

# Surface Changes of Corona-Discharge-Treated Polyethylene Films

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**ABSTRACT:** Morphological and chemical changes of the surface of low-density polyethylene (LDPE), linear middle-density polyethylene (L-MDPE), and their 80/20 blend were studied by different techniques after corona-discharge treatment in air and subsequent annealing. The surface tension was determined by wetting; the roughness was measured by atomic force microscope (AFM), and the surface chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS), whereas the low-molecular-mass fraction washed off by chloroform by FTIR. The surface tension of the films increases with the electrode current. The surface roughness depends primarily on the polymer type and is less affected by the corona treatment. At the initial stage of annealing, posttreatment-type oxidation and hydrophobic recovery are competing. The former is more pronounced in L-MDPE, the latter in LDPE. After annealing at 50°C for 160 days, hydrophobic recovery becomes predominant in each film studied, which is accompanied by significant smoothening of the surface. According to XPS and FTIR results, this is due to the migration of low-molecular-mass components (oligomers, oxidized polymer fractions, and additives) to the surface. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1529–1541, 2000

**Key words:** polyethylene; corona-discharge treatment; annealing; surface tension; AFM; XPS

## INTRODUCTION

Polyethylene (PE) is one of the most widely used packaging materials due to its suitable properties (e.g., nontoxic, easily processible, reprocessable, cold-resistant, resistant to moisture, etc.). To in-

crease the printability of the products (like films or bottles), i.e., to increase the low-surface energy inherent in the nature of the base polymer, an additional processing step is required. Corona discharge in air is the most widely used online commercial treatment of PE films.<sup>1,2</sup> According to Briggs,<sup>2</sup> its main effect is the oxidation of the surface, during which ketone, aldehyde, carboxylic, and ester groups are formed together with OH, nitrate, and nitrite groups. Owens<sup>3</sup> attributed the resulting enhanced self-adhesion of surface-treated PE to the interfacial H-bonding between keto and enol tautomers of carbonyl

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groups. Briggs and Kendall<sup>4</sup> confirmed the role of enolic OH in the autoadhesive bonding. About 4% of the O/C atomic ratio (determined by XPS) was reported<sup>2</sup> as a requirement for excellent ink adhesion to LDPE, but only about 0.4% of the surface carbonyl atoms were estimated to be converted into potential enolic OH groups. Carley and Kitze<sup>5</sup> studied the corona-treated PE surface by reacting it with diphenyl picryl hydrazyl. They found a close correlation between the adhesion and wetting properties of the polymer film, and the concentration of fairly stable RO<sub>2</sub>R and RO<sub>3</sub>R peroxide structures formed by the treatment.

Kim and Goring<sup>6</sup> disclosed that the irregularities (bumps) formed on PE surface during corona-discharge treatment in the presence of oxygen can be removed by dipping the polymer into solvents, and the material removed contains a considerable amount of methylene group besides carbonyl groups, indicating that the chemical reactions involve oxidation and scission of the polymer as well. The low-molecular-mass degradation products can cause subsequent adhesion problems. Although these materials are dissolved by some ink systems, they can hinder lamination and heat sealing.<sup>7</sup> Blythe et al.<sup>8</sup> observed that heating air-discharge-treated LDPE films to 80°C for 3 min results in the loss of autoadhesion without the loss of oxygen functionalities determined by XPS.

The surface energy can decrease also at ambient temperature with increasing storage time, resulting in a loss of printability. The hydrophobic recovery, which is observed not only in PE, is explained by different mechanisms in the literature. One of the recoveries is the rearrangement within the modified layer by overturning the functional groups from the surface toward the bulk.<sup>1</sup> Das-Gupta<sup>9</sup> suggested a thermally driven diffusion process. Tóth et al.<sup>10</sup> proved that the recovery process observed, for instance, in silicone rubber treated by plasma in air is predominantly due to the migration of low molecular silicon oil components to the surface rather than to group reorientation. Surface blooming of some additives (particularly slip and antistatic agents) was suggested as another explanation.<sup>7</sup>

The aim of the present work was a comprehensive study of (a) the effect of air-corona-discharge treatment on the surface properties of PE films containing antioxidants and slip agent, and (b) the reason for loss in printability during annealing at ambient temperature and 50°C.

**Table I Processing Conditions of the Films Investigated**

Polymer	Temperature (°C)	Rotor Speed (rpm)	Film Speed (m/min)
LDPE	160–170	83	8
L-MDPE	200–210	82	14
LDPE/L-MDPE 80/20	180–190	84	10

## EXPERIMENTAL

### Materials and Sample Preparation

**Polymers.** Low-density polyethylene (LDPE; Tiplen FB 2223;  $\rho = 0.921 \text{ g/cm}^3$ ), ethylene-1-hexene copolymer [linear middle-density polyethylene (L-MDPE), Tiplen FS 340;  $\rho = 0.934 \text{ g/cm}^3$ ], and their blend of LDPE/L-MDPE 80/20 (hereinafter denoted as blend) produced by Tisza Chemical Work (TVK) were investigated.

**Additives.** Hindered phenol antioxidant and oleamide slip agent were added to LDPE, hindered phenol, and phosphite antioxidants, as well as Zn-stearate slip agent to L-MDPE.

Films of about 40- $\mu\text{m}$  thickness were processed by extrusion-blow molding under conditions given in Table I in two parallel lines. In one line, the surface of the film was treated by corona discharge excited in air.<sup>2</sup> The energy of discharge was controlled by changing the electrode current at the same film speeds; 2 and 4 A were applied to obtain 38 and 46 mN/m film surface tensions, respectively.

The films were annealed at ambient temperature (23–25°C) and at 50°C. Changes of the surface tension were studied as a function of annealing time. The structure of the surface layer was analyzed the next day after processing and after annealing at 50°C for 160 days.

