Modification of Polyolefin Films Surface with Sodium Hypochlorite

O. Iguerb,[1] S. Demoustier-Champagne,[1] J. Marchand-Brynaert,[2] D. Daoust,[1] M. Sclavons,[1] J. Devaux[1]

[1]*Université Catholique de Louvain (UCL), Unité de Chimie et de Physique des hauts Polymères, Croix du Sud 1, Louvain-La-Neuve, BE-1348, Belgium*
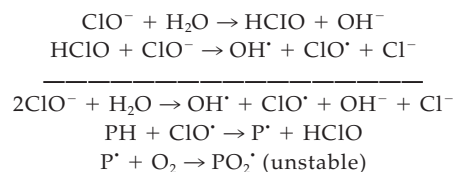[2]*Université Catholique de Louvain (UCL), Unité de Chimie Organique et Médicinale, Place Louis Pasteur, 1, B-1348. LLN, Belgium*

ABSTRACT: Surface modification of high-density-polyethylene (HDPE) and linear-low-density polyethylene (LLDPE) films is promoted by sodium hypochlorite solutions using two different processes (I and II). Such an oxidation system introduces limited amounts of carbonyl–carboxyl and hydroxyl groups onto the surface of hydrocarbon polymers. FTIR, XPS, and SEM were used to assess the efficiency of the oxidation. The hydrophilicity of the studied surfaces was investigated by the sessile drop technique and the Wilhelmy plate and a plausible oxidation mechanism is proposed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1184–1197, 2006

$$ClO^- + H_2O \rightarrow HCIO + OH^-$$
$$HClO + ClO^- \rightarrow OH^\bullet + ClO^\bullet + Cl^-$$
_____
$$2ClO^- + H_2O \rightarrow OH^\bullet + ClO^\bullet + OH^- + Cl^-$$
$$PH + ClO^\bullet \rightarrow P^\bullet + HClO$$
$$P^\bullet + O_2 \rightarrow PO_2^\bullet \text{ (unstable)}$$

Key words: hydrophilic polymers; polyethylene (PE); surfaces; oxidation; hypochlorite

INTRODUCTION

Polyolefins and olefinic copolymers are among the most widely used polymeric materials, but suffer from a major drawback: adhesive bonding is difficult and usually requires special surface pretreatment. Not surprisingly, adhesion to polyolefin has been the subject of a considerable number of researchs and reviews.[1–4] Commercially, important treatments of polymer surfaces such as metallizing, bonding, painting, and printing require good substrate adhesion.

For polyolefins as polyethylene (HDPE, LLDPE, LDPE. . .) and polypropylene exhibiting essentially nonpolar surfaces, these treatments are rather difficult to perform. Thus, these polymers must be surface modified to introduce polar functional groups promoting adhesion.[5] Procedures for modification of polyolefin surfaces commonly require hard and nonselective oxidation processes. Examples include Cr (VI) in sulfuric acid, SO_3 in sulfuric acid, and HNO_3 and flame or plasma treatments.[6–14]

The oxidation of low-density polyethylene (LDPE) by chromic acid was investigated by Ferguson, Rasmussen et al.[15–17] The number and the nature of the surface functional groups introduced by the treatment (>50% of carboxyl groups) and the dynamic processes occurring at the surface when placed in contact with different solvents or gases have been studied. For example, upon heating in air or argon, the carboxylic acid groups were shown to become buried in regions of the interface that cannot be probed by contact angle measurements. Reversibly, the surface acids were recovered by heating the (LDPE) samples in boiling water.

In our work, we were interested in studying similar possibilities of oxidizing C—H bond of hydrocarbon polymers under mild conditions[18,19] by using sodium hypochlorite (NaClO). Besides scientific interest, the demonstration of some reactivity of a nontoxic, not dangerous and unexpensive oxidant toward a polyolefin could potentially provide the basis for further studies, leading to enhanced biodegradability.[20] In this way, sodium hypochlorite is known as a nonspecific oxidant.[21] It attacks the hydroxyl and ether functions and can also cleave C—C and C—H bonds. These reactions depend essentially on the pH and temperature of the reaction medium.[22,23]

Previous work[24] reported that powders of HDPE and LLDPE hydrophilized by sodium hypochlorite treatment behave as efficient filtration aids in food industry especially for beer. In the present study, we

Correspondence to: O. Iguerb (iguerb@poly.ucl.ac.be).

attempt to chemically understand the surface modification mechanism. In this way, hypochlorite oxidation of high-density polyethylene (HDPE) and linear-low-density polyethylene (LLDPE) have been investigated. The oxidation is proven to be mild, and the level of functional groups introduced onto the polymer surfaces remains low. The efficiency of such a wet treatment of HDPE and LLDPE films for adhesion enhancement (pretreatment) has been studied by wetting dynamics Wilhelmy plate method, FTIR spectroscopy, XPS spectroscopy, and Scanning Electron Microscopy (SEM).

EXPERIMENTAL

Materials

Sodium hypochlorite solution of 13% active chlorine (C = 152.16 g/L), sodium hydroxide, ethanol, n-hexan, deuterated tetrachloroethane, diiodomethane, dodecylbenzenesulfonic acid salt, and deuterated water analytical grade were obtained from Acros Chemicals (Belgium) and used as received. HPLC grade water was obtained by purification with a Milli-Q plus system, hereafter referred as Milli-Q. High-density-polyethylene HDPE (M_w = 75,700) and linear-low-density-polyethylene LLDPE (M_w = 55,700) films with intrinsic viscosities of 1.02 and 0.71, respectively, in 1,2,4-trichlorobenzene were prepared by pressing powders purchased from Mobil Plastics (Belgium). The powder was molded at 200°C between two sets of steel plates, aluminum polyimid sheets to give 0.1-mm thick films.

Molar mass distributions are measured by Steric Exclusion Chromatography (SEC) using a Waters Alliance GPC/V 2000 instrument equipped with differential refractive index detection. Two Styragel HT6E and one Styragel HT2 columns are used. The SEC is carried out at 135°C in 1,2,4-trichlorobenzene and stabilized with BHT (2 g/L). At a flow rate of 1 mL/min, polymer concentration is 2 g/L. Filtered samples are injected into the system with an injection volume of 323 μL. Narrow PS standards covering the entire MM (Molecular Mass) range of the samples are used for calibration purpose. Mark-Houwink relationships are used for universal calibration.[25]

Sodium hypochlorite surface oxidation

Two different processes I and II were used to perform surface modifications of HDPE and LLDPE films by NaClO solutions.

In process I, 10 × 10 mm^2 polyolefin films were first cleaned by ultrasonication using ethanol and n-hexan. The samples were dried in vacuum oven for 12 h at 70°C. These freshly cleaned samples were immersed in a closed batch-type reactor containing aqueous Na-

ClO solution of 13% active chlorine (C = 152.16 g/L), under stirring at 80 ± 0.1°C. At the end of the reaction, the films were rinsed several times with Milli-Q water to eliminate salts formed at the treated polymer surface and dried in a vacuum oven for 24 h at 40°C.

In process II, the films were rinsed only with propan-2-one before oxidation reaction. Moreover, the sodium hypochlorite solution was renewed after regular periods of reaction time (5 h). At the end of the reaction, the treated films were rinsed in a bath of Milli-Q water during 10 min. The washing and drying were carried out in the same way as in process I.

Methods

Wetting static measurements

The sessile drop technique and the measurement of contact angle by an image analysis system were used. The measurements were carried out with Milli-Q distilled water for evaluating hydrophilicity of treated and untreated samples at room temperature. The water droplet volume was always kept in the range of 1–3 μL to prevent gravitational distortion of the spherical profile. Each reported value is the average of at least ten measurements on different regions.

Wetting dynamics measurements

Wetting with Milli-Q water was investigated using the Wilhelmy plate method,[26] with a DCA 322 equipment from Cahn Instruments (Cerritos, CA). The measurements were performed at room temperature. The water container was closed with a lid, pierced with a small hole for the suspension wire ensuring a relative humidity of 95% about 1 cm above the water surface. Repeated cycles of immersion and emersion (advancing–receding) were performed at a speed of 50 μm/s and the contact angles (Θ_{adv} and Θ_{rec}) were recorded. For a cycle of immersion–emersion, the measured contact angles are called Θ_{adv} and Θ_{rec}, respectively. In certain cases, a pause could be realized in the air between two successive immersion–emersion cycles to check if the film surface undergoes any modification between successive immersions. The variation of the measured cosΘ is generally reported as a function of the position scale referring to the distance between the bottom of the plate and the position (X) of three-phase contact line.[27] In the present work, four successive cycles were performed. In both cycles 1 and 2, the sample is immersed and emerged without pause. However for cycle 3, a pause of 5 min was observed before immersion–emersion in the bath of water, followed by a pause of 20 min in air before immersion–emersion (cycle 4).

