Polyethylene Adhesion: Pretreatment with Potassium Permanganate

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Synopsis

Two major events occur in the modification of polyethylene (PE) surfaces by treatment with acidic $KMnO_4$ solutions: The polymer surface is coated with a porous MnO_2 layer and corroded, by oxidation. In both cases the resulting surfaces may be bonded with epoxy; the average peeling force for LDPE/epoxy/LDPE adhesive joints thus obtained may reach > 1.6 kN m^{-1} and is limited by adherend cohesive failure. Modified LDPE surfaces and disassembled joints were examined by transmission and ATR-IR spectrophotometry, to show that corroded, nonwettable LDPE contains appreciable amounts of polar groups, reactive towards epoxy amine components.

INTRODUCTION

Polyethylene (PE) and other polymer surfaces may be modified by various methods,[1-3] which aim at improving adhesion, painting, dyeing, and other characteristics of these materials but preserving their bulk (thermal, electrical, mechanical) properties.

Oxidative surface modification procedures have been widely studied and used.[4-7] These procedures have some advantages (low cost, adequacy to large surface treatments) and disadvantages (environmental problems associated with the chemical reagents used, long required times).

This laboratory has been investigating PE surface modification by treatment with aqueous potassium permanganate solutions.[8-10] This treatment leads to PE surface oxidation and coating with Mn (IV) hydrous oxide. Both consequences contribute to an increase of PE surface energy and might well improve PE adhesion.

The preparation and characterization of $KMnO_4$-treated PE surfaces is described in this work. This material was used in the preparation of adhesive joints, which properties are also reported.

EXPERIMENTAL

Technical-grade PE film and tubing was used throughout this work. The identity of the samples was checked by IR, melting point, and density measurements. LDPE crystallinity is 57% and HDPE crystallinity is 80%, as determined by X-ray diffraction. Other reagents are analytical grade.

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PE samples were washed with detergent solution and rinsed with water and ethanol, wiped with tissue paper and dried for 1 h, at 60°C. Clean, dry films were immersed in the surface-modification, coating baths (aqueous, $KMnO_4$ + nitric or sulfuric acid solutions at 80°C), under the conditions (time, concentration) given ahead. The films were then removed from the bath, rinsed with distilled water and dried. Films were weighted before and after these treatments, to determine weight gain or loss.

Adhesive joints were prepared with LDPE films treated following three different procedures: (i) Procedure I: Films were immersed in $0.2M$ $KMnO_4$ + $0.2M$ HNO_3 aqueous solution at 80°C for 10 min, rinsed, and air-dried. The result is dark films, with weight gains of 0.3 ± 0.1 g m^{-2}. (ii) Procedure II: Films were immersed in $0.1M$ $KMnO_4$ + $0.2M$ HNO_3 aqueous solution at 80°C for 12 h. In this case the initial dark coating peels off, leaving a thin, clear tan coating. (iii) Procedure III: The same as II but followed by washing with $6M$ HCl. These films do not show any discoloration and are transparent.

LDPE films loose weight during treatment by procedures II and III: -50 and -260 mg m^{-2}, respectively; this shows that films are corroded, to an appreciable extent: On the average, a layer 0.3 μm thick of polymer is removed by this teatment.

Adhesive joints were prepared in the following way: two LDPE film pieces were coated, on one side each, with general-purpose, household Araldite (Ciba-Geigy) epoxy resin. The epoxy-coated film surfaces were juxtaposed and passed between variable-gap aluminum rolls. These joints were cured under a pressure of 540 Pa, for 30 min at 85–90°C or for 24 h at room temperature. Joints were evaluated by using the T-peel test[11] and using a MEN-500 (São Paulo) testing machine.

Fractured joint and other polymer surfaces were examined by transmission and ATR-IR, in an IR 408 Shimadzu instrument, using a JASCO ATR-6 attachment and both 5 and 22 mm KRS-5 crystals. We found that the use of 2 mm crystal brings a remarkable improvement in the quality of spectra. Transmission spectra were taken by scratching the surfaces with inox blades and using the resulting powder to prepare KBr pellets (5 : 1000 wt %). Films exposed to isolated Araldite hardener and to n-butylamine were washed with toluene, ethanol, and water, and dried with tissue paper or at 80°C, 30 min, prior to IR spectra measurements.

MnO_2 surface area was determined by the ZIA (zinc ion-exchange ability) method.[12] Low-angle X-ray scattering measurements were done in a Phillips PW-1140 instrument; gyration radii were calculated by Guinier's method.[13]

Fractured surfaces were examined in a Carl Zeiss polarizing microscope, with a Miranda camera attached. MnO_2 coatings on PE were gold-coated and examined in a JEOL, JSM-25 SII scanning electron microscope.