## METHODS

The surface of the films was visualized by atomic force microscope (AFM) in noncontact mode<sup>11</sup> by using a Nanoscope III AFM (Digital Instruments). The applied scan ranges changed from 25 to 1000  $\mu\text{m}^2$  areas. The surface roughness was determined by calculating the root-mean-square of heights (rms).

The chemical structure of the films in the surface layer was investigated by X-ray photoelectron spectroscopy (XPS or ESCA)<sup>12,13</sup> by using a Kratos XSAM800 spectrometer with MgK $\alpha_{1,2}$  radiation. The X-ray gun was operated at 12 kV and 15 mA. The pressure in the sample analysis chamber was  $10^{-9}$  mbar. The spectra were recorded in fixed radiation ratio (FRR) mode. The spectrometer was calibrated against the Au $_{7/2}$  line fixed at 84.0 eV.<sup>14</sup> The linearity of the energy scale was checked by the dual Al/Mg electrode method by using the Ag3d $_{5/2}$  line.<sup>14</sup> The data acquisition and processing were performed by a Sun SPARC IPX workstation and the Kratos Vision 2000 data system. The overview spectra were taken between 50 and 1300 eV with energy steps of 0.5 eV. The detailed spectra of the lines of interest (C1s, O1s, Zn2p, N1s, P2p) were registered with energy steps of 0.1 eV. The C KLL, O KLL, and Zn LMM Auger peaks were recorded by using the Bremsstrahlung component of the exciting radiation, with an energy step of 0.2 eV. The spectra were referenced to the hydrocarbon-type C1s line (BE = 285 eV). For determining the chemical bonding of the carbon atoms, the C1s line was decomposed to four components with energies of 285 eV (C1: C—C and C—H), 286.5 eV (C2: C—OH and C—O—C), 287.9 eV (C3: C=O and O—C—O), and 289.2 eV (C4: carboxyls).<sup>15</sup> The sampling depth extends up to about 10 nm.<sup>16</sup> (Note that the calculated atomic concentrations are given with one tenth of atomic percentage precision in this work because of the importance of the changes of the atoms present only in low concentrations and for mathematical correctness).

Further investigations were carried out by dissolving the low-molecular-mass fraction from the surface by dipping a 5-g piece of film in 150 cm<sup>3</sup> chloroform at ambient temperature for 5 min. The amount of the dissolved material was determined gravimetrically after evaporation of the solvent. Although the thickness of the layer affected by the dissolution process must exceed that investigated by XPS, it is supposed that the penetration rate of chloroform in PE is not high enough to dissolve the low-molecular components from the whole cross section at ambient temperature in 5 min. We assume that mainly the exuded components are removed by this process.

The chemical composition of the fraction dissolved by chloroform was analyzed by FTIR spectroscopy after evaporation of the solvent by using a Mattson Galaxy 3020 FTIR spectrometer (Matt-

son Instruments, Inc.—Unicam Ltd.) with a FIRST Enhanced V1.52 software. The intensity of the absorption peaks at 1378 cm<sup>-1</sup> (methyl C—H deformation vibration), 1731 cm<sup>-1</sup> (ester C=O stretching vibration), 1660 cm<sup>-1</sup> (amide—I band), and 1082 cm<sup>-1</sup> (P—O—R vibration) were determined<sup>17</sup> and related to the absorption peaks at 1465 cm<sup>-1</sup> (CH<sub>2</sub> scissors vibration) or 721 cm<sup>-1</sup> (noncrystalline CH<sub>2</sub> rocking vibration) as internal standards.

The surface tension of the films was measured by a wetting technique according to ASTM D 2578–84 by using mixtures of formamide and cellosolve of different compositions.

## RESULTS AND DISCUSSION

### Effect of Surface Treatment

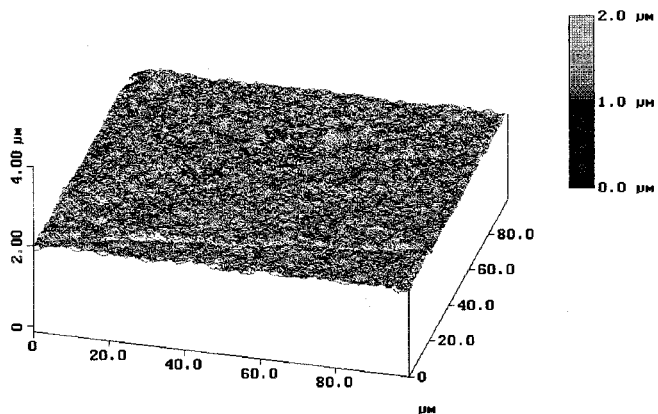
The AFM images of the untreated, as-processed films are compared in Figure 1. LDPE has a smooth surface, whereas the roughness of the L-MDPE film is quite remarkable. The blend of the two polymers has a heterogeneous surface morphology with roughness between those of the two components. The rms values depend on the area investigated (Table II) but the trend is similar at each level.

The effects of corona-discharge treatment on the surface characteristics of the PE films studied by AFM, XPS, and by determination of the surface tension are summarized in Table III. Although the surface tension increases with increasing electrode current, the roughness of the films remains practically the same. For illustration, the AFM images of L-MDPE films treated by different electrode currents are compared in Figure 2.

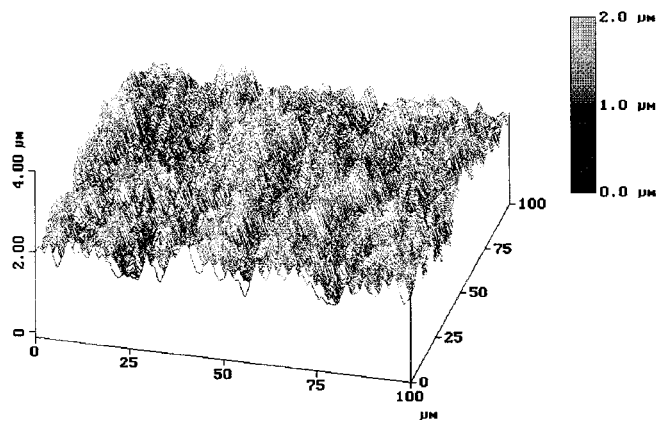
The XPS analyses revealed some surface oxidation even for the untreated PE films. This is attributed to the oxidation of the polymer melt passing from the extruder to the air during blow-molding. For comparison, the surface of additive-free L-MDPE powder was also investigated, and a very weak O1s line was found, being at about the detection limit.