Surface energy measurement

The surface energy of water before and after wetting dynamics measurements of treated and untreated surfaces of HDPE and LLDPE films were measured by Kruss Interfacial-Tensiometer K8600 by using the Noui method.[28]

X-ray photoelectron spectroscopy

XPS spectra were recorded using SSX-100 Spectrometer (model 206 from surface Science Instruments) equipped with an aluminum anode (10 kV, 20 mA) and a quartz monochromator. Charge stabilization was achieved using an electron flood gun set at 6–8 eV and placing a grounded nickel grid 2–3 mm above the sample surface. The analyzed area was 1.4 mm^2 and the pass energy was 150 eV for survey analysis. Photoelectrons were collected at an angle of 55° with the normal to the sample surface. The order of peak analysis was C_{1s}, O_{1s}, Cl_{2p}, Na_{1s}, and C_{1s} again followed by a final survey scan.

Scanning electron microscopy

High-resolution images were obtained by field-effect gun scanning electron microscopy (FE-SEM) (982 Gemini from Leo). For morphological studies using SEM, the samples were covered by a thin layer of chromium (6 nm).

FTIR spectroscopy

The treated and untreated films were dried in a vacuum oven for 24 h before being analyzed. Infrared spectra were recorded at room temperature on a FTIR Spectrometer type 1760 of Perkin–Elmer. Ten scans at a resolution of 2 cm^{-1} were signal averaged for each sample.

When needed, the IR spectra of the overlapping band were mathematically analyzed by an iterative curve fitting method developed in the software Igor provided by Wavemetrics Inc.[29]

Sodium hydroxide (NaOH 0.1N) was used to convert acids into sodium carboxylates (COO^- Na^+) and a solution of sodiumdodecylsulfate in D_2O to convert O—H into O—D.

Oxidized LLDPE and HDPE films were submitted to Soxhlet extraction in methanol for 12 h to eliminate the stearates, which could be used as additives. After drying the samples in vacuum oven for 24 h, they were immersed in NaOH solution during 15 min.

The samples were analyzed by FTIR spectroscopy after drying in vacuum oven during 72 h. The oxidized samples were immersed during 60 h in a solution of dodecylbenzenesulfonic acid salt in D_2O, dried
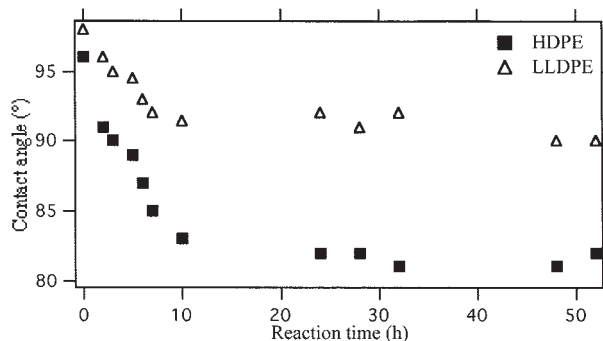

Figure 1 Evolution of contact angle measured by sessile drop technique as a function of reaction time for HDPE and LLDPE films treated by process I.

in vacuum oven during 72 h and analyzed by FTIR spectroscopy.

UV spectroscopy

The oxidant concentration (sodium hypochlorite) was determined using UV_vis_IR CARY 500 scan spectrometer from Varian, after regular periods of reaction time. The spectrometer was calibrated by establishing an initial (reference) absorbance with Milli-Q distilled water. The absorbance decrease at 292 nm, corresponding to the disappearance of hypochlorite ion (ClO^-), was measured for several diluted solutions of the oxidant. In fact, after a given reaction time, 1 mL of NaClO was taken from the reactor and diluted in 500 mL of Milli-Q distilled water.

Nuclear magnetic resonance (NMR)

The characterization of different species formed by oxidation on the surface was performed using ^{13}C and ^1H NMR spectroscopy. The spectra were obtained at 135°C, using a Bruker-Advance 500 pulsed NMR spectrometer at 125 and 500 MHz equipped with a high-temperature probe. Polymer solutions are prepared by dissolving 150 mg of polymer in 3.5 mL of deuterated tetrachloroethane. Detailed parameters of the experiment are as follows: pulse angle, 90°; relaxation time, 15 s; acquisition time, 1.5 s; and number of scans, 10,000. The chemical shifts assigned to various functionalities follow the literature.[30,31]

RESULTS

Contact angles–sessile drop technique

The water contact angles measured as a function of the reaction time by the sessile drop technique, for HDPE and LLDPE treated with process I, are presented in Figure 1. After such a treatment, evolution of contact angles as a function of reaction time shows two be-
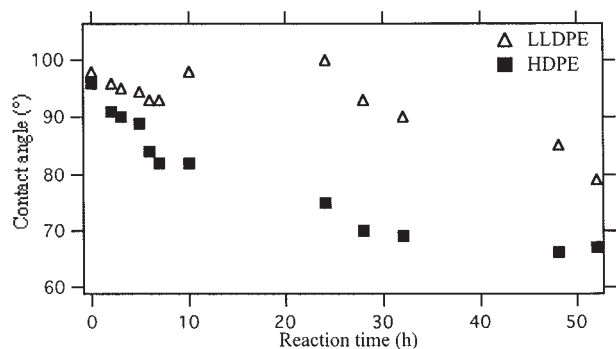
Figure 2 Evolution of contact angle measured by sessile drop technique as a function of reaction time for HDPE and LLDPE films treated by process II.

haviors. From 0 to 10 h, a slight decrease of the contact angle was observed for HDPE and LLDPE-treated films, compared with untreated films. After 10 h of reaction time, the contact angle remains constant in spite of increasing reaction time (85° for HDPE and 92° for LLDPE, respectively).

UV spectroscopy measurements of the oxidative solution showed that the absorption at 292 nm assigned to ClO^- species decreases by 80% after 10 h. This impoverishment, resulting from the thermal instability of hypochlorite solutions (eq. 1), could explain the break onto the oxidation process.

$$2ClO^- \rightarrow ClO_2^- + Cl^- \ (T° > 40°C)$$
$$ClO^- + 1/2\,O_2 \rightarrow ClO_2^- \tag{1}$$
$$ClO^- + O_2 \rightarrow ClO_3^-$$
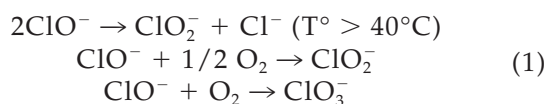
Crystallization of NaCl on the walls of the vessel witnesses that, at least, the first reaction of (eq 1) occurs.

To verify this explanation, process II was designed in which successive additions of hypochlorite solution were performed. The plot of contact angles into HDPE and LLDPE treated by this process II (renewing of of NaCl after each 5 h of reaction) is represented in Figure 2.

For HDPE films treated with process II, an important decrease of the contact angle was measured when the reaction time increased. After 24 h of reaction time, the contact angle decreased from 100° to 67°.

However, whatever the process, hydrophilicity of LLDPE films remained lower than HDPE films, and the contact angle of LLDPE decreased only down to 82° after 52 h.

Interestingly, it has been verified that the surface hydrophilicity values remained the same for samples analyzed immediately after treatment and 20 days after treatment. By comparison with the results reported in the case of oxidized polymers by flame, plasma, or corona treatments, this represents a remarkable surface stability.

XPS

No important modification of the C_{1s} peak shape was noted, indicating that the sample did not undergo degradation nor contamination during analysis.[32]

The binding energy scale was set by fixing the component of C_{1s} peak (due to carbon only bound to carbon and hydrogen) at 284.8 eV. A Shirley-type nonlinear background subtraction was used.[33] Intensity ratios were converted into molar concentration ratios by using the sensitivity factors proposed by the manufacturer (Scoffield emission cross sections, variation of the electron mean free path according to the 0.7 power of the kinetic energy, and constant transmission function).

A plot of O/C ratio *versus* reaction time for oxidized HDPE and LLDPE is presented in Figure 3. After successive additions of oxidative solution (process II), the quantity of oxygen is higher by comparison with process I. Again, the modifications induced on HDPE are more important than on LLDPE by using both processes I and II. One can easily see that a certain amount of oxygen was introduced on HDPE and LLDPE-treated surfaces proving that oxidation has occurred.

A quantification of the various functions created at the surface by the oxidation processes on HDPE and LLDPE films has been attempted.