Contact angles were determined by the immersed bubble method.[14]

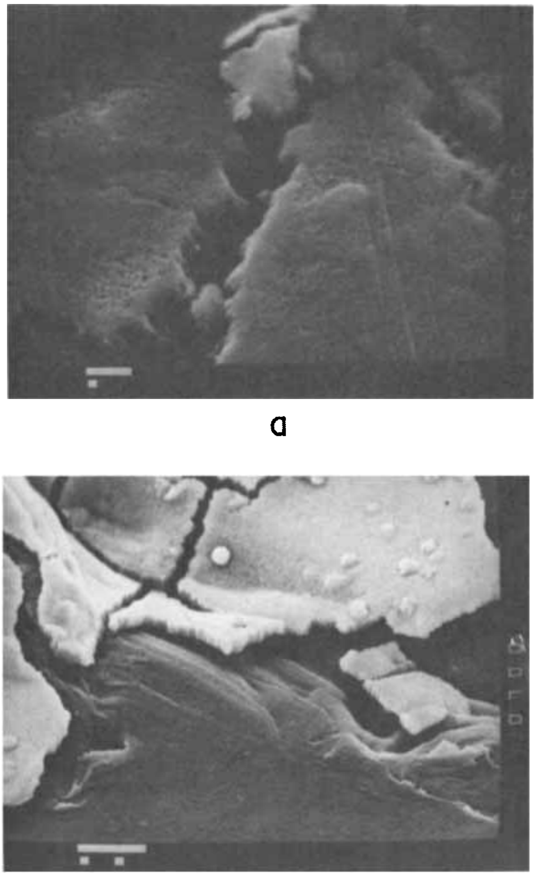
RESULTS

PE Coating with Hydrous MnO_2. When PE slabs or films are immersed in aqueous, acidic $KMnO_4$ warm solutions, they are coated with hydrous Mn(IV) oxide.[15] The amount of coating oxide depends on the immersion time, temperature, coating bath composition, and substrate, as shown in Table I.

TABLE I
Weight and Surface Area of MnO_2 Coatings on LDPE and HDPE

	LDPE[a]		LDPE[b]		LDPE[c]		LDPE[d]		HDPE[b]	
Time (h)	Weight (mg/cm^2)	Surf. area (m^2/g)	Weight (mg/cm^2)	Surf. area (m^2/g)	Weight (mg/cm^2)	Surf. area (m^2/g)	Weight (mg/cm^2)	Surf. area (m^2/g)	Weight (mg/cm^2)	Surf. area (m^2/g)
1	0.089	187	0.078	121	0.081	71			0.054	208
2	0.140	143	0.123	79	0.105	59	0.136	149	0.087	118
3							0.191	117		
3.5	0.232	87	0.240	36	0.240	51			0.125	109
4							0.187	126		

[a] Coating bath: 0.2M $KMnO_4$ and 0.2M H_2SO_4, $t = 80°C$; drying at room atmosphere.
[b] The same as a but dried at 60°C for 1 h.
[c] The same as b but aged for 100 days at room temperature.
[d] The same as b but coating bath: 0.2M $KMnO_4$ and 0.2M HNO_3.



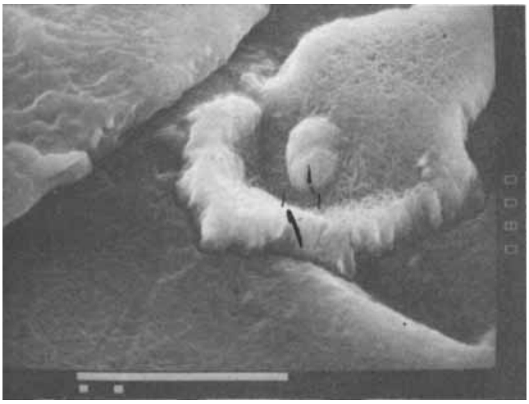
a

b1

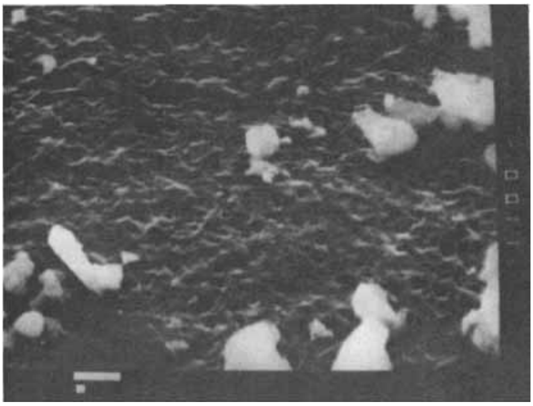
Fig. 1. Scanning electron micrographs of the LDPE surfaces pretreated with potassium permanganate: (a) procedure I; (b1 and b2) procedure II; (c) procedure III.