The concentration of oxygen in the surface layer increases on corona-discharge treatment, and a higher current results in higher oxygen concentrations (Table III). Comparing the O contents of the samples with the same surface tension, the values for LDPE and the blend are similar, whereas it is lower in L-MDPE. The differ-

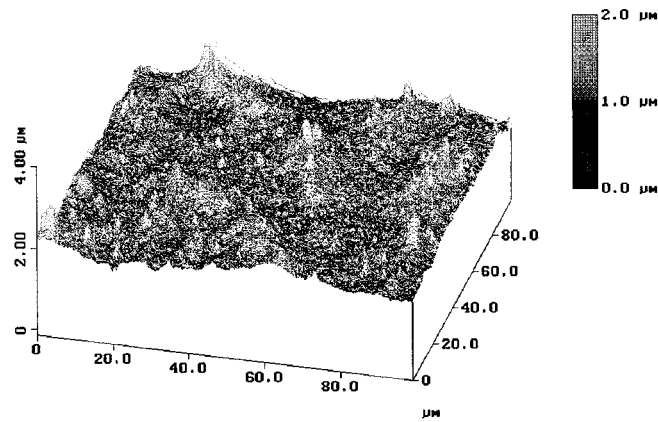
a)



b)



c)



**Figure 1** Effect of polymer type on the surface roughness of untreated films measured after processing. (a) LDPE; (b) L-MDPE; (c) LDPE/L-MDPE 80/20.

**Table II The Effect of Corona Discharge Treatment on the Surface Roughness of Films Determined by AFM After Processing**

Polymer	Electrode Current (A)	Rms ( $\mu\text{m}$ )		
		1000 $\mu\text{m}^2$	Surface Area 400 $\mu\text{m}^2$	25 $\mu\text{m}^2$
LDPE	—	62.7	42.4	13.1
	2	57.7	29.0	—
	4	92.3	39.3	15.5
L-MDPE	—	303.2	182.3	—
	2	293.7	178.7	—
	4	254.0	134.4	—
LDPE/L-MDPE 80/20	—	107.6	56.9	22.1
	2	130.9	40.8	19.3
	4	142.9	61.4	15.2

ences are smaller when the percentages of the C2 component of the C1s line (C—OH and C—O—C portions given in Table IV related to the total carbon) are compared, which suggests that the surface tension after processing may be in connection primarily with the OH group concentration. From the concentration of the carboxyl-type carbon atoms (C4 component of C1s line in Table IV related to the total carbon), it can be deduced that the degradation is more advanced in LDPE and in the blend than in L-MDPE. The difference can originate either from the higher film speed of L-MDPE during processing (Table I) or from the higher amorphous fraction of LDPE.

Nitrogen could not be detected in L-MDPE, indicating that N-containing functionalities incorporated from air remain under detection level. Therefore, it is accepted that the nitrogen mea-

sured on the surface of LDPE and blend films originates from the oleamide additive migrated to the surface during processing. Also, the higher O concentrations in these polymers can partly be attributed to the presence of the amide groups. This conclusion seems to be confirmed by the differences in the concentration of C3 (C=O and O—C—O) component of C1s line. Zn—stearate does not migrate to the surface in the processing step, as no line for Zn could be observed in the spectrum. These results are in agreement with the literature,<sup>18,19</sup> where a higher surface migration rate was reported for oleamide in PE than for the larger molecules (e.g., erucamide) and the saturated derivatives (e.g., stearamide).

The corona-discharge treatment promotes blooming of the phosphite antioxidant, because the surface layer of the untreated films does not contain

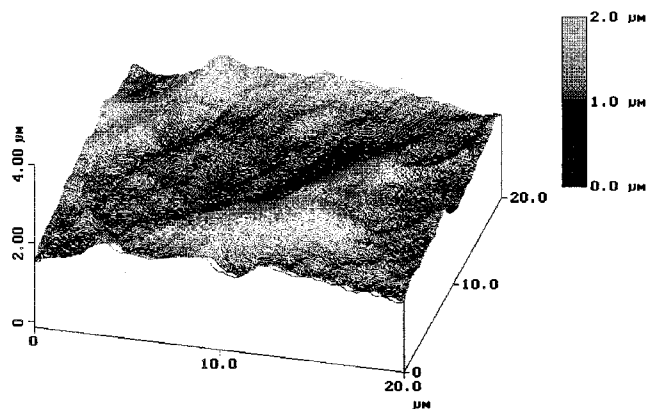
**Table III Surface Characteristics of the Films Determined After Processing**

Polymer	Electrode Current (A)	Tension (mN/m)	Roughness <sup>a</sup> ( $\mu\text{m}$ )	Composition by XPS (Atomic %)				
				C	O	Zn	N	P <sup>b</sup>
LDPE	—	—	42.4	97.3	2.3	0.	0.4	—
	2	38	29.0	88.3	10.8	0	0.9	—
	4	46	39.3	81.8	17.0	0	1.2	—
L-MDPE	—	—	182.3	99.4	0.6	0	0	—
	2	38	178.7	91.0	9.0	0	0	+
	4	46	134.4	86.8	13.2	0	0	—
LDPE-MDPE 80/20	—	—	56.9	98.6	1.4	0	0	—
	2	38	40.8	88.0	10.7	0	1.3	+
	4	46	61.4	80.6	18.7	0	0.7	+