Several works have already treated this problem by taking into account the shape of the asymmetric C_{1s} peak of polyethylene (HDPE, LLDPE).[34,35] In the present work, a new procedure to decompose the C_{1s} peak is proposed. The peak recorded on a treated film is decomposed by subtraction of the peak recorded on untreated film. The resulting background is processed by a classical peak-fitting procedure.

As shown in Table I, fine analysis (decomposition) of the C_{1s} peaks revealed new components at 286.1–286.8 eV due to C—O functions and 288.6–289.2 eV attributed to O—C=O and CC=O functions.[36–38] The same effect was also corroborated from appearance of O_{1s} peak (Table I), while the peaks at 532.1 eV due to
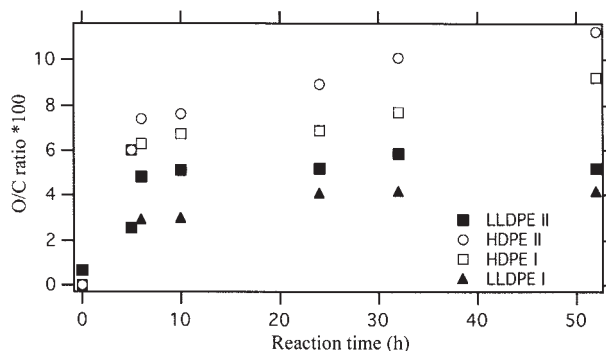

Figure 3 O/C ratio of oxidized HDPE and LLDPE *versus* reaction time by using processes I and II.

TABLE I
Quantified XPS Analysis of HDPE and LLDPE Surfaces Modified by Process I

Time (h)	O/C (10^2)	Cl_{2p}	$\begin{matrix}C=O\\O-C=O\end{matrix}$	C—O	C—(C,H)	Θ_{adv1}
HDPE (atomic %)						
0	0	—	—	—	—	101
5	5.98	0.86	0.72	1.88	97.40	91
6	6.31	0.80	0.70	1.87	97.43	87
10	6.75	0.99	1.09	1.92	96.99	82
24	6.85	0.53	1.09	1.94	96.97	82
32	7.69	0.45	1.14	2.02	96.84	81
52	9.22	0.55	1.26	2.15	96.59	82
LLDPE (atomic %)						
0	0.65	0	—	—	—	98
5	2.57	0.27	0.27	0.47	99.26	95.5
6	2.96	0.42	0.30	1.15	98.55	93
10	2.98	0.72	0.36	1.25	98.39	99
24	4.09	0.15	0.42	1.40	98.18	103
32	4.19	0.24	0.44	1.86	97.70	93
52	4.18	0.10	2.47	10.76	86.77	83

Θ_{adv1}, water contact angle in first advance.

C—O and O—C=O groups are also promoted to higher energies with increasing reaction time, with a simultaneous rise in their area. Similar results were obtained with LLDPE-oxidized films (Table I), but the quantities of oxygenated carbon seems lower by comparison with HDPE.

Table II shows the results obtained by using process II. In this case, the surface oxidation was more efficient, as previously seen from the contact angle measurements.

Quantitative analysis revealed the formation of various species characterizing the oxidized polyolefin surface. In fact, acid, ester, ketone, hydroxyl, or ether groups were observed. In addition, chlorination of the treated surface seemed to occur, but the concentration of Cl_{2p} on treated surfaces remained rather low: 1.22% for LLDPE and 1.07% for HDPE were the maximum values.

FTIR spectroscopy

As shown here before by XPS spectroscopy, the processes I and II led to surface oxidation of both HDPE and LLDPE films. In this section, we attempted to follow this oxidation by FTIR spectroscopy.

TABLE II
Quantified XPS Analysis of HDPE and LLDPE Surfaces Modified by Process II

Time (h)	O/C (10^2)	Cl_{2p}	$\begin{matrix}O=O\\O-C=O\end{matrix}$	C—O	C—(C,H)	Θ_{adv1}
HDPE (atomic %)						
0	0	0	—	—	—	101
5	5.98	0.77	2.11	3.7	94.19	93
6	7.39	1.07	2.38	5.85	91.77	91
10	7.61	1.07	2.57	4.95	92.48	90
24	8.93	0.65	1.45	4.09	94.46	70
32	10.09	0.93	2.43	7.30	90.25	59
52	11.26	0.68	3.14	7.58	89.28	67
LLDPE (atomic %)						
0	0.6	0	—	—	—	100
5	2.57	0.07	1.17	4.16	94.67	99
6	4.82	0.10	1.22	4.30	94.48	98
10	5.15	0.70	1.54	4.32	94.15	96
24	5.21	0.76	1.83	5.58	92.59	95
32	5.88	1.22	2.08	6.55	91.37	83
52	5.16	0.45	2.89	7.62	89.49	89

Θ_{adv1}, water contact angle in first advance.
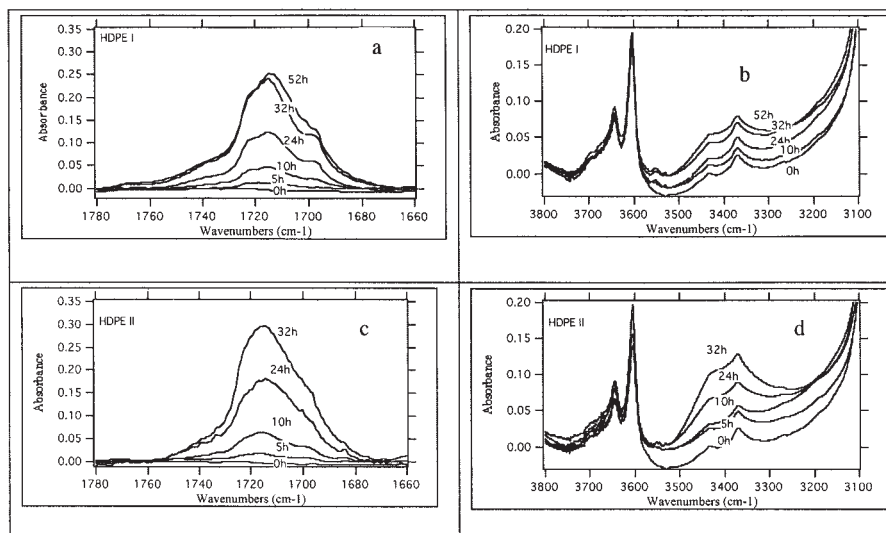
Figure 4 FTIR spectra of oxidized HDPE (a, b) with process I and (c, d) with process II.

Generally, oxidation of polymers produces complex mixtures of products. Chemical changes resulting from oxidation process involve the formation of functional groups specific to the type of polymer, and at rates which are strongly dependent on the chemical structure of the polymer.

The FTIR spectra recorded from native and treated HDPE and LLDPE films, after normalization at 1368 cm^{-1}, showed that the most affected bands lie in spectral ranges corresponding to stretching modes of carbonyl (1780–1660 cm^{-1}) and of hydroxyl (3800–3100 cm^{-1}) groups.

Figure 4(a) displays FTIR spectra in the 1780–1660 cm^{-1} region for HDPE films treated by process I and compared with the native HDPE film. Modified samples exhibited a broad band, growing with reaction time and centered at 1714 cm^{-1}, which is typical of carbonyl groups in oxidized polyolefins.[39–41]

In the range applicable to hydroxylated oxidation products (Fig. 4(b)), there was an increase of two weak maximums at 3435 and 3370 cm^{-1}. These wavenumbers indicate well the formation of hydroxylated functions. Similar results were reported in the literature for the complex IR absorption of oxidized polyethylene.[39–41]

Treatment of HDPE by process II (Figs. 4(c) and 4(d)) led to the appearance of the same peaks with higher intensities. As a result, stronger modifications occurred in the carbonyl and hydroxyl regions by comparison with process I.

The IR spectra of the overlapping band were mathematically analyzed by an iterative curve fitting method (so-called deconvolution) as described in the experimental part. The absorption bands in the carbonyl (1780–1660 cm^{-1}) frequency range and in a region characteristic of the polymer used as reference were approximated by Lorentzian functions.[28]

The deconvolution of oxidized HDPE spectrum after 32 h of reaction time with process II is illustrated in Figure 5.

Four elemental peaks centered at 1740, 1722, 1715, and 1700 cm^{-1} were obtained on all HDPE and LLDPE-treated samples.

The second derivative method described by Donohue and coworkers[42] was also used. Similar results were obtained with both methods. The curve-fitting analysis was therefore extended to all HDPE and LLDPE samples treated with both processes I and II.