Surface Area and Morphology of MnO_2 Coatings. MnO_2 surface area was determined by the ZIA method, and is also given in Table I. We find that the use of HNO_3 in the coating bath yields higher surface areas, which do also depend on the nature of the substrate. Surface areas are decreased by increasing the sample immersion time, by drying and aging. Electron scanning micrographs reveal that the MnO_2 coatings are made of porous, fractured slabs laying over the substrate polymer. There are no indications of discrete particles being formed and grown, in the coating process (Fig. 1).

Scanning micrographs of surfaces modified by procedure III reveal the presence of MnO_2 particles [Fig. 1(c)], scattered through the surface. These are certainly much more resistant to dissolution in acid than most of the oxide coating. The discoloration imparted to LDPE by these particles can only be noticed if many (6–10) films are piled up and observed against a light source. The surfaces pictured in Figure 1(c) are rough, as opposed to untreated, blown LDPE films surfaces. This may be ascribed to LDPE corrosion, in the surface



b2



c

Fig. 1. (*Continued from the previous page.*)

modification process. The corroded, rough surface should make a positive, mechanical contribution to the adhesive joints stability.

MnO_2 coatings on LDPE were also examined by low-angle X-ray scattering, as shown in Table II. The determined gyration radii were found to *decrease* as the samples were aged. This is the result to be expected if these gyration radii refer to pores and not to particles, as indeed is indicated by the electron micrographs.

TABLE II
Gyration Radii of Hydrous Mn (IV) coatings on LDPE[a]

Immersion time (min)	R_0 (Å)
120	46.4
180	31.5
240	29.0

[a] Coating bath: $0.2M$ KMnO_4 + $0.2M$ HNO_3.

TABLE III
Contact Angle Measurements on LDPE Films Surface-Modified by Immersion in $KMnO_4$ Solutions

Modification procedure	Immersion time[a]	θ_a (deg)	θ_r (deg)
II	10 min	74 ± 3	68 ± 3
II	10 min	74 ± 2	69 ± 3
II	30 min	69 ± 1	60 ± 2
III	30 min	72 ± 2	63 ± 2
II	12 h	b	45
III	12 h	b	40

[a] Prior to taking contact angle readings.
[b] Not measured due to difficulty to obtain bubble adhesion.
[c] Average of measurements taken on two different film regions.

Contact Angle Measurements. Contact angles were determined using bubbles in the 5–30 μL volume range. The results thus obtained are in Table III. LDPE-modified surfaces are more wettable than untreated surfaces; the wettability increases as a function of sample immersion time, in water (before taking readings). This last observation shows that the modified surfaces are mutable by water: In the case of surfaces obtained by procedure II this is ascribed to MnO_2 surface hydration[16]; in the case of procedure III this may be understood assuming that (i) the scattered MnO_2 particles remaining at the surface undergo hydration, making the overall surface more hydrophilic and (ii) polar, oxidized PE groups migrate towards the surface, to minimize the PE–water interfacial energy.[17] The susceptibility of the modified surfaces towards drying is itself indicated by the following visual observations: Films taken from the solutions used are highly wettable; they lose wettability upon drying and show further contact angle changes when wetted, as shown in Table III.

Adhesive Joint Mechanical Stability. Adhesive joints prepared with LDPE films prepared by procedures I, II, and III, joined with epoxy adhesive, were subjected to a peel test, the results of which are in Table IV. All three

TABLE IV
Peel Strength of Adhesive Joints Prepared by Bonding Two LDPE Films (Previously Treated with $KMnO_4$ Solution) with Epoxy

Procedure used for LDPE treatment	Peel strength (kN m^{-1} [min-aver-max])	
	200-μm-thick film	300-μm-thick film
I	[0.2–0.4–0.6][a]	—
II	> 1.5[b]	> 1.6[b]
III	—	> 1.0[c]
Untreated LDPE	—	< 0.01

[a] Failure occurs at the MnO_2/LDPE interface. Average displacement rate, 100 mm min^{-1}.
[b] Cohesive failure of the adherend. Average displacement rate, 50 mm min^{-1}. Adherend dried at 80–85°C; joint cured for 30 min at 85–90°C.
[c] Complex failure, both interfacial and cohesive (adherend). Experimental conditions as in b.