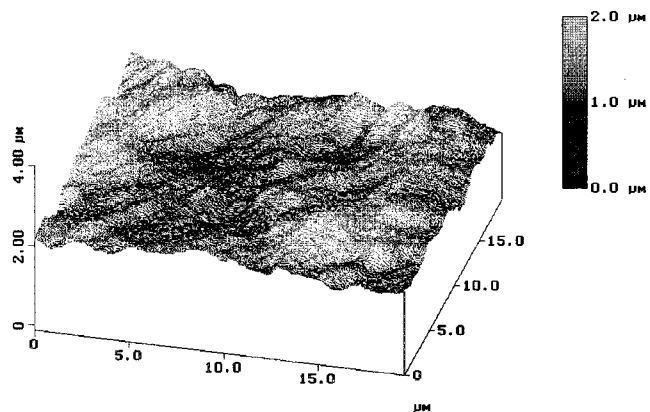
<sup>a</sup> 200–400  $\mu\text{m}^2$  area.

<sup>b</sup> P2p line: +, present (trace); —, absent.

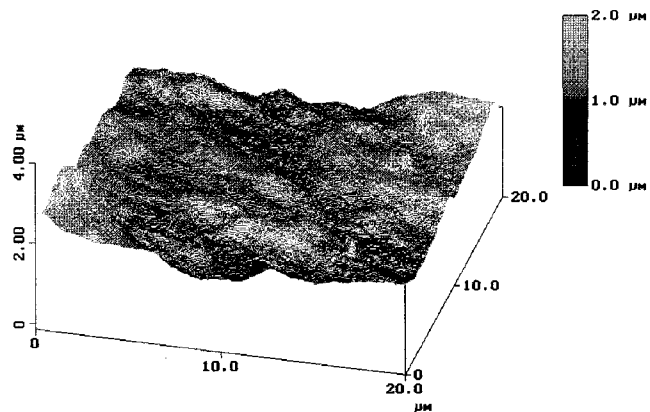
a)



b)



c)



**Figure 2** Effect of corona-discharge treatment on the surface roughness of L-MDPE films. (a) Untreated; (b) treated by 2 A; (c) treated by 4 A.



**Table IV** Decomposition of the C1s Peak Determined by XPS

Polymer	Electrode Current (A)	C1s Components (%)							
		After Processing				After Annealing at 50°C for 160 Days			
		C1 (C—C, C—H)	C2 (C—OH, C—O—C)	C3 (C=O, O—C—O)	C4 (carboxyl)	C1 (C—C, C—H)	C2 (C—OH, C—O—C)	C3 (C=O, O—C—O)	C4 (carboxyl)
LDPE	—	92.8	6.1	0.8	0.2	90.0	9.4	0.6	0.1
	2	83.5	12.1	3.1	1.3	73.7	21.2	4.0	1.1
	4	76.7	15.4	5.0	2.9	65.7	27.5	5.1	1.7
L-MDPE	—	94.1	5.6	0.3	0	88.4	9.7	0.1	1.8
	2	84.6	13.1	1.5	0.9	83.7	14.7	0.2	1.5
	4	80.3	14.9	2.7	2.1	83.0	15.2	0.3	1.5
LDPE/ L-MDPE	—	94.2	5.4	0.4	0.1	90.0	9.4	0.2	0.3
	2	81.6	14.3	2.3	1.8	81.4	15.6	1.4	1.6
	80/20	4.4	74.6	16.8	4.6	76.0	19.4	2.3	2.3

phosphorous, but it appears in the corona-treated films (L-MDPE and blend), although in small concentration (some tenth of atomic percentage). The behavior of the phenolic antioxidants cannot be determined by this method, as the products of corona discharge include a wide variety of oxidized groups (Table IV).

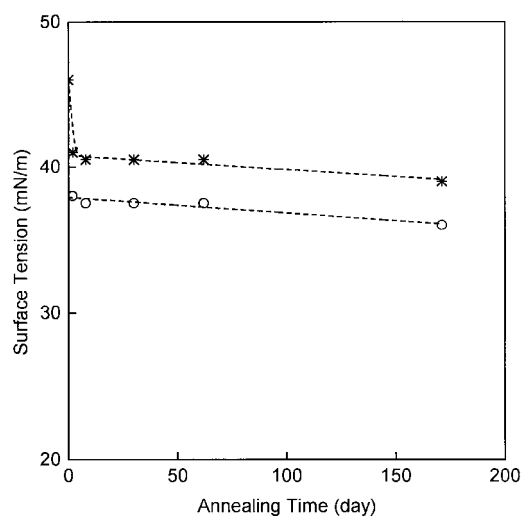
Summarizing the above results, we can conclude that the air-corona-discharge treatment results in surface oxidation and an increase in the surface energy of PE films. This is accompanied by surface segregation of the oleamide slip agent and the phosphite antioxidant. The roughness of the films is more affected by the type of the polymer than by the corona treatment.

### Effect of Annealing

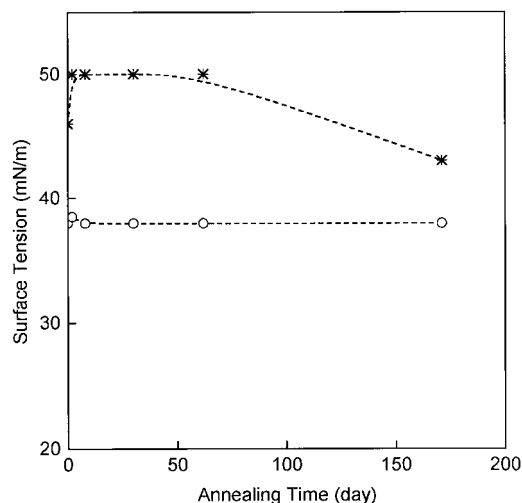
The surface tension ( $\gamma$ ) of the corona-treated films does not remain constant during annealing. The direction of changes depends on the polymer type and the temperature. At ambient temperature, the surface tension of LDPE (Fig. 3) and the blend films show an immediate decrease after treatment. The rate is the highest at the initial period of annealing, and the drop of  $\gamma$  is larger for the films treated by higher current. The behavior of L-MDPE differs from that, as the surface tension increases after processing and starts to decrease only in a later period of annealing (Fig. 4). The changes are really pronounced also in this case at higher initial  $\gamma$ . The trends of surface energy variations are similar at 24 and 50°C, but the rate is faster at the latter temperature (a decrease of  $\gamma$

can be observed already after 7 days in the case of L-MDPE treated by 4 A).