In oxidized polyethylene, the peak at 1715 cm^{-1} is characteristic of C=O stretching in carboxylic acid groups.[43] The peak intensity increased with increasing the reaction time. The first important shoulder at 1722 cm^{-1} is assigned to stretching of carbonyl groups in saturated aliphatic ketones.[28,44]

The second shoulder near 1700 cm^{-1} may be due to α, β unsaturated ketones[45] or to dimeric carboxylic acids as reported by Coleman et al.[46] However, bands
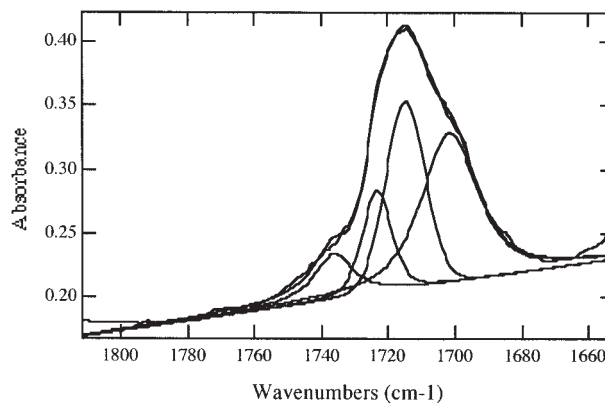

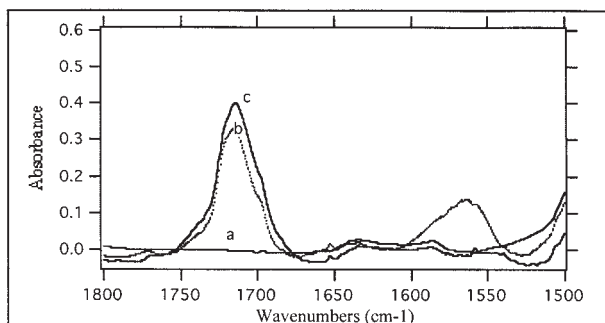**Figure 5** FTIR curve-fitting of HDPE treated for 32 h with process II.

Figure 6 FTIR spectra of (a) HDPE, (b) HDPE oxidized for 52 h and neutralized, and (c) HDPE oxidized for 52 h in 1780–1500 cm^{-1} region.

attributed to vinylene systems were not observed. Consequently, the peak at 1700 cm^{-1} was only assigned to carboxylic acids and not to α, β unsaturated ketones.

Finally, the peak at 1740 cm^{-1} is assigned to stretching of carbonyl groups of esters.[28] Generally, the stretching of C=O in aldehyde is reported[41] at 1733 cm^{-1}; however, the peak was not observed in IR spectra of oxidized HDPE.

The assignment of complex absorption in IR spectra of oxidized polyolefin samples was extensively followed using various derivatization techniques, for instance the ones first proposed by Carlsson et al.[47,48] In the present work, only two simple experiments were undertaken. The reagents used are, on the one hand, sodium hydroxide (NaOH 0.1N) to convert acids into sodium carboxylates (COO⁻ Na⁺), and on the other hand, deuterated water (D₂O) (with sodium dodecylbenzenesulfonic acid salt ($C_{18}H_{29}NaO_3$) as wetting agent) to convert O—H into O—D functions.

A neutralization of oxidized films (HDPE, 52 h, II) with alkali solution led to some modifications. The FTIR spectrum of neutralized HDPE in 1780–1500 cm^{-1} range is shown in Figure 6. A decrease of the intensity of the peak assigned to carboxylic acids at 1715 cm^{-1} was observed and in addition, a new band characteristic of C=O of carboxylates (COO⁻) appeared near 1560 cm^{-1} as a consequence of the conversion of carboxylic acids into carboxylic acid salts. The partial conversion of the peak at 1715 cm^{-1} suggested an overlap of C=O stretching of acids and ketones. A partial neutralization of the carboxylic groups is quite improbable in our conditions.

The FTIR spectra of oxidized samples immersed in D₂O (with sodium dodecylsulfate used as surfactant) showed that the absorbance of the broad bands at 3813, 3435 and 3370 cm^{-1} slightly decreased. The yields of this method remained, however, unsufficient to confirm the assignment of hydroxyl and carbonyl species in the oxidized HDPE.

A comparative analysis was performed with LLDPE-treated films using processes I and II as presented in Figure 7. The band centered at 1715 cm^{-1} is narrower than in HDPE films oxidized with the same process. In addition, shoulders near 1741, 1722 and 1699 cm^{-1} were observed. A parallel development in the hydroxyl stretching range (Fig. 7(b)) showed that in comparison between treated and native LLDPE, no important changes occurred.

For LLDPE films treated with process I (Figs. 7(a) and 7(b)), a broad band with a maximum at 1715 cm^{-1} was obtained in the 1780–1660 cm^{-1} range, with two weak shoulders at 1699 and 1740 cm^{-1}. In the hydroxyl region (3800–3100) cm^{-1}, bands similar to those observed on HDPE treated with process II can
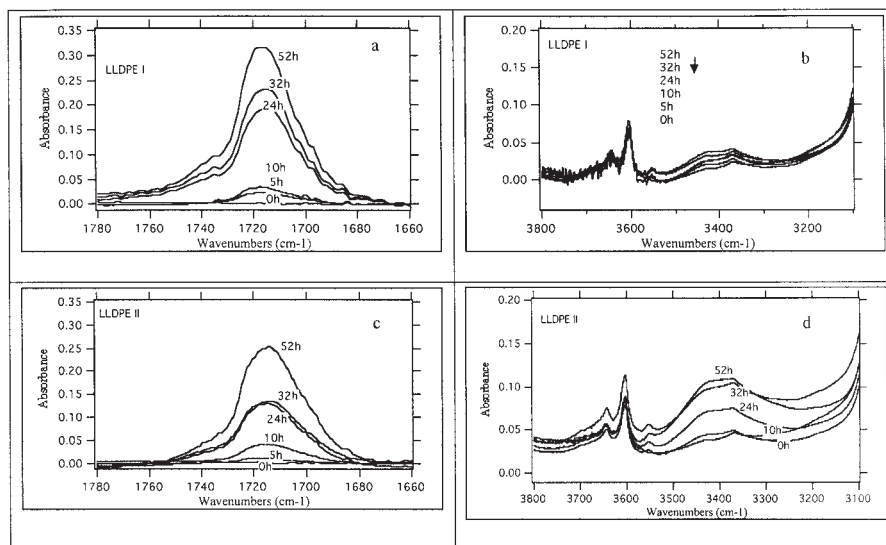

Figure 7 FTIR spectra of oxidized LLDPE (a, b) with process I and (c, d) with process II.
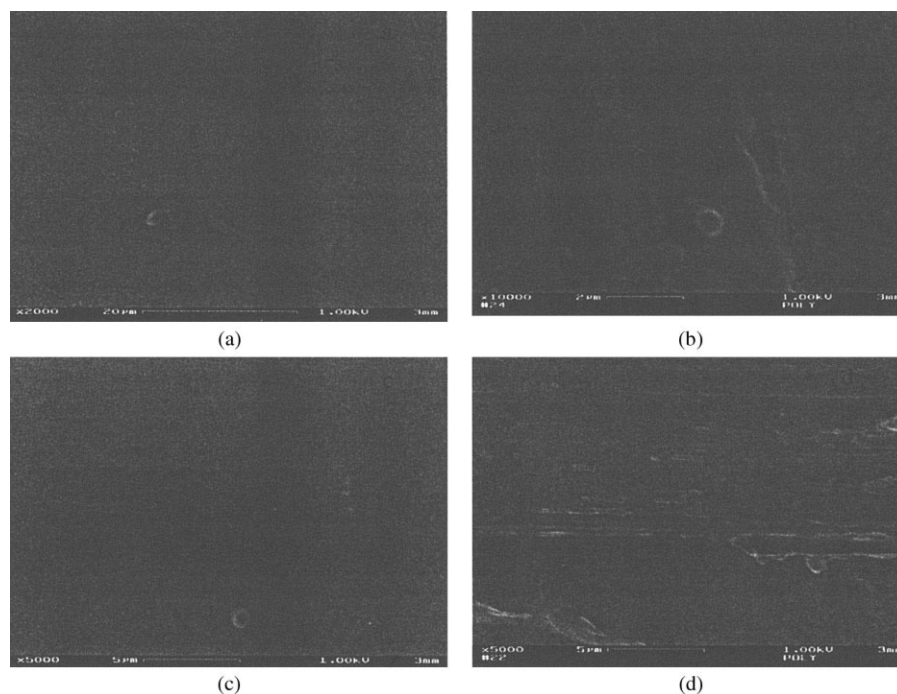
Figure 8 SEM images of (a) untreated HDPE film, (b) HDPE film treated for 24 h by process I, (c) untreated LLDPE film, and (d) LLDPE film treated for 24 h by process I.

be observed in Figures 7(c) and 7(d) for LLDPE treated by process II. As a result, it can be concluded that similar species (acids, esters and ketones) were created on both LLDPE and HDPE-oxidized surfaces.