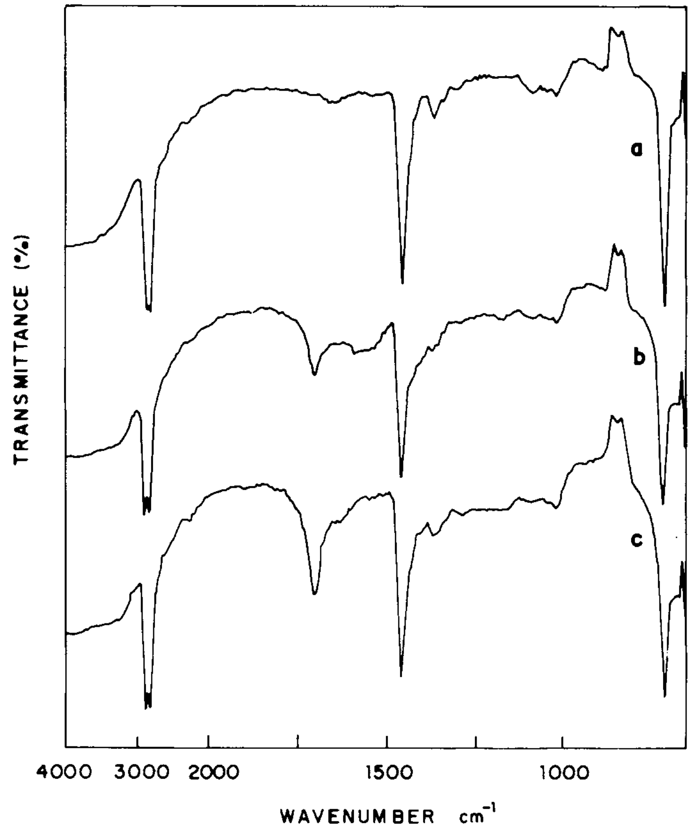


Fig. 2. ATR-IR spectra of: (a) LDPE virgin film; (b) the same, modified by procedure I; (c) the same, modified by procedure II; (d) the same, modified by procedure III.

procedures give useful joints; procedures II and III give joints in which adherend cohesive failure is observed.

Surfaces of LDPE Modified by Procedures I, II, and III. Reflectance spectra of LDPE coated with MnO_2 according to procedure I (Fig. 2, curve b) shows large absorbances at 3500–3000 and 1600 cm^{-1}, assigned to oxide-bound OH groups[18]; these bands lose intensity upon drying under air at 100°C, for 2 h. Drying does also eliminate a weaker band at 910 cm^{-1}, for which a definite assignment was not found, in the literature.

Reflectance spectra of LDPE surfaces modified by procedures II and III show little difference from LDPE virgin films (Fig. 2, curves c and d), except for the bands at ca. 1700 cm^{-1}, assigned to ν_{CO} from keto, carboxylic, or ester groups.[5-7]

The spectrum of MnO_2-coated LDPE has a broad absorption band at 1570 cm^{-1}, which disappears when the films are washed with 6*M* HCl; the 1700 cm^{-1} band intensity increases, at the same time (see Fig. 2, curves c and d). The 1570 cm^{-1} band may be assigned to carboxylate groups.[7,19] Even though the spectral bands assigned to polar groups are rather intense, these LDPE surfaces are not well wetted by water (see Table III). The existence of polar groups detected in IR-ATR spectra together with a low surface wettability may be understood assuming that: (i) Polar groups are located in crevices or pits, apolar groups being spread over the upmost surface layers; this composite surface may well be poorly wetted if the apolar surface area fraction is larger than the polar one.[14] (ii) The polar groups may be within the depth sampled by ATR-IR (2 μm)[20,21] but beneath the 10-Å-thick outermost layer, which determines wetting behavior. This last assumption is based on the reported redistribution of polar groups between oxidized polyethylene surface and bulk[22,23]; wettable, oxidized PE becomes nonwettable when heated above 80°C, under air, as expected considering the solid trend to minimum surface energy.

LDPE films treated by procedures II and III were treated with the isolated epoxy resin hardener (which contains —NH— groups), with a pure amine (*n*-butylamine) and with ammonium hydroxide (Fig. 3). As a result of these treatments, spectral changes are detected at 1700, 1620, 1540, and 1430–1400 cm^{-1}. The decrease in signal intensity at 1700 cm^{-1} is assigned to the consumption of carboxylic acid groups; the newly formed band at 1620 cm^{-1} is assigned to the formation of alkylammonium groups,[24,25] which may also contribute to absorbance around 1540 cm^{-1}. Carboxylate groups also absorb at ca 1540 cm^{-1} (ν_{as} COO^-).[25,26] The 1430–1400 cm^{-1} bands observed after treating oxidized LDPE with NH_4OH and butylamine is assigned to contributions of carboxylate[25,26] (ν_s COO^-) and ammonium[26] (δ NH_4^+) modes. We

