

Surface Modification of Low-Density Polyethylene (LDPE) Film and Improvement of Adhesion Between Evaporated Copper Metal Film and LDPE

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ABSTRACT: To improve the interfacial adhesion between evaporated copper film and low-density polyethylene (LDPE) film, the surface of LDPE films was modified by treating with chromic acid [$K_2Cr_2O_7/H_2O/H_2SO_4$ (4.4/7.1/88.5)]/oxygen plasma. Chromic-acid-etched LDPE was exposed to oxygen plasma to achieve a higher content of polar groups on the LDPE surface. We investigated the effect of the treatment time of chromic acid in the range of 1–60 min at 70°C and oxygen plasma in the range of 30–90 sec on the extent of polar groups created on the LDPE. We also investigated the surface topography of and water contact angle on the LDPE film surface, mechanical properties of the LDPE film, and adhesion strength of the evaporated copper metal film to the LDPE film surface. IR and electron spectroscopy for chemical analysis revealed the introduction of polar groups on the modified LDPE film surface, which exhibited an improved contact angle and copper/LDPE adhesion. The number of polar groups and the surface roughness increased with increasing treatment time of chromic acid/plasma. Water contact angle significantly decreased with increasing treatment time of chromic acid/plasma. Combination treatment of oxygen plasma with chromic acid drastically decreased the contact angle. When the treatment times of chromic acid and oxygen plasma were greater than 10 min and 30 sec, respectively, the contact angle was below 20°. With an increasing treatment time of chromic acid, the tensile strength of the LDPE film decreased, and the film color changed after about 10 min and then became blackened after 30 min. With the scratch test, the adhesion between copper and LDPE was found to increase with an increasing treatment time of chromic acid/oxygen plasma. From these results, we found that the optimum treatment times with chromic acid and oxygen plasma were near 30 min and 30 sec, respectively. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1677–1690, 2001

Key words: surface modification; plasma; chromic acid; metallized polymer

INTRODUCTION

Polyethylene (PE) has been widely used because it has many good properties including a high

chemical resistance, a high impact strength, flexibility, and low cost. However, the nonpolar property of PE limits its applications in composites and coatings because of the lack of adhesion. Various attempts have been made to improve the adhesion property of PE, for example, by chemical etching,^{1–3} corona discharge,⁴ and plasma treatment.^{5–7} Nuzzo and Smolinsky⁸ reported a procedure to modify the surface of PE film with a com-

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combination of gas discharge and wet chemical techniques.

When a polymer is soaked in a heavily oxidative chemical liquid and treated under suitable conditions, polar groups are introduced on the polymer surface, and the surface characteristics are improved. Various types of heavily oxidative chemicals, such as chromic anhydride/tetrachloroethane, chromic acid/acetic acid, chloratesulfuric acid, and potassium dichromate/sulfuric acid have been investigated. Other methods of treatment, such as oxidation with NO, cycloalkyl chromate treatment, potassium permanganate treatment, sodium hypochlorite treatment, chlorosulfonation treatment, and flame treatment in the presence of halogen have been proposed. The most effective and common chemicals among these candidates is potassium dichromate/sulfuric acid. The surface of polyolefin is activated by treating it with the liquid through the formation of polar groups such as >C=O , —OH , —COOH , and SO_3H . Rasmussen et al.⁹ determined these polar groups qualitatively in detail.

Plasma treatment is a convenient way to modify the surface ($\sim 25\text{--}50\text{\AA}$) of a polymer for improved adhesion of vacuum-deposited metals. The plasma treatment of polymers before metallization has been shown to enhance the adhesion of the metal layers.¹⁰ Plasma treatments have been applied to modify the polymer surface to improve the adhesion strength of many polymers without affecting the bulk properties. X-ray photoemission analysis of plasma-modified PE has indicated no detectable chemical effects for argon plasmas, whereas oxygen and nitrogen plasmas have created new chemical species that altered the chemical reactivity of the PE surface for vacuum-deposited Ag.¹¹

Metallized polymers are extensively used for a variety of applications.¹² The chemical composition of the polymer surface before metal deposition has been found to control the adhesion of the metal films to the substrate.¹³

Generally, when low-density polyethylene (LDPE) has been surface modified by simple treatment with chromic acid or oxygen plasma, the effects of modification have not been sufficient to improve adhesion between metal and LDPE. We describe in this article a procedure to modify the surface of LDPE film with a combination of chromic acid and oxygen plasma treatments. The influence of oxygen plasma treatment after chromic acid treatment on the introduction of polar

groups, topography, water contact angle, mechanical properties, and adhesion strength of vacuum-deposited Cu on LDPE were investigated.