SEM

The analysis of oxidized LLDPE and HDPE samples by scanning electron microscopy showed no differences between native and oxidized films treated with process I with increasing reaction time. The treated surfaces appeared smooth without visible deterioration (Fig. 8). In contrast with process I, a new morphology was obtained onto surfaces of HDPE and LLDPE oxidized by process II, as illustrated in Figure 9.

After 24 h (Fig. 9(a)), the morphology of HDPE revealed clearly a spherulitic macrostructure. An etching process, due to a selective degradation of the amorphous phase between lamellae, could explain this surface modification. After 32 h of reaction time (Fig. 9(b)), an heterogeneous surface was observed and cracks appeared. These cracks could be assigned to an intense etching of the amorphous phase between spherulites.

Molecular mass of oxidized films was analyzed by SEC and showed a decrease of M_w after 24 h of reaction time. As an example, M_w decreased from 76,000 to 30,000 and 28,000 for HDPE and M_w fell from 56,000 to 30,000 and 22,000 for LLDPE treated by processes I and II, respectively. This indicates that chain scissions

occur during oxidation processes. It may also occur that the oxidative treatment of high-density polyethylene leads to significant formation of low-molecular weight products (chains), which can migrate out of the polymeric sample. Figure 9(c) showed oxidized LLDPE films, using process II after 24 h of reaction time. The oxidized surface exhibited more significant cracks after 32 h (Fig. 9(d)). The results obtained by SEM analysis illustrate that oxidation with process II induced distinct morphologies on LLDPE and HDPE, respectively.

It is important to notice here that after 52 h of treatment (process II), the mechanical properties of the oxidized films of HDPE and LLDPE were severely deteriorated (results not shown).

Wetting dynamics

The Wilhelmy plate method study (Fig. 10) showed that for HDPE films oxidized by process II (successive addition of oxidative solution), important changes of the contact angle are observed when the reaction time increases.

For native HDPE (Fig. 10(a)), upon the first immersion, $\cos\Theta$ was close to -0.2 and during the first emersion, $\cos\Theta$ was close to 0.2 forming a hysteresis loop. This behavior does not change during the second, third, and fourth cycles, witnessing that there is no change of wettability.
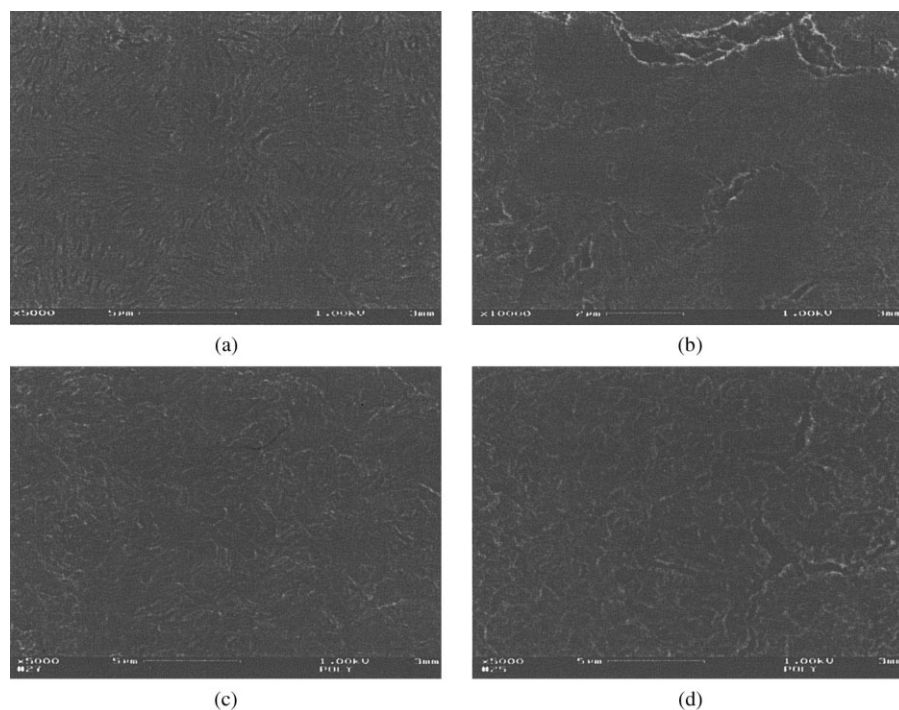
Figure 9 SEM images of (a) HDPE film after 24 h, (b) HDPE after 32 h, (c) LLDPE after 24 h, and (d) LLDPE film after 32 h, by process II.

After 10 h (Fig. 10(b)) of reaction time, the shape of the hysteresis became wider, where $\cos\Theta_{adv} = 0$ and $\cos\Theta_{rec} = 1$. The decrease of Θ_{rec} is an indication of an increase of hydrophilicity by immersion. From 24 h of reaction time, the wetting behavior of HDPE changed with the reaction time. Figure 10(c) showed that
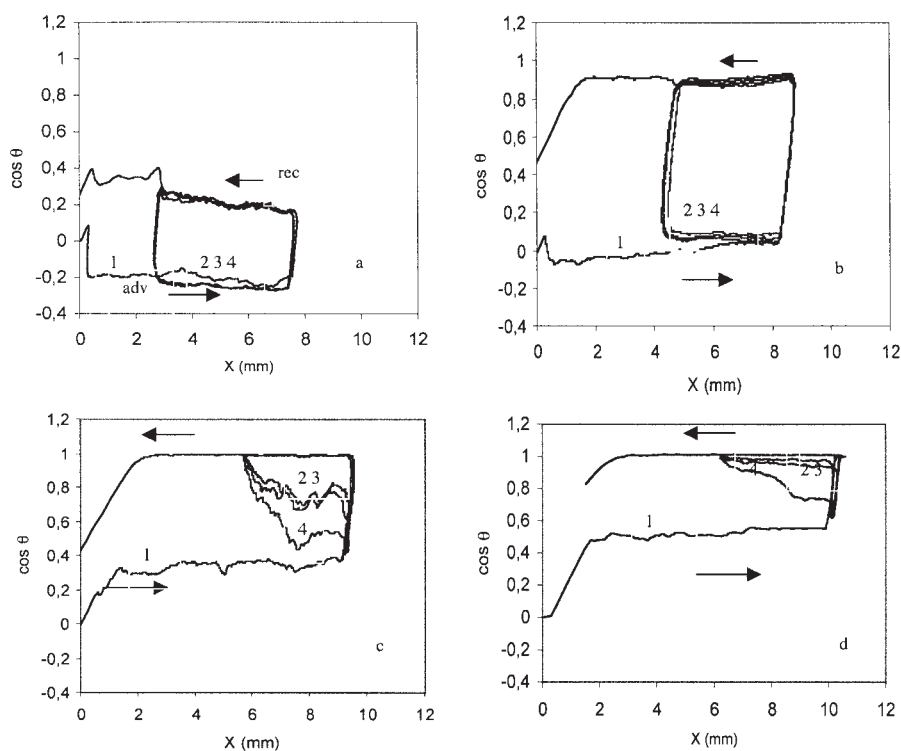