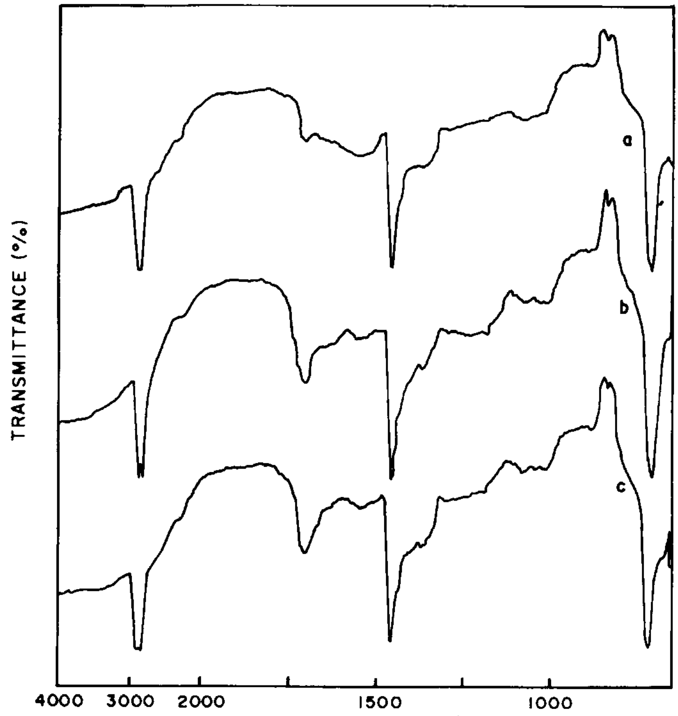


Fig. 3. ATR-IR spectra of LDPE films modified by procedure III and treated with: (a) araldite hardener; (b) butylamine; (c) ammonium hydroxyde, 25 wt % (immersion during 30 min, room temperature).

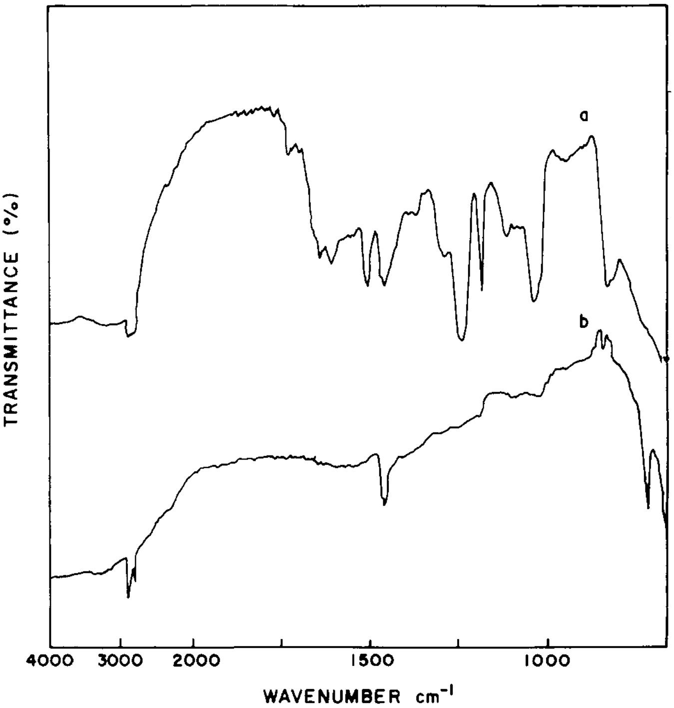


Fig. 4. ATR-IR spectra of: (a) multicoated LDPE/MnO_2/LDPE joint; (b) LDPE film coated with MnO_2 (prepared by procedure I, peeled off). In the two cases IR radiation incidence was on the surface containing MnO_2.

may thus conclude that the polar carboxylic groups are accessible to the reagents used, forming ammonium and alkylammonium carboxylates.

Examination of the Surfaces Obtained by Joint Fracture. Adhesive joints prepared with films treated by procedure I are fractured so as to yield a LDPE film and an MnO_2/epoxi/MnO_2/LDPE multilayer film. Thus failure occurs at one of the LDPE/MnO_2 interfaces. The surface of the PE film obtained by joint failure was examined by ATR-IR spectrophotometry (curve b, Fig. 4); surface material was also removed by scratching with a blade, and its transmission IR spectrum was obtained (curve a, Fig. 5). These spectra may be compared to spectra of pure polyethylene and of epoxy resin. It is clear that the bound-and-peeled-off LDPE surface contains appreciable amounts of epoxy. This resin can only reach LDPE surface if it is able to permeate the MnO_2 oxide layer.