The changes of the surface tension indicate the occurrence of two parallel processes at the initial stage of annealing: postoxidation and hydrophobic recovery. The observed increase of the surface tension of L-MDPE can be attributed to postoxidation of the polymer. The physical processes resulting in hydrophobic recovery are slower and come into effect only at a later period of annealing. For LDPE and blend films, the recovery is the dominant process, which most probably obscures



**Figure 3** Changes of the surface tension of LDPE films as an effect of annealing at ambient temperature. Electrode currents of corona treatment: (○) 2 A; (\*) 4 A.



**Figure 4** Changes of the surface tension of L-MDPE films as an effect of annealing at ambient temperature. Electrode currents of corona treatment: (○) 2 A; (\*) 4 A.

the postoxidation. The rate of recovery increases at 50°C, compared to ambient temperature, resulting in a faster and more extensive decrease of the surface tension of each polymer ( $\gamma$  values measured after 160 days of annealing are given in Table V).

To determine the reasons of the hydrophobic recovery (loss of printability), the surface characteristics of the PE films annealed at 50°C for 160 days were analyzed in detail. The AFM measurements revealed that the recovery is accompanied by smoothening of the surface (cf. Tables III and V). For illustration, the AFM images taken before and after annealing are compared in Figure 5 for

LDPE treated by 4 A, and in Figure 6 for LDPE/L-MDPE blend treated by 2 A. The most significant decrease in surface roughness is observed for L-MDPE, although the rms values remain the highest for this polymer even after annealing.

The effect of annealing on the composition of the surface layer depends on the polymer type and the conditions of the corona treatment (cf. Tables III and V). The O/C ratio determined by XPS increases for each untreated PE sample upon annealing. An increase of the O/C ratio can be observed also for the corona-treated LDPE films. In the case of L-MDPE and blend films, the changes measured after annealing are affected by the intensity of corona-discharge treatment. The O/C ratio of films treated by 2 A remained practically unaltered after annealing for 160 days, whereas that of the films treated by 4 A decreased significantly. As seen in Figure 7, a linear relationship exists between the changes of the concentration of O and those of the C1 component of the C1s line: with increasing concentration of O in the top layer, the hydrocarbon type C concentration decreases. It is noted that despite the decrease of  $\gamma$ , the concentration of the C2 component (C—OH and C—O—C) of C1s line increases upon annealing. It can be an indication of the appearance of phenolic antioxidant.

As it was discussed above, the processes resulting in the changes of the surface characteristics during annealing are complex: postoxidation runs parallel with hydrophobic recovery. The increase of the O/C ratio suggests that postoxidation, as well as segregation of oxidized polymer fragments, and additives are the dominant processes. The

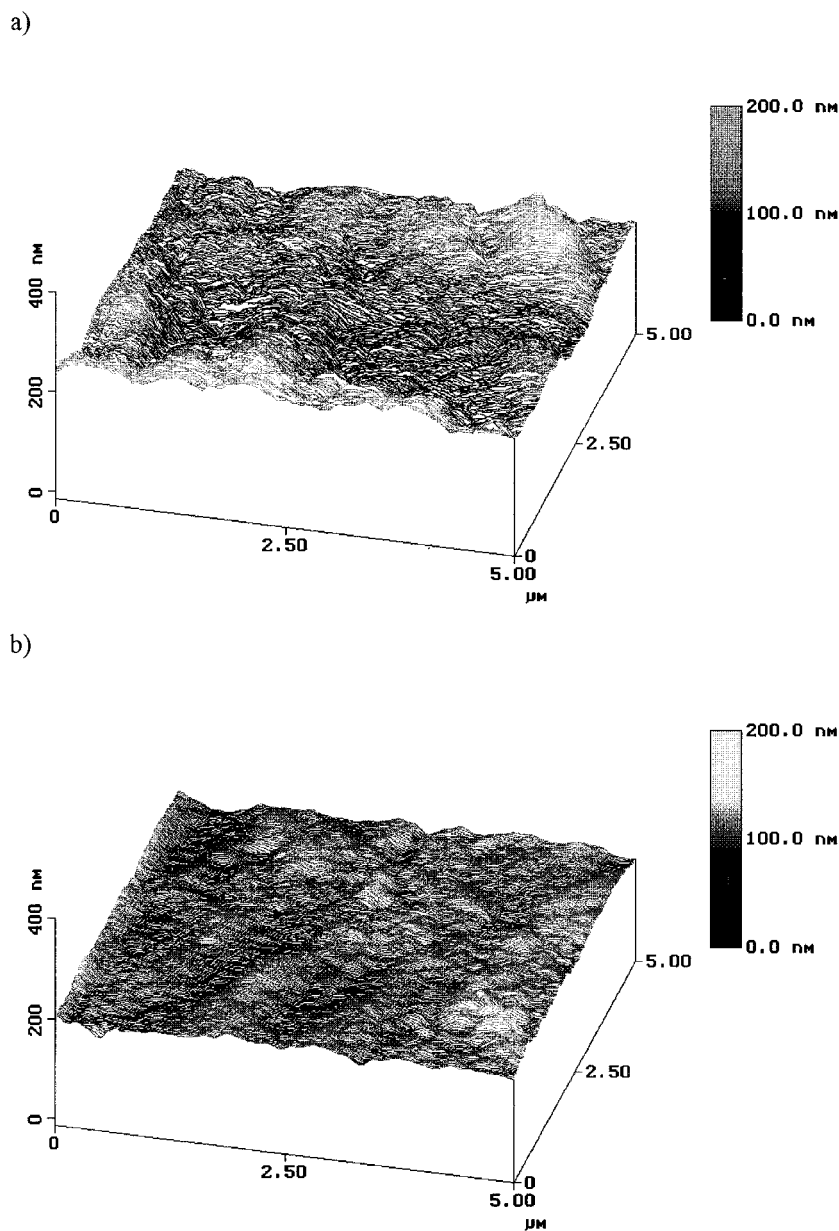
**Table V.** Surface Characteristics of the Films Determined After Annealing at 50°C for 160 days