Figure 10 Plot of $\cos\Theta$ versus X during repeated cycles for HDPE-oxidized films by process II after (a) 0 h, (b) 10 h, (c) 24 h, and (d) 32 h of reaction time.
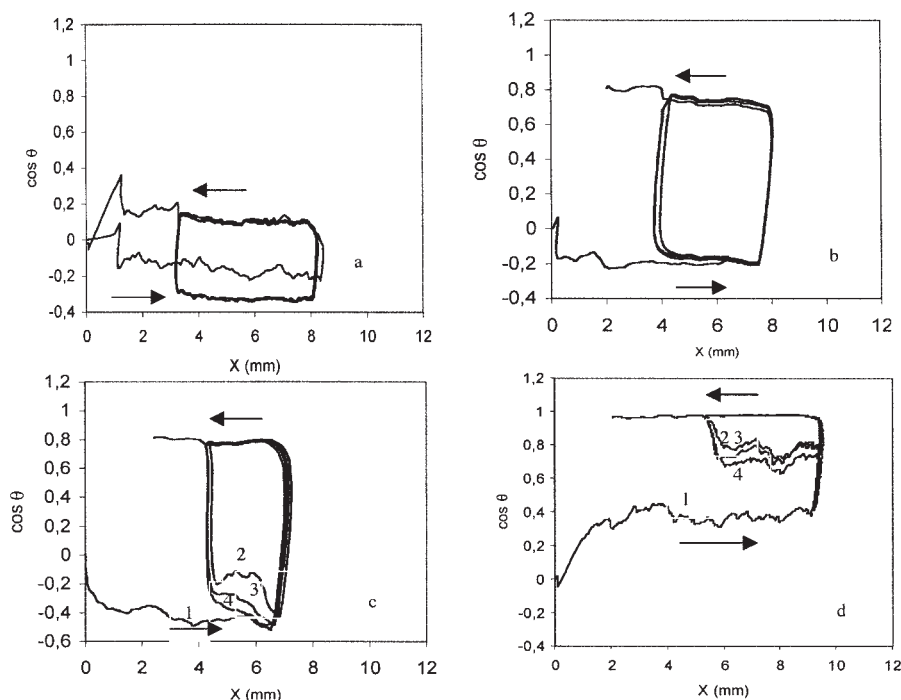
Figure 11 Plot of cosΘ versus X during repeated cycles for and LLDPE-oxidized films by process II after (a) 0 h, (b) 10 h, (c) 24 h, and (d) 32 h of reaction time.

$\cos\Theta_{adv1}$ recorded during the first immersion was equal 0.3 and $\cos\Theta_{rec1} = 1$. When a second cycle was performed without dwell (cycle 2), the contact angle in second advance Θ_{adv2} strongly decreased ($\cos\Theta_{adv2} = 0.8$ and $\cos\Theta_{rec2} = 1$). When the emerged sample was subject to a pause of 5 min in air before being immersed again (cycles 3), $\cos\Theta_{adv3}$ was equal to 0.8. It remained close to the value obtained during the second advance (Θ_{adv2}).

When the emerged sample was subject to a dwell of 20 min in air (cycle4), $\Theta_{adv4.}$ slightly increased ($\cos\Theta_{adv4} = 0.6$) and $\cos\Theta_{rec4}$ remained constant and equal to $\cos\Theta_{rec3}$, $\cos\Theta_{rec2,}$ and $\cos\Theta_{rec1}$.

A treatment during 32 h (Fig. 10(d)) was also performed. The wetting behavior of oxidized HDPE was strongly changed upon repeating cycles, and was affected by pauses between cycles in advancing. While Θ_{rec} was always equal to zero ($\cos\Theta_{rec} = 1$), $\cos\Theta_{adv}$ recorded during the first immersion was equal to 0.5. For the subsequent cycles (2 and 3), $\cos\Theta_{adv2}$ and $\cos\Theta_{adv3}$ were similar and equal to 0.9. For the last cycle,[4] $\cos\Theta_{adv4}$ varied as a function of sample position, and the slope was influenced by the duration of the dwell, following the previous emersion with a minimum value of $\cos\Theta_{adv4}$ at 0.7. However $\cos\Theta_{rec}$ remains equal to 1.

For LLDPE, the variation of cosΘ during repeated immersion–emersion cycles, measured with the Wilhelmy plate method, was significantly different from HDPE behavior (Fig. 11). The shrinkage of the hys-

thresis loop was not obtained before 32 h of treatment.

For native LLDPE (Fig. 11(a)), the shape of the hysteresis loop remained constant upon repeated cycles, Θ_{adv} and Θ_{rec} were not affected ($\cos\Theta_{adv1} = -0.3$ and $\cos\Theta_{rec1} = 0.2$). After 10 h (Fig. 11(b)) of reaction time, the shape of the hysteresis was slightly affected, $\cos\Theta_{adv} = -0.2$ and $\cos\Theta_{rec} = 0.8$. The decrease of Θ_{rec} is an indication of an increase of hydrophilicity with immersion. As shown in Figure 11(c), after 24 h of reaction time, the wetting behavior of LLDPE slightly changed with the reaction time. $\cos\Theta_{adv1}$ recorded during the first immersion was equal -0.3 and $\cos\Theta_{rec1} = 0.8$. When a second cycle was performed without dwell (cycle 2), the contact angle in second advance Θ_{adv2} decreased ($\cos\Theta_{adv2} = -0.1$ and $\cos\Theta_{rec2} = 0.8$). When the emerged sample was subject to a pause of 5 or 20 min in air before being immersed again (cycles 3 and 4), $\cos\Theta_{adv}$ was equal to -0.2 and $\cos\Theta_{rec} = 0.8$.

The wetting behavior of LLDPE-treated films (Fig. 12(d)) was also dependent on reaction time and it was affected by repeating cycles and dwells especially for a long reaction time of 32 h: $\cos\Theta_{adv1}$ recorded during the first immersion is equal to 0.4 and $\cos\Theta_{rec} = 1$. For the subsequent cycles (2, 3 and 4), $\cos\Theta_{adv}$ remained equal to 0.8 and $\cos\Theta_{rec} = 1$.

Surface energy parameter

Pretreatment of a nonpolar polymer such as polyethylene or polypropylene with flame or corona creates

functional polymer groups that can enter into hydrogen bonding as either donor or acceptor groups. If no pretreatment is employed, the surface behavior of a nonpolar polymer is characterized by a dispersive term (Y_s^d), the Lifshitz-Vanderwaals component[49] After pretreatment, an additional parameter is required, Y_s^p, which characterizes the polar component of the surface energy.[50,51] The total surface energy of a substance (Y_s) is related to these parameters by eq. (2).

$$Y_s = Y_s^d + Y_s^p \qquad (2)$$

The measurement of contact angle Θ is the best available method for determining the parameters Y_s^d and Y_s^p of a solid. They are linked by eq. (3).

$$1 + cos\ \Theta = 2((Y_s^d Y_1^d)^{0.5} + (Y_s^p\ Y_1^p)^{0.5})/Y_{1v} \qquad (3)$$

To solve eq. (3), two independent measurements have to be performed using two different liquids. In this work, MilliQ water and diiodomethane were used. Y_l^d, Y_l^p are dispersive and polar surface energy components of the liquid respectively. Y_{1v} is the total surface energy of the liquid. The polar surface energy component (Y_s^p), as determined for unmodified and oxidized films, are obtained using eq. (3). The traces of normalized Y_s^p for HDPE and LLDPE films were shown in Figure 12.

Y_s^p of LLDPE surfaces treated with both processes seems to be constant despite increasing reaction time. However, Y_s^p of HDPE oxidized by process II are more important than those obtained by process I. In addition, with a same process, Y_s^p on HDPE is higher than on LLDPE.

Nuclear magnetic resonance (NMR)

The analysis of oxidized HDPE and LLDPE films by nuclear magnetic resonance at 135°C was tentatively carried out in solution of deuterated tetrachloroeth-
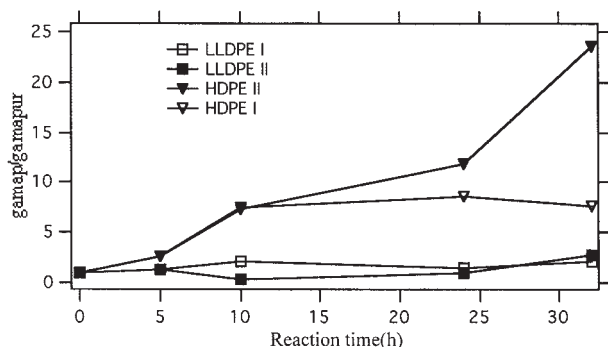

Figure 12 Evolution of normalized gama polar as a function of reaction time using processes I and II for HDPE and LLDPE-treated films.
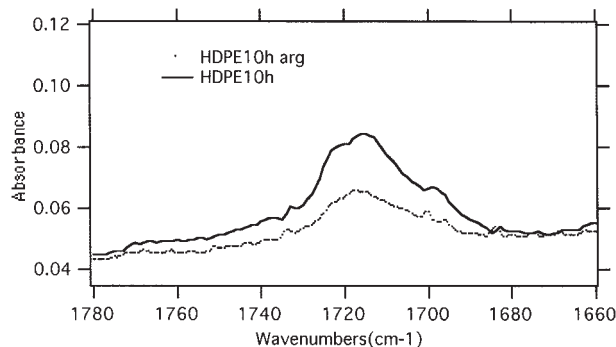

Figure 13 FTIR spectra of HDPE and HDPE oxidized for 10 h with oxygen and (−) in argon in 1780–1660 cm^{-1} region.

ane. Only ^{1}H NMR gave visible results. A weak signal appeared at 4 ppm, which can be assigned to a chlorinated chain (—CH—Cl) and/or to an ester (R—CO—O—CH$_2$—R) group (figure not shown). Carboxylic (—CH$_2$—COOH) and ketone (CH$_2$—CO—CH$_2$—) functions whose signals appeared at 2.18 ppm largely prevailed over aldehyde (—CHO) whose signal appears at 9.7 ppm.