Now, if the MnO_2-coated LDPE films prepared by procedure I are dried for 2 h at 100°C and bound with epoxy, the resulting joints peel off at the epoxy–MnO_2 interfaces. Reflectance spectra of the MnO_2 surfaces peeled from epoxy does not reveal any important epoxy contribution (curve b, Fig. 4).

Surfaces Obtained by Fracture of Joints Weakened under Water. Adhesive joints prepared with LDPE surfaces modified by procedures II and III were immersed in water at 80°C, for 120 h and disassembled by peeling, manually. Reflectance spectra of both fractured surfaces show intense absorptions characteristic of epoxy resin (Fig. 6). Scratching the surface with tissue

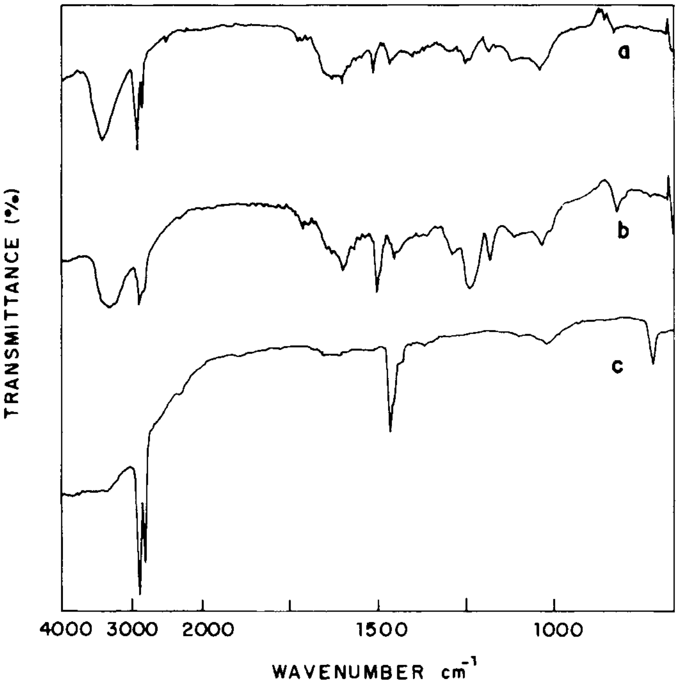


Fig. 5. Transmission IR spectra of the powders obtained by scratching the following surfaces, with a blade: (a) LDPE surface obtained by failure of a LDPE/MnO_2/epoxi/MnO_2/LDPE joint, at the LDPE, at the LDPE/MnO_2 interface; (b) surface of epoxi film, prepared by curing the resin in between virgin LDPE films; (c) virgin LDPE film.

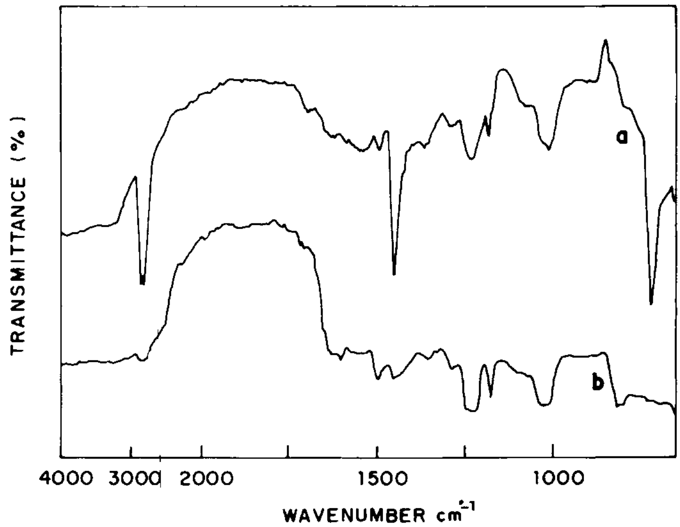


Fig. 6. ATR-IR spectra of the two surfaces obtained by peeling a joint prepared using procedure III and weakened under water (80°C, 120 h).

paper does not cause major spectral changes, showing that polyethylene-bound epoxy is not easily removed and that the joint fails by adhesive rupture.

Another feature of the spectra **a** and **b** in Figure 6 is the low intensity of the 1700 cm^{-1} band, as compared to spectra of LDPE treated by procedures II and III. This parallels the spectral changes described in the previous section and shows that alkyl–ammonium carboxylate is formed, probably making an ionic contribution to LDPE–epoxy adhesion, which resists exposure to water.