Polymer	Electrode Current (A)	Tension (mN/n)	Roughness <sup>a</sup>	Composition by XPS (Atomic %)				
				C	O	Zn	N	P <sup>b</sup>
LDPE	—	—	12.7	96.6	3.4	0	0	—
	2	33	23.9	84.6	14.0	0	1.4	—
	4	37	14.4	80.3	18.7	0	1.0	—
L-MDPE	—	—	26.4	91.0	5.8	3.2	0	—
	2	32	41.6	87.5	9.0	3.5	0	+
	4	39	46.0	87.6	9.5	2.9	0	+
LDPE/L-MDPE 80/20	—	—	22.2	93.9	4.4	1.7	0	+
	2	32	19.7	88.0	10.4	1.2	0.4	+
	4	37	14.9	82.6	13.9	2.6	0.9	+

<sup>a</sup>200–400  $\mu\text{m}^2$  area.

<sup>b</sup> P2p line: +, present (trace); –, absent.





**Figure 5** Effect of annealing at 50°C for 160 days on the surface roughness of LDPE film treated by corona discharge at 4 A.

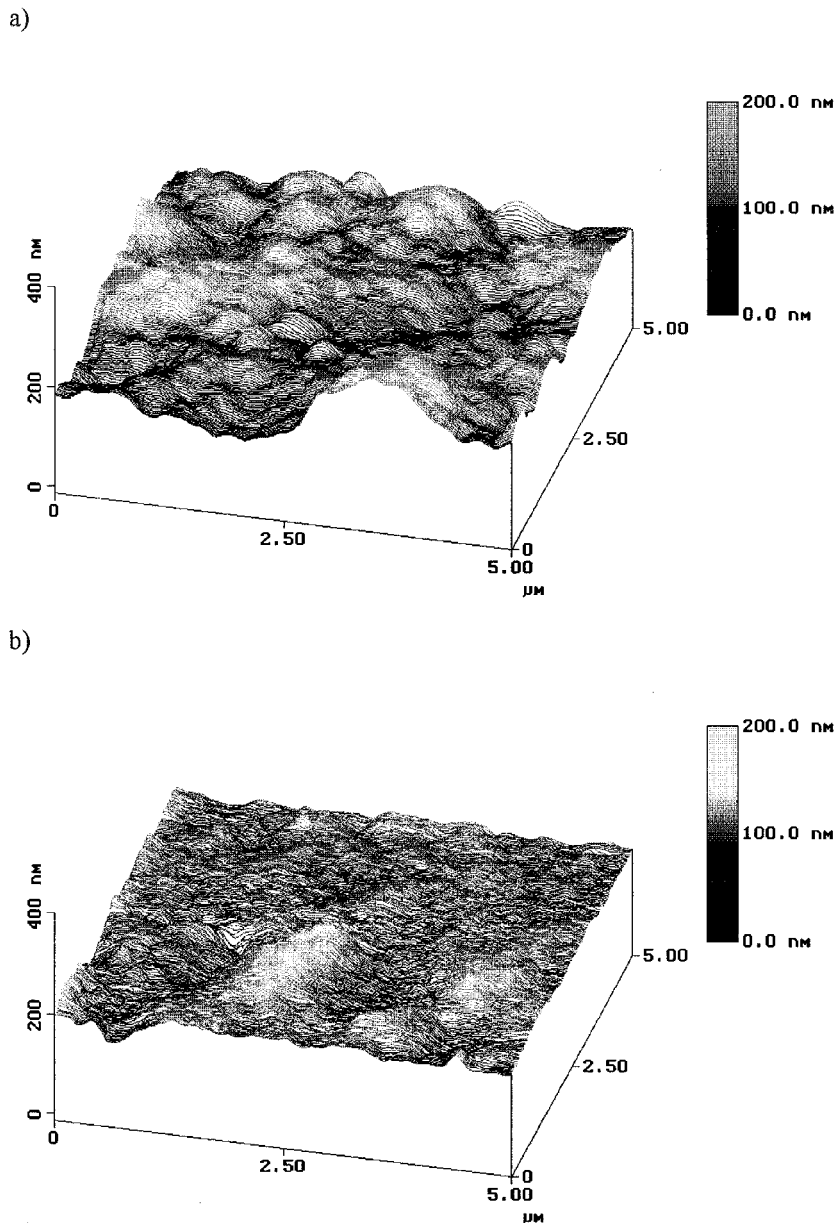
increase in the concentration of the C1 component (in L-MDPE and blend treated by 4 A) is an indication for oligomer migration to the surface.

The additive blooming is confirmed by the presence of specific atoms in the XPS spectra. Thus, the appearance of Zn reveals the migration of the slip agent from the bulk to the surface. Similarly, surface segregation of oleamide and the phosphite antioxidant is proven by the N1s and P2p lines in the spectra, respectively.