These results confirm the XPS and FTIR observations that the main species created on oxidized polyethylene using sodium hypochlorite are ketones, esters, and acids.

DISCUSSION

All the results clearly underlined the occurrence of oxidation on LLDPE and HDPE film surfaces in both processes (I and II), using sodium hypochlorite as the oxidant.

In fact, quantitative XPS and FTIR analyses showed that carbon atoms became simply (C—O) or doubly (C=O) linked with oxygen and that new functionalities appeared as ketones and carboxylic acid and esters on the oxidized surfaces. The hypochlorite treatment can thus be explained only by oxidation by "active oxygen". No conclusive results were obtained to support significant chlorination.
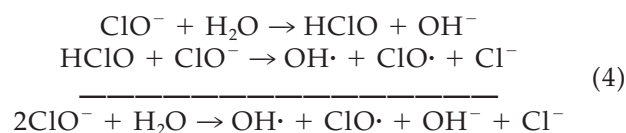
To determine the role of oxygen gas in the oxidation mechanism, a film of HDPE was oxidized during 10 h by process I under argon flux, and the results were compared with a sample oxidized in air by the same process. A very significant decrease of the intensity of carbonyl groups in the 1780–1660 cm^{-1} region was clearly observed (Fig. 13) by FTIR spectroscopy.

A great amount of salts was formed during the oxidation process and did not allow a complete argon feeding during the last hours of treatment. Actually, the argon flux couldn't be maintained more than 7 h in the reactor. Consequently, the low intensity of car-

bonyl band may be due to traces of oxygen present in the reactor. Similar results were obtained with LLDPE.

As shown by FTIR and XPS studies, the amount of new functionalies was always more important into oxidized HDPE than LLDPE films by both processes. It is proposed that the larger concentration of antioxidant present in LLDPE may explain this behavior. In this way, a comparison was made between FTIR spectra of a film of HDPE oxidized during 10 h and a second film in which 0.2% of Irganox 1010 ® was added before molding and oxidation. The FTIR spectra in the 1780–1660 cm^{-1} region showed that the peak centered at 1715 cm^{-1} did not appear in the second spectrum (a peak at 1745 cm^{-1} in the second spectrum was assigned to Irganox 1010®). In addition, the analysis of antioxidant concentration for native HDPE and LLDPE films showed indeed that HDPE contains less than 0.001%, whereas LLDPE contains 0.012% of antioxidant.

Thus, both previous results suggest that air could be the main oxidizing agent in these hypochlorite oxidation processes. To clarify the role of hypochlorite, a treatment of HDPE and LLDPE films was performed in the same conditions of pH (pH = 12) and temperature (80°C) in the absence of sodium hypochlorite. No oxidation occurred on the treated surfaces. This result emphasizes the role of hypochlorite in the initiation step (classical radical mechanism) of oxidation. Indeed, Singh[52] has reported that ClO$^-$ ions give hypochlorite radical (ClO·) and hydroxyl radical (OH·) under similar conditions of temperature and pH following eq. (4).

$$ClO^- + H_2O \rightarrow HClO + OH^-$$
$$HClO + ClO^- \rightarrow OH\cdot + ClO\cdot + Cl^-$$
$$\overline{}$$
$$2ClO^- + H_2O \rightarrow OH\cdot + ClO\cdot + OH^- + Cl^-$$

$$(4)$$

A treatment of HDPE and LLDPE films by a generator of hydroxyl radicals ($Na_2S_2O_8$ in aqueous solution) showed, by different surface analyses, that no changes have occurred. This underlines the major role played by ClO· in our oxidation processes.

At this stage, it was reasonable to propose the hypothesis of an initiation of the oxidation mechanism by abstraction of a (tertiary) hydrogen atom by the hypochlorite radical only as shown by eq. (5) Molecular oxygen reacts afterwards with the polymer radical (P·) following a classical air oxidation mechanism.[43]

$$PH + ClO\cdot \rightarrow P\cdot + HClO$$
$$P\cdot + O_2 \rightarrow PO_2\cdot \text{ (unstable)}$$

$$(5)$$
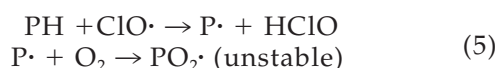
The decrease of contact angles measured by static or dynamic methods for both HDPE and LLDPE films indicated that a reaction has occurred at the surface and that new functions have been created following a kinetics on HDPE, which is different from LLDPE. The HDPE-treated film became more rapidly hydrophilic than the LLDPE film using both processes, probably because of a difference in antioxidant concentration. The results obtained by the sessile drop technique were slightly different from those obtained by dynamic measurements. This behavior may be explained by the heterogeneity of the treated surfaces, clearly visible by SEM.

The study of hydrophilicity by wetting dynamics method showed a decrease of cosΘ$_{adv}$. Moreover, cosΘ$_{adv}$ varied with X in the hysteresis loop with increasing pause duration for HDPE and LLDPE. This behavior may not be attributed to a dissolution of oxidized fragments[53] as reported in the case of oxidized PS by plasma. In fact, the surface energy of water in which HDPE and LLDPE films have been immersed was analyzed by Noui method[28] before and after contact angle measurements. The obtained value remained equal to 70 mN/m. Accordingly, the created species remained attached to the HDPE and LLDPE surface films; no release of any species was observed. The decrease of cosΘ$_{adv}$ as a function of X may thus be attributed to evaporation of the water film retained at the oxidized surface during immersion and the concomitant compaction of the macromolecules and/or reorientation of functionalized fragments toward the bulk. As reported by Schronerr and Julius Vansco,[54] the new functionalities created at the treated surface become somewhat buried in certain regions of the interface that can't be probed by contact angle measurement.

This interpretation is in agreement with the effect of pause duration on the hysteresis loop and in particular with the very low appearance of hysteresis in case where a short or no pause was performed between immersion–emersion (cycles 2 and 3 respectively, in Fig. 10(d)) obtained with long reaction time. This behavior is well illustrated (Fig. 10(d)) with a film of HDPE oxidized during 32 h, which already showed O/C atomic ratio of 5.88 determined by XPS (Table II). The reorganization of the sample surface in contact with the polar medium (water) tends to bring the functionalized polymer chains at the surface and to increase the surface hydrophilicity.

The decreasing of Θ$_{adv}$ as a function of the reaction time could then be assigned to solvating of the solid surface and/or reorientation of functionalized segments. Even after a pause of 20 min, water remains retained at the surface.

For HDPE and LLDPE, an important decrease in receding contact angle (Θ$_{rec}$) was also observed, indicating an increase of hydrophilicity. The hydrophilicity seems to be more important for HDPE than for LLDPE showing that the amount of water retained on the treated HDPE films is higher.

CONCLUSIONS

Two convenient and economical surface treatments (processes I and II) of high-density-polyethylene and of linear-low-density-polyethylene by wet chemistry have been proposed for improving the polymer hydrophilicity. Treatments with sodium hypochlorite solution at 80°C and pH = 12 under air atmosphere led to surface oxidation as ascertained by the usual surface analyses (XPS, FTIR, static, and dynamic wetting measurements). The XPS analysis showed that the amount of oxygen introduced on oxidized surfaces increases with increasing reaction time, and a decomposition of C_{1s} and O_{1s} peaks showed that carbon may be linked to oxygen by simple or double bond, leading to the formation of different functions (carboxylic acids, ketones, and esters). In addition, traces of chlorine have been measured on treated surfaces.

The water contact angles and gamma polar measured by static and dynamics wetting revealed that the hydrophilicity of HDPE and LLDPE treated by process II is more important compared with that obtained by process I. The morphology of oxidized films was characterized by scanning electron microscopy. SEM images showed that there is no main change during process I. In contrast, chain scission was observed by SEC on both HDPE and LLDPE. They are accompanied by an etching on HDPE films and cracks on LLDPE films when they are treated by process II.

All the analyses showed that LLDPE exhibits weak reactivity compared with HDPE for both processes. This behavior has been attributed to an antioxidant concentration effect.