EXPERIMENTAL

Materials and Treatment

LDPE films (thickness ~ 0.5 mm) were made by compression molding with LDPE pellet (LG Co., Korea). Film samples were cut into pieces of about 10×5 cm. After refluxing in hexane for 2 h, the films were rinsed with pure hexane and dried in a vacuum. Chromic acid [$\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ (4.4/7.1/88.5 wt %)] was freshly prepared by the dissolution of potassium dichromate (Aldrich Chem) in hot concentrated sulfuric acid (98%; Aldrich Chemical Co.) prior to use. The LDPE film samples were etched with chromic acid at 70°C for different treatment times, ranging from 1 to 90 min. After acid treatment, the film samples were exposed to oxygen plasma for 30–90 sec at room temperature with a direct current (DC) sputtering system (pressure = 1.8×10^{-1} Torr, voltage = 610 V, current = 1.75 A). The various surface-modified LDPE film samples prepared in this way are identified in Table I. The copper was deposited onto the LDPE films for 3 min with a DC sputtering system (pressure = 7.9×10^{-3} Torr, voltage = 275 V, current = 2 A).

Characterization

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the control and modified LDPE films were obtained on a Nicolet impact 400D FTIR spectrophotometer. For each sample, 32 scans at 2 cm^{-1} resolution were collected in the reflectance mode. Films were placed on the ATR crystal and held tightly in place with pressure on the plate. Electron spectroscopy for chemical analysis (ESCA) was performed with a PerkinElmer PHI 558 spectrophotometer. Photoelectrons were excited by monochromatized $\text{AlK}\alpha$ radiation, and measurements were made at a 55° take-off angle. The apparatus used for static contact angle measurements was an ERMA contact angle meter. Advancing-type contact angles of water were measured for treated and untreated samples at room temperature with the sessile drop technique. Constant volume droplets of 0.2 cm^3 distilled water were delivered from the tip of

Table I Sample Codes, Treatment Conditions, Surface Characteristics, Contact Angles, and Tensile Properties of Surface-Modified LDPE

Sample Code	Treatment time (Acid ^a /Plasma ^b ; min/sec)	Surface Characteristic				Contact Angle	Tensile Properties			
		ESCA		ATR-FTIR			Strength at Break		Elongation at Break	
		O1s/C1s	S2p/C1s	>C=O ^c / —CH ₂ — ^d	—SO ₃ H ^e / —CH ₂ ^d		MPa	Rate ^f	%	Rate ^f
C0/P0	0/0	0.05	0	0	0	95	15.36	0	768.13	0
C0/P30	0/30	0.18		0.43		47.5				
C0/P60	0/60	0.15		0.42		49				
C0/P90	0/90	0.14		0.39		47				
C1/P0	1/0	0.14	0.009	0.35	0.42	83	15.00	2.3	756.15	1.5
C1/P30	1/30	0.23		0.62		27.5				
C1/P60	1/60	0.20		0.60		28				
C1/P90	1/90	0.22		0.68		26				
C10/P0	10/0	0.16	0.011	0.70	1.61	74	14.30	6.9	706.95	7.9
C10/P30	10/30	0.34		0.91		18.5				
C10/P60	10/60	0.33		0.87		20				
C10/P90	10/90	0.33		1.03		19				
C30/P0	30/0	0.21	0.015	1.5	2.92	69	13.80	10.1	682.60	11.1
C30/P30	30/30	0.47		1.75		16.5				
C30/P60	30/60	0.45		1.60		18				
C30/P90	30/90	0.44		1.70		16				
C60/P0	60/0	0.19	0.013	3.12	3.39	66	8.96	41.6	116.55	84.8
C60/P30	60/30	0.38		3.23		17				
C60/P60	60/60	0.35		3.31		15				
C60/P90	60/90	0.36		3.45		14				

^a Chromic acid = K₂Cr₂O₇ = H₂O = H₂SO₄ = 4.4 = 7.1 = 88.5 wt %, treatment temperature = 70°C.

^b Oxygen plasma = 610 V, 175 mA, 1.8 × 10⁻¹ Torr.

^c C=O peak = 1590–1850 cm⁻¹.

^d —CH₂— peak = 1390–1480 cm⁻¹.

^e —SO₃H peak = 950–1300 cm⁻¹.

^f Drop rate (%).

a 1-mL syringe onto the film sample, and the dwell time was 5 sec. The scanning electron micrographs of untreated and treated LDPE films were obtained with a JEOL JSM 5400 microscope. Tensile strength of the LDPE films was measured by an Instron universal testing machine (Tinius Olsen, series 1000) at room temperature at a crosshead speed of 500 mm/min. The adhesion between copper and PET film was examined with the scratch tester (Revetest, CSEM Co., Switzerland) with 0–20 N of force. The LDPE samples were cooled with liquid nitrogen just before the examination to prevent the depression of LDPE in the course of scratching. The scratched LDPE film samples were examined with an electron microscope (TMGIII 613U W/Ace).