Morphology of Surfaces Obtained by Joint Failure. Joints prepared with LDPE modified by procedure III were disassembled as described in the previous section and examined. Micrographs are in Figure 7. Some textures are observed, which show that the polymer surface is ondulated and/or it displays an ordering pattern, perhaps associated with the mechanical action causing failure. These textures disappear when the film pieces are heated to 120°C, under air, which eliminates the possibility that they are formed by material unmiscible with LDPE, as cured epoxy.

DISCUSSION

The procedures described in this paper yield PE surfaces which can be bonded with a household epoxy adhesive.

Procedure II gives the best joints; three contributions to the stability of these joints are probably important: One is the reaction between carboxylic groups and resin amine groups. The other two are related to polyethylene corrosion: The weight loss of the films indicates that surface, weakly bound layers[27] are totally or partly removed. Since these layers are held responsible for the weakness of polymer-adhesive joints, their removal is highly desirable. Moreover, permanganate etching (although in more drastic conditions) generates a number of surface topographical features in PE, as described by Olley and Basset.[28] These artifacts are sites for mechanical interlocking of polyethylene and epoxy resin, making a contribution to adhesive joint stability. We believe that the textures observed by optical microscopy in failed joints, in this work, reveal surface topographic heterogeneities which can make a mechanical contribution to joint stability.

An interesting point is the effect of drying on the Mn (IV) oxide permeability to epoxy resin. This may be assigned to oxide layer pore diameter decrease and also to a decrease in oxide wettability, associated with loss of water. In this regard, our contact angle data show that MnO_2-coated LDPE becomes more wettable when kept beneath water.

There are literature reports on the performance of PE–adhesive–PE joints, prepared using PE surfaces treated with chromic acid (30 min, 70°C) and O_2 plasma (5–30 min, 25–50 W).[29] Peeling tensions thus obtained are, respectively (minimum–average–maximum) 0.2–0.8–3.0 and 0.2–2.4–15 kN m^{-1}. As we had substrate cohesive rupture (with procedures II and III), a comparison of average and maximum values is not possible, but our minimum values are greater than 1 kN m^{-1}. Joints prepared using procedure I have lower average and maximum peeling tensions, but the minimum (which is probably the most relevant one) is equal to that obtained in chromic acid and plasma treatments.

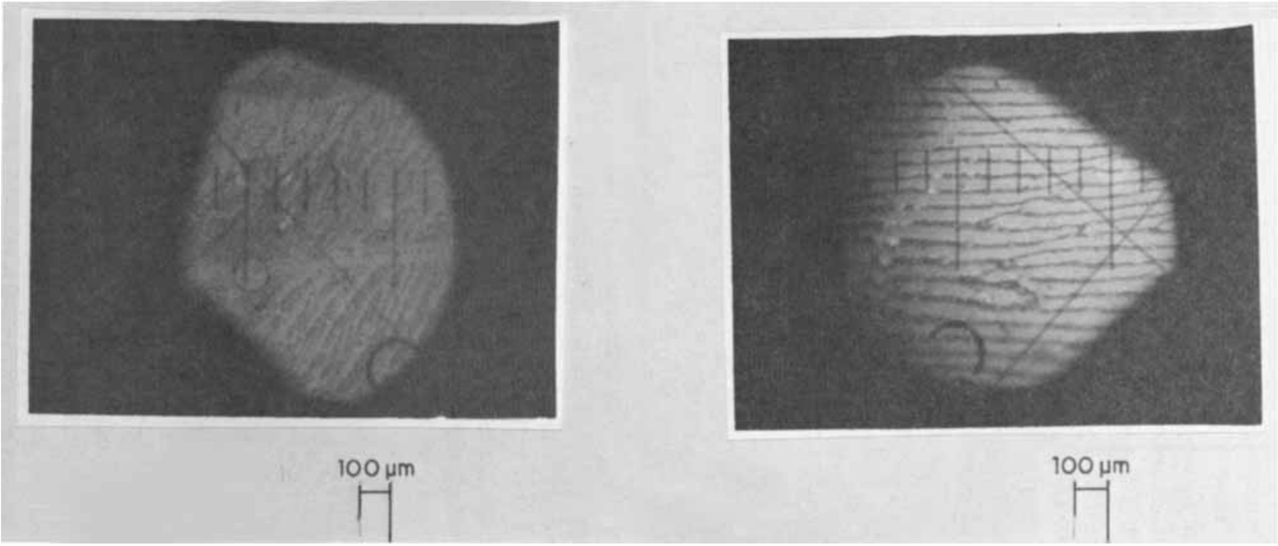


Fig. 7. Optical micrographs of LDPE surfaces obtained by mechanic fracture of adhesive joint assembled with films prepared using procedure III.