Dipping of the annealed films in chloroform for 5 min yielded a soluble fraction (exudate) of 0.27–

0.75% w/w concentration (Table VI). The lowest portion was obtained for L-MDPE, and the highest one for LDPE. A direct relationship can be established between the exudate concentration and the surface roughness of the annealed films (Fig. 8). The lower the rms values are, the higher the exudate ratio is. This result proves that recovery of the polymer surface is a consequence of migration of the low-molecular-mass components to the surface.

The composition of the exudate was studied by FTIR spectroscopy. The spectra are complex, re-

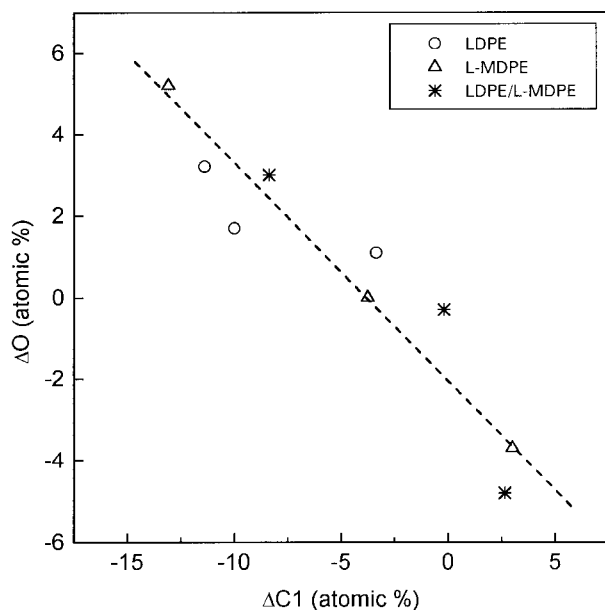


**Figure 6** Effect of annealing at 50°C for 160 days on the surface roughness of LDPE/L-MDPE 80/20 film treated by corona discharge at 2 A.

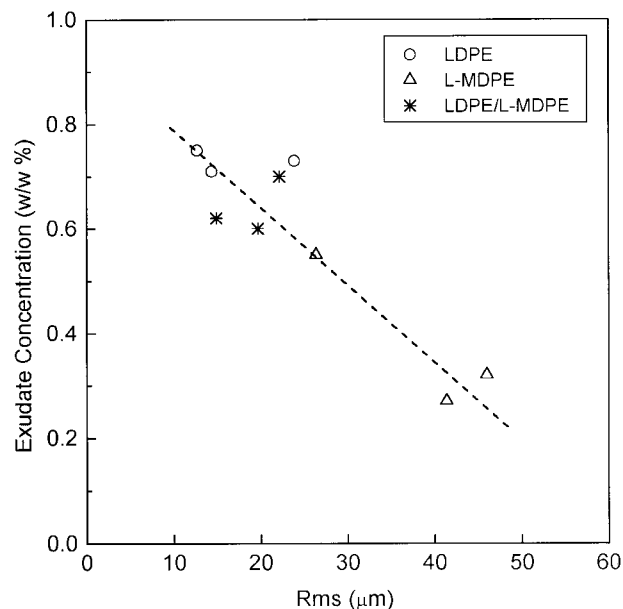
vealing the characteristic absorption peaks of hydrocarbon chains, as well as stabilizers and slip agents added to the polymers (Table VI). The hydrocarbon peak absorptions are high, and the  $\text{CH}_2$  rocking vibration gives an absorption peak at  $720\text{ cm}^{-1}$ , indicating noncrystalline hydrocarbon chains.<sup>17,20</sup> The absorption of the methyl group related to that of the methylene group ( $A_{\text{CH}_3}/A_{\text{CH}_2}$ ; relative  $\text{CH}_3$  absorption) increases with the concentration of exudate, as seen in Figure 9. This shows that not only the portion of the exudate is

the lowest in L-MDPE, but its relative methyl concentration as well.

The ester-type carbonyl absorption at  $1731\text{ cm}^{-1}$  shows an opposite trend, as compared to that of the  $\text{CH}_3$  group: its concentration is the highest in the exudate of L-MDPE and decreases with increasing amounts of dissolved material (Fig. 10). The  $\text{C}=\text{O}/\text{CH}_2$  values are affected primarily by the polymer type and less significantly by the conditions of corona treatment. The  $\text{C}=\text{O}$  absorption at  $1731\text{ cm}^{-1}$  can originate from the



**Figure 7** Relationship between the changes of the C1 component of C1s line and those of the intensity of O1s line determined by XPS before and after annealing of the films at 50°C for 160 days.



**Figure 8** Relationship between the concentration of the fraction dissolved by chloroform in 5 min and the roughness of the film surface measured by AFM (200–400  $\mu\text{m}^2$  area) after annealing at 50°C for 160 days.

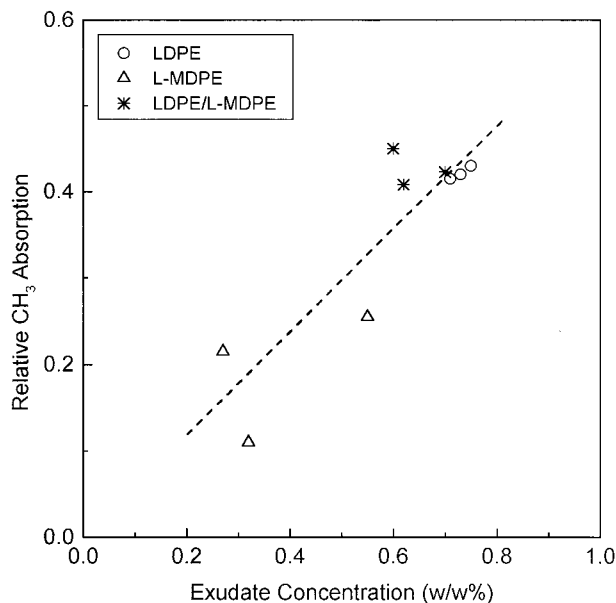
oxidized, fragmented parts of the polymer, as well as from the primary antioxidant added to L-MDPE, and so, to the blend. Considering the compositions of the films, and comparing the relative ester carbonyl absorptions of the different PE exudates, it can be deduced that the relatively high ester C=O in the dissolved fraction of L-MDPE originates primarily from blooming of the phe-

nolic antioxidant, besides the oxidative decomposition of the polymer. The antioxidant added to LDPE does not contain any ester group; therefore, the C=O absorption at  $1731\text{ cm}^{-1}$  can originate only from oxidized oligomers.