RESULTS AND DISCUSSION

Table I presents the sample code, treatment conditions, surface characteristics, contact angles, and tensile properties of the samples. The IR spectra of chromic-acid-treated and untreated LDPE films are shown in Figure 1. From the IR analysis of the chromic-acid-treated LDPE films, the appearance of strong bands at 1700–1712 cm⁻¹ confirms the presence of the carbonyl group (>C=O) of a —COOH group. A band at 1620–1627 cm⁻¹ corresponds to a >C=O group adjacent to an olefinic double bond or enolic >C=O group. The appearance of a strong band at 1170–1180 cm⁻¹ is assigned to the sulfoxide group (>S=O) of sulfonic acid. All these absorption peaks were absent

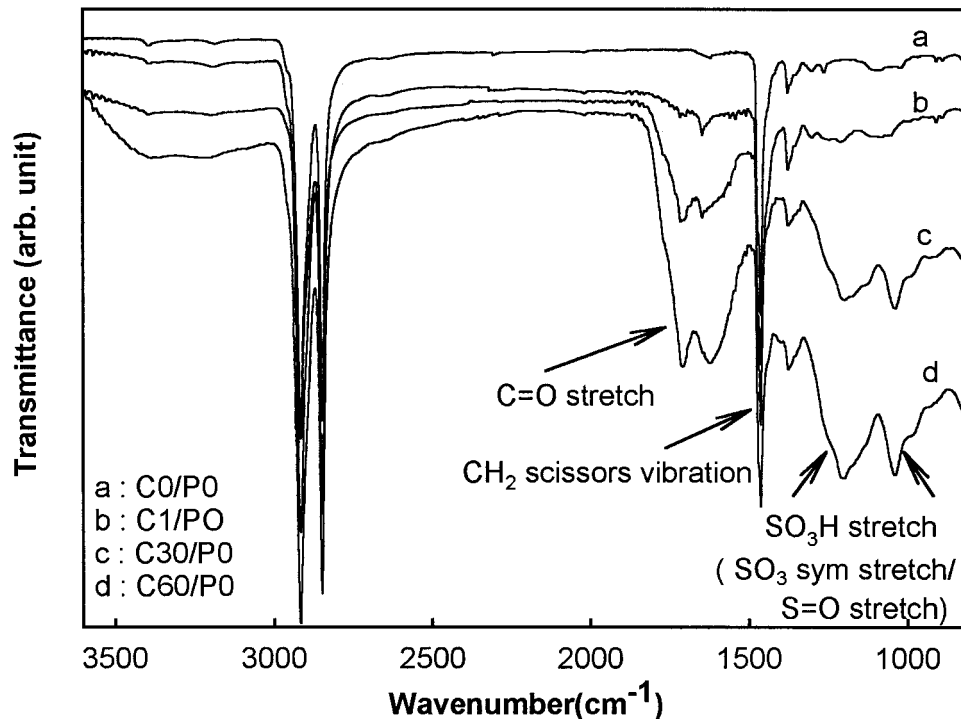


Figure 1 Typical ATR-FTIR spectra of LDPE film for samples (a) C0/P0, (b) C1/P0, (c) C30/P0, and (d) C60/P0.

in the virgin LDPE film. As the chromic acid treatment time increased, the characteristic peak intensities of the carbonyl and sulfoxide groups increased (see Table I and Fig. 1).

Figure 2 shows the IR spectra of chromic acid (30 min)/oxygen plasma (0, 30, 60, and 90 sec) treated LDPE film samples: C30/P0, C30/P30, C30/P60, and C30/P90. At a fixed chromic acid treatment time (30 min), the intensity of the carbonyl group increased with increasing oxygen plasma treatment time; however, sulfoxide groups were not changed (see Table I and Fig. 1). This indicates that oxygen plasma oxidized the chromic-acid-oxidized LDPE surface further to give a higher content of polar carbonyl groups.

Generally, ESCA measurement is very useful for the characterization of polymer surfaces. Quantitative results on the surface atomic concentration are presented in Table I. Figure 3 shows a typical ESCA spectra for the untreated LDPE (C0/P0), chromic-acid-treated LDPE (C30/P0), oxygen-plasma-treated LDPE (C0/P30), and chromic-acid/oxygen-plasma-treated LDPE (C30/P30) samples. ESCA spectra of samples C30/P0 and C30/P30 showed the expected C1s (285.1 eV),