A plausible mechanism is proposed with chain reaction initiated by hypochlorite radical and followed by a classical air-oxidation by molecular oxygen.

It has been checked that the surface hydrophilicity values remained the same for samples analyzed immediately after treatment and 20 days after treatment.

To our knowledge, this mechanism has no precedent, as all the previously reported surface oxidation reactions of polyethylene by wet chemistry made use strong inorganic acids as oxidants.[54–63]

References

1. Tomasetti, E.; Daoust, D.; Legras, R.; Bertrand, P.; Rouxhet, P. G. J Adhes Sci Technol 2001, 15, 1589.
2. Gilbert, C.; Carlsson, D. J.; Kenth, M.; Johansson, S. Surf Interface Anal 1993, 20, 441.
3. Yang, P.; Deng, J. Y.; Yang, W. T. Polymer 2003, 44, 7157.
4. Shadpour, M. E.; Hajipour, A. R.; Mahdavian, A. R.; Zadhoush, A.; Ali-Hosseini, F. A. Eur Polym J 2001, 37, 1199.
5. Brewis, D. M. Prog Rubber Plastic Technol 1985, 1, 1.
6. Feast, W. J.; Munro, H. S., Eds.; Polymer Surfaces; Wiley: Chichester, 1987.
7. Baszkin, A.; Deym, M.; Nishino, M.; Ter-Minassian- Saraga, L. Prog Colloid Polym Sci 1976, 61, 97.
8. Holmes-Farley, S. R.; Reamy, R. H.; Nuzzo, R.; McCarthy, T. J.; Whitesides, G. M. Langmuir 1987, 3, 799.
9. Olsen, D. A.; Osteraas, A. J. J Polym Sci Part A: Polym Chem 1913 1969, 7.
10. Fonseca, C.; Perena, J. M.; Fatou, J. G.; Bello, A. J Mater Sci 1985, 20, 3283.
11. Melby, L. R. Macromolecules 1978, 11, 50.
12. Klausner, M.; Loh, I. H.; Baddour, R. F.; Cohen, R. E. Polym Mater Sci Eng 1987, 56, 227–231.
13. Strobel, M.; Corn, S.; Lyons, C. S.; Korba, G. A. J Polym Sci Part A: Polym Chem 1987, 25, 1295.
14. Ogita, T.; Ponomarev, A. N.; Nishimoto, S.; Kagiya, T. J. Macromol Sci Chem 1985, A22, 1135.
15. Ferguson, G. S.; Whitesides, G. M. In Modern Approaches to Wettability. Stirred, M. E.; Lobe, G. I. Eds Plenum New York 1992, p. 143, and references therein.
16. Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. J Am Chem Soc 1977, 99, 4736.
17. Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. J Am Chem Soc 1977, 99, 4746.
18. Hill, C. L., Ed.; Activation and Functionalization of Alkanes; Wiley: NewYork, 1989.
19. Barton, D. H. R.; Csuhai, E.; Doller, D.; Balavoine, G. J Chem Soc Chem Comm 1990, 24, 1787.
20. Guillet, C. J., Ed; Polymers and Ecological Problems; Plenum: New York, 1973.
21. Amin, G. C.; Wadekar, S. D. Ind J Tex Res 1977, 3, 20.
22. Wilson, I.; Kelly, H. C. Inorg Chem 1982, 21, 1622.
23. Shenai, V. A.; Sharma, K. K. J Appl Polym Sci 1976, 20, 377.
24. Biebuyck, J. J.; Daoust, D.; Devaux, J.; Rahier, G. J. Eur. Pat. 00870258 (2000).
25. Scheinert, W. Angew Makromol Chem 1977, 63, 117.
26. Wilhelmy, L. Ann Phys 1863, 119, 177.
27. Tomasetti, E.; Rouxhet, P. G.; Legras, R. Langmuir 1998, 14, 3435.
28. Noüi, L. D. P. J Gen Physiol 1919, 1, 521.
29. Maddams, V. F. Appl Spectros 1980, 34, 245.
30. Randall, J. C. Polymer Sequence Determination-Carbon-13 NMR Method; Academic Press: New York, 1977.
31. Liu, W.; Ray, D. G., III; Rinaldi, P. L. J Magn Reson 1999, 140, 482.
32. Dengris, P. B.; Gerin, P. A.; Rouxhet, P. G. Colloid Surf B 1995, 4, 199.
33. Shirly, D. A. Phys Rev B 1972, 5, 4709.
34. Murakami, T.; Kuroda, S.; Osawa, Z. J Colloid Interface Sci 1998, 200, 192.
35. Paynter, R. W. Surf Interface Anal 1999, 27, 103.
36. Beamson, G.; Briggs, D. High-Resolution XPS of Organic Polymers, The Scienta ESCA 300 Database; John Wiley and Sons: Chichester, 1992.
37. Dewez, J. L.; Doren, A. Y.; Scheneider, J.; Rouxhet, P. G. Biomaterials 1995, 20, 547.
38. Gerin, P. A.; Dengis, P. B.; Rouxhet, P. G. J Chem Phys 1995, 92, 1043.
39. Handbook of Vibrational Spectroscopy; Chalmers, J. M.; Griffith, P. R., Eds.; Wiley: Chichester, 2002; Vol. 4, p 2514.
40. Severini, F.; Landro, L. D.; Galfetti, L.; Meda, L.; Ricca, G.; Zenere, G. Macromol Symp 2002, 181, 225.
41. Singh, R. P.; Mani, R.; Sivaram, S.; Lacoste, J.; Vaillant, D. J Appl Polym Sci 1993, 50, 1871.
42. Ioannis, G.; Economou, Y.; Cui, F.; Donohue, M. D. Macromolecules 1997, 24, 5058.
43. Lemaire, J.; Gardette, J. L.; Lacoste, J.; Delprat, P.; Vaillant, D. J Am Chem Soc 1996, 35, 577.
44. Carlsson, D. J.; Wiles, D. M. Macromolecules 1969, 2, 587.

45. Domke, W. D.; Steinke, H. J Polym Sci Part A: Polym Chem 1986, 24, 2701.
46. Coleman, M. M.; Graft, J. F.; Painter, P. C. Specific Interaction and the Miscibility of Polymer Blends; Technomic: Lanaster, PA, 1991.
47. Carlsson, D. J.; Dobbinj, C. J. R.; Jensen, P. T.; Wiles, D. M. In Polymer Stabilization and Degradation; Klemchuk, P. P., Ed., ACS Symposium Series 280; American chemical Society: Washington, DC, 1985; p 359.
48. Carlsson, D. J.; Rousseau, R.; Zhang, C.; Wiles, D. M. ACS Symp Sci 1988, 364, 376.
49. Good, R. J. J Adhesion Sci Technol 1992, 6, 1269.
50. Good, R. J. J Colloid Interface Sci 1975, 52, 308.
51. Good, R. J.; Chaudhury, M. K.; Van Oss, C. J. in Fundamentals of Adhesion; Lee, L. H., Ed; Plenum Press: New York, 1991; Chapter 4.
52. Singh, O. P. Textile Dyer Printer 1982, 17, 35.
53. Dupont-Gillain, C. C.; Adriaensen, Y.; Derclaye, S.; Rouxhet, P. G. Langmuir 2000, 16, 8194.
54. Schronerr, H.; Julius Vansco, G. J Polym Sci Part B: Polym Phys 1998, 36, 2483.
55. Bergbreiter, E. D.; White, N.; Zhou, J. J Polym Sci Part A: Polym Chem 1992, 30, 389.
56. Fonseca, C.; Perena, J. M.; Fatou, J. G.; Bellov, A. J Mater Sci 1985, 20, 3283.
57. Ogata, Y.; Kumura, M.; Kondo, A. Y. Bull Chem Soc Jpn 2057 1981, 54.
58. Louni, Z. A.; Seux, R. Wat Res 1987, 21, 335.
59. Shenai, V. A.; Gotmare, V. D. Textile Dyer and Printer 1988, 2, 17.
60. Shenai, V. A.; Naik, V. G. Textile Dyer and Printer 1986, 30, 17.
61. Shenai, V. A.; Narkhede, A. S. Textile Dyer and Printer 1987, 20, 17.
62. Van Oss, C. J.; Giese, R. F. R.; Li, J. Z.; Morris, J.; Chaudhury, M. K.; Good, R. J. J Adhesion Sci Technol 1992, 6, 413.
63. Hambardzumyan, A.; Biltresse, S.; Dufrêne, Y.; Marchand-Brynaert, J. J Coll Inter Sci 2002, 252, 443.