The FTIR study of the dissolved fraction confirmed the results of the XPS analyses, because the additives detected by XPS could be recognized

**Table VI.** FT-IR analysis of the Fraction Dissolved by Chloroform (dipping for 5 min) After Annealing the Films at 50°C for 160 Days

Polymer	Electrode Current (A)	Amount (w/w%)	Exudate			
			FTIR Characteristics			
			$A_{1378}/A_{1465}$ ( $\text{CH}_3$ )	$A_{1731}/A_{721}$ (C=O)	$A_{1082}/A_{721}$ (P—O)	$A_{1660}/A_{721}$ (amide-I)
LDPE	—	0.75	0.435	0.483	—	0.453
	2	0.73	0.420	0.420	—	0.739
	4	0.71	0.415	—	—	—
L-MDPE	—	0.55	0.255	1.118	1.261	—
	2	0.27	0.215	1.329	1.170	—
	4	0.32	0.110	1.223	0.617	—
LDPE/L-MDPE 80/20	—	0.70	0.423	—	—	—
	2	0.60	0.450	0.683	0.863	0.675
	4	0.62	0.408	0.820	1.486	0.947



**Figure 9** Relationship between the concentration and the relative methyl absorption (determined at  $1378\text{ cm}^{-1}$  by FTIR) of the fraction dissolved by chloroform in 5 min after annealing at  $50^\circ\text{C}$  for 160 days.

also in the exudates. The O/C ratio determined by XPS and the absorption at  $1731\text{ cm}^{-1}$  do not, and need not, correlate directly, because the ester carbonyl is only a part of the total oxygen content. The amide-I absorption of oleamide at  $1660\text{ cm}^{-1}$  is relatively strong in the exudate of LDPE and the blend. The results given in Table VI indicate that the corona-discharge treatment promotes the migration of oleamide to the surface. The absorption peak at  $1082\text{ cm}^{-1}$  (P—O bond) confirms the blooming of the phosphite stabilizer. The C=O group absorption of Zn-stearate at  $1538\text{ cm}^{-1}$  is relatively weak. It could also be detected in the samples containing L-MDPE, although the intensity is difficult to determine reliably.

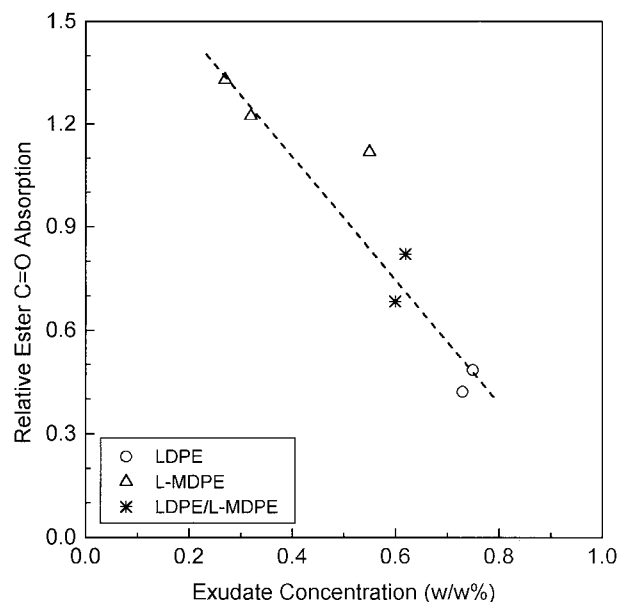
Summarizing the results, it can be concluded that the hydrophobic recovery of the investigated PE films is a result of migration of low-molecular-mass substances oligomers, oxidized polymer fragments, and additives to the surface, which can be removed by dipping in a solvent. The recovery is accompanied by the decrease of surface roughness.

## CONCLUSION

The effects of air-corona-discharge treatment and subsequent annealing of PE films were studied by

different techniques. LDPE, L-MDPE, and their 80/20 blend were investigated. From the results of the experiments, the following conclusions were drawn:

1. The surface of the PE films oxidizes to some extent even without corona treatment. The roughness of the film surface depends on the polymer type. LDPE has a much smoother surface than L-MDPE, that of the blend film is between those of the pure polymers.
2. The degree of surface oxidation and the surface tension of the films increase with increasing electrode current of corona-discharge treatment. The surface roughness remains primarily dependent on the polymer type even after treatment. Some of the additives (e.g., oleamide and phosphite stabilizer) migrate to the surface during processing; others cannot be detected the next day, after processing.
3. During annealing at ambient temperature and  $50^\circ\text{C}$ , post-treatment-type oxidation and hydrophobic recovery of the surface can be observed. The former is more pronounced in L-MDPE, and the latter is the dominant process in LDPE at the initial stage.
4. After a long annealing time, the hydropho-



**Figure 10** Relationship between the concentration and the relative ester carbonyl absorption (determined at  $1731\text{ cm}^{-1}$  by FTIR) of the fraction dissolved by chloroform in 5 min after annealing at  $50^\circ\text{C}$  for 160 days.

bic recovery prevails in each polymer investigated, which results in an essential decrease of the surface tension and roughness. It originates from the migration of the low-molecular-mass components (oligomers, oxidized polymer fragments, and additives) to the surface.

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