CONCLUSIONS

1. PE surfaces are coated with hydrous Mn (IV) oxide, by immersion in aqueous permanganate solutions. Extended treatment leads to surface corrosion and weakly-bound layers removal.

2. Different procedures of LDPE treatment with permanganate give surfaces bondable with epoxy, and joints of characteristics comparable to chromic acid and plasma treatments.

3. Permanganate-treated LDPE surface bonding with epoxy has contributions from adherend–adhesive ionic groups interaction and of mechanical interlocking; LDPE surface carboxylic groups are used up in adhesive joint formation, giving ionic bonds which resist extended exposure to hot water.

References

1. S. Yamakawa, *J. Appl. Polym. Sci.*, **20**, 3057 (1984).
2. K. Rossmann, *J. Polym. Sci.*, **19**, 141 (1956).
3. R. H. Hansen and H. Schonhorn, *J. Polym. Sci. B*, **4**, 203 (1966).
4. N. A. de Bruyne, *Nature*, **10**, 262 (1957).
5. J. R. Rasmussem, E. R. Stedronsky, and G. M. Whitesides, *J. Am. Chem. Soc.*, **99**, 4736 (1977).
6. J. C. Ericksson, C. G. Goländer, A. Baszkin, and L. Ter-Minassian-Saraga, **100**, 381 (1984).
7. H. R. S. Farley, R. H. Reamey, T. J. McCarthy, J. Deutch, and G. M. Whitesides, *Langmuir*, **1**, 725 (1985).
8. A. F. Rubira and F. Galembeck, in *Proceedings of the IV Japan–Brazil Symposium on Science and Technology*, Rio de Janeiro, Brazil, 1984, p. 341.
9. F. Galembeck, S. E. Galembeck, H. Vargas, C. A. Ribeiro, L. C. M. Miranda, and C. C. Ghizoni, in *Surface Contamination*, K. L. Mittal, Ed., Plenum, New York, 1979, Vol. 1, p. 57.
10. A. F. Rubira, A. C. da Costa, and F. Galembeck, *Colloids Surfaces*, **15**, 63 (1985).
11. Standard method of test for peel resistance of adhesives (T-Peel Test), ASTM, 1876–72.
12. A. Kozawa, *J. Electrochem. Soc.*, **106**, 552 (1959).
13. A. Guinier and G. Fournet, *Small Angle Scattering of X-Rays*, Chapman and Hall, London, 1955.
14. A. W. Adamson, *Physical Chemistry of Surfaces*, 4th ed., Wiley, New York, 1983.
15. A. F. Rubira, M. G. de Oliveira, N. F. Leite, C. C. Cesar, H. Vargas, and F. Galembeck, in *Proceedings of the 4th International Meeting on Polymer Science and Technology*, La Plata, Argentina, 1985, p. 373.
16. J. W. Murray, *J. Colloid Interf. Sci.*, **46**(3), 357 (1974).
17. D. R. Gagnon and T. J. McCarthy, *J. Appl. Polym. Sci.*, **29**, 4335 (1984).
18. M. A. Baltanás, A. B. Stiles, and J. B. Katzer, *J. Catal.*, **88**, 362 (1984).
19. B. C. Mehrota and R. Bohra, *Metal Carboxilates*, Academic, London, 1983.
20. D. A. Saucy, S. J. Simko, and R. W. Sinton, *Anal. Chem.*, **57**, 871 (1985).
21. J. A. Gardella Jr., G. L. Grobe, W. L. Hopson, and E. M. Eyring, *Anal. Chem.*, **56**, 1169 (1984).
22. A. Baszkin and L. Ter-Minassian-Saraga, *Polymer*, **15**, 759 (1974).
23. A. Bazkin and L. Ter-Minassian-Saraga, *Polymer*, **19**, 1083 (1978).
24. A. Yerger and G. M. Barrow, *J. Am. Chem. Soc.*, **77**, 4474 (1955).
25. M. Avram and G. H. D. Mateescu, *Infrared Spectroscopy—Applications in Organic Chemistry*, Wiley-Interscience, New York, 1972.
26. R. M. Silverstein, G. C. Bassler, *Spectrometric Identification of Organic Compounds*, 2nd ed., Wiley, New York, 1962.
27. N. J. De Lollis, in *Adhesives, Adherends, Adhesion*, R. E. Krieger, Ed., Plenum, New York, 1980, Chap. 2.
28. R. H. Olley and D. C. Basset, *Polymer*, **23**, 1707 (1982).
29. S. Yamakawa and F. Yamamoto, *J. Appl. Polym. Sci.*, **25**, 41 (1980).

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