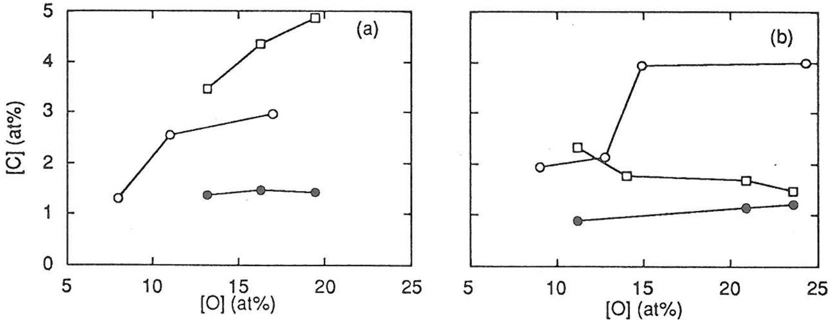

Figure 2: The concentration of carbon in particular functional groups (□- OH; o - C=O; • - COOH) on corona (a) and plasma (b) treated PE, as a function of the overall oxygen concentration, [O].

To further pursue and expand the above-cited work, we have used CD-XPS, the results of which are shown in Fig. 2. The concentration values of all investigated groups, and their dependence on the overall oxygen concentration [O] are seen to differ strongly for plasma- and corona-treated samples. The latter possess a relatively high concentration of OH groups, which increases markedly with rising [O] value; a similar trend is noted for C=O groups, while the concentration of COOH groups remains nearly constant. The plasma-treated samples contain more C=O and less OH groups than their corona-treated counterparts, while the COOH concentration rises slightly with increasing [O] value.

Despite appreciable changes in the surface composition, there is no evidence that specific functional groups can create a maximum in the peel strength with increasing oxygen concentration. Moreover, the very different behavior of plasma- and corona-treated samples suggests that there is no single functional group which can be held responsible for a strong or weak interfacial interaction.

The following set of experiments further supports this conclusion: The functional groups were masked by a derivatizing group, after which the films were used for peel strength measurements; the results for plasma-oxidized samples are summarized in Table 1.

Table 1. Peel force F_p (in N/m) for plasma-oxidized and derivatized PE (untreated control: F_p = 1 N/m).

	Treatment duration (s)		
Sample	15	20	35
underivatized, plasma-treated ([O] value in at%)	130 (8)	>200 (13)	90 (15)
COOH	4	4	4
C=O	4	4	5
OH	10	66	35

The peel strength F_p is seen to drop markedly for all derivatized samples, only the masking of OH groups showing any measurable dependence on the degree of oxidation. From this, it appears that all the investigated functional groups contribute more or less equally to create an interfacial interaction which is strong enough to provide a measurable adhesion.

The results presented above suggest that rather unspecific interaction forces are responsible for the adhesion. Fowkes /1/ investigated the role of Lewis acid-base interactions in interfacial phenomena; these interactions are asymmetric, that is, an acid interacts only with a base, but not with another acid. Assuming this type of interaction, it would be sufficient to block or transform either the acidic or the basic sites in order to block all interactions.

To test this hypothesis, we performed adsorption experiments in which plasma-treated samples were exposed to strongly basic (pyridine) and to acidic (chloroform) vapors, respectively: Due to the adsorption of the base, acidic sites on the surface are blocked, and vice-versa. After this treatment, peel strength measurements were carried out with "symmetric" as well as with "asymmetric" sample pairs (Table 2): In the "asymmetric" experiment, a film exposed to the base was joined with a film treated with the acidic vapors; the resulting peel strength is seen to be higher than for a "symmetric" pair, but lower than in the case of only plasma-treated samples.

Table 2. Peel force F_p for plasma-oxidized PE with adsorbed Lewis acid (chloroform) or Lewis base (pyridine) .

Film1	Film 2	F_p (N/m)
plasma-treated	plasma-treated	130
chloroform	chloroform	23
pyridine	pyridine	2
chloroform	pyridine	45
plasma-treated	untreated PE	1.5

This observation suggests that acid-base interactions are largely responsible for bonding forces in the autoadhesion of oxidized PE. While the nature of these forces seems to be relatively clear from these experiments, the reason for the sharp peel strength maximum with rising [O] value is perhaps less readily understood. A possible explanation is a weak boundary layer, composed of low molecular weight products, on the surface after treatment. However, our observations suggest another possible explanation: We have noticed that some samples with rather poor bonding adhered strongly when stored together in contact for a certain period of time. Moreover, the storage conditions were found to dramatically influence the results (Table 3).

Table 3: Duration required to achieve $F_p > 200$ N/m for plasma-oxidized PE (plasma treatment time 35 s; initial value of $F_p = 90$ N/m)

Storage condition	Storage duration (hours)
10^{-4} Torr	3
10 Torr, 40°C	48
atmosphere, 20°C	120
air, 98 % rel. humidity	no change

When storing the samples in vacuum, the initially low peel strength ($F_p = 90$ N/m) increases to a value of > 200 N/m over a period of 3 hours; that is, the two strips of PE could not be separated without destruction. On the other extreme, storing the samples in air of high relative humidity was found not to affect the peel strength. Similar results were also obtained for samples treated with corona, from which we conclude that water molecules strongly influence the interfacial interaction.

The surface of PE is found to become increasingly hydrophilic with increasing [O] value resulting from corona- or a plasma-treatment. From this, and from the above-mentioned, there are two competing effects which can influence the strength of adhesion: (i) A rising concentration of functional groups increases the number of sites which contribute to the adhesion, and this raises the peel strength. (ii) At the same time, hydrophilicity increases and with it the amount of water adsorbed on the surface from the ambient atmosphere. This latter phenomenon is difficult to avoid while preparing the samples for the peel experiment (even if all amenable processing were carried out in a glove box under dry, inert gas), and it drastically lowers the peel strength. It is therefore quite conceivable that the superposition of both effects is responsible for the observed maximum in the peel strength.

CONCLUSION

The autoadhesion of low-pressure plasma- or corona-oxidized PE appears to be largely determined by acid-base interactions, both acidic and basic surface sites being formed by the oxidation process. An inhibition of either of these can dramatically reduce the measured bond strength. The autoadhesion can also be drastically reduced by the adsorption of water molecules from the ambient air.

REFERENCES

1. F. M. Fowkes, J. Adhesion Sci. Technol., 1 (1987) 7
2. S. Sapieha, J. Cerny, J. E. Klemberg-Sapieha, and L. Martinu, J. Adhesion (in press)
3. L. J. Gerenser, J. F. Elman, M. G. Mason, and J. M. Pochan, Polymer 26 (1985) 1162
4. J. M. Pochan, L. J. Gerenser, and J. F. Elman, Polymer 27 (1986) 1058
5. R. A. Dickle, J. S. Hammond, J. E. de Vries, and J. W. Holubka, Anal. Chem. 54 (1985) 2045
6. D. Briggs and C. R. Kendall, Int. J. Adhesion and Adhesives, Jan. (1982) 13
7. J. E. Klemberg-Sapieha, L. Martinu, S. Sapieha, and M. R. Wertheimer, in "The Interfacial Interactions in Polymeric Composites", G. Akovali (Ed.), Kluwer Academic Publishers, 1993