O1s (534.2 eV), and S2p (171.8 eV) peaks. The ESCA spectrum of sample C0/P30 showed C1s and O1s peaks. However, the ESCA spectrum of the control LDPE sample C0/P0 showed the expected C1s peak and the very small unexpected O1s peak. This indicates that the control LDPE was already oxidized a little. The deconvoluted ESCA spectra of C1s, O1s, and S2p for samples C0/P0, C30/P0, C0/P30, and C10/P30 are shown in Figure 4. The deconvoluted C1s spectra of chromic-acid/oxygen-plasma-treated LDPE (sample C10/P30) showed peaks at 285.1, 286.3, 287.0, and 287.9 eV that could be assigned to $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, >C=O , and $-\text{COO}-$, respectively. The deconvoluted O1s spectra of chromic-acid/oxygen-plasma-treated LDPE (sample C10/P30) showed peaks at 534.2, 535.8, and 536.7 eV that could be assigned to >C=O , $-(\text{O}=\text{S}=\text{O})-$, and $-\text{O}(\text{C}=\text{O})-$, respectively. The S2p spectrum of samples C30/P0 and C10/P30, on the other hand, showed peaks at 171.8, 173.8, and 174.9 eV that could be assigned to sulfide, sulfoxide, and sulfone groups, respectively. Figure 5 shows the effect of chromic acid treatment time on the O1s/C1s value for samples C0/P0, C1/P0, C10/P0, C30/P0, and

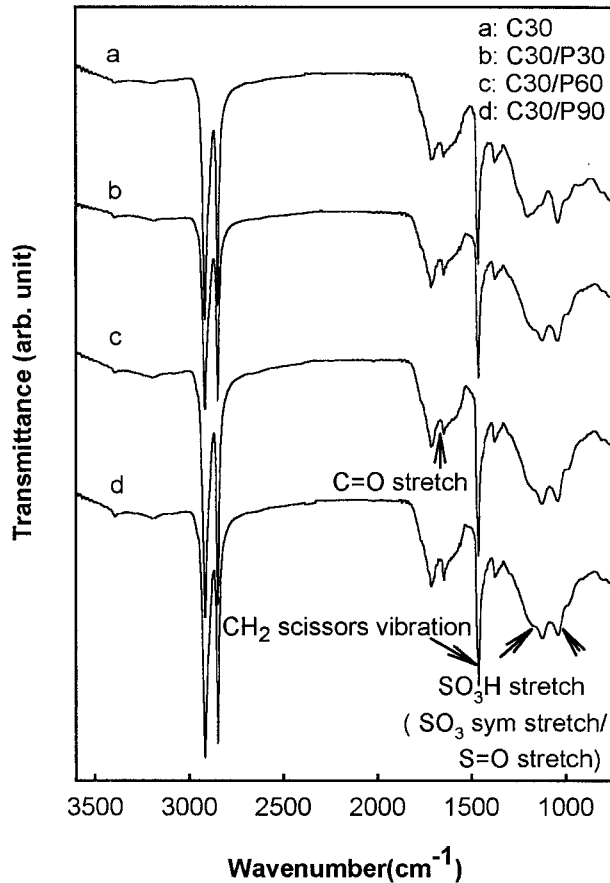


Figure 2 Typical ATR-FTIR spectra of LDPE film for samples (a) C30/P0, (b) C30/P30, (c) C30/P60, and (d) C30/P90.

C60/P0. The O1s/C1s value increased suddenly with increasing chromic acid treatment time and then gave the almost maximum value at 30 min. The increase of the S2p/C1s value showed same trend as the O1s/C1s value (see Table I). The effect of plasma treatment time on the O1s/C1s value for samples C30/P0, C30/P30, C30/P60, and C30/P90 is shown in Figure 6. With increasing plasma treatment times up to 30 sec, the O1s/C1s value increased and then almost leveled off or decreased a little.

To ascertain the extent of damage on the LDPE film surface by treatment with chromic acid at 70°C, LDPE samples were viewed under a scanning electron microscope. The scanning electron microscopy (SEM) micrographs of etched and untreated LDPE films are shown in Figure 7. The control LDPE film (C0/P0) had a fairly smooth surface as shown in Figure 7(a). Pitting and sur-

face roughening were observed for the chromic-acid-treated LDPE films. This was caused by the fact that the amorphous portion between spherulites was more easily etched than the spherulite itself. With an increasing treatment time of chromic acid, erosion propagated inside the film, resulting in the formation of bigger pits on the surface. Both the depth and the frequency of the occurrence of pits increased with increasing treatment time [see Fig. 7(c–f)]. Figure 7(b) shows the roughness of LDPE surface for sample C0/P90 treated with 90 sec of oxygen plasma. The effect of oxygen plasma on the topography of LDPE film surface was feeble within 60 sec; however, the surface of the LDPE film sample roughed significantly after 60 sec of plasma treatment. The color of the LDPE film changed to yellow after about 10 min of chromic acid treatment and then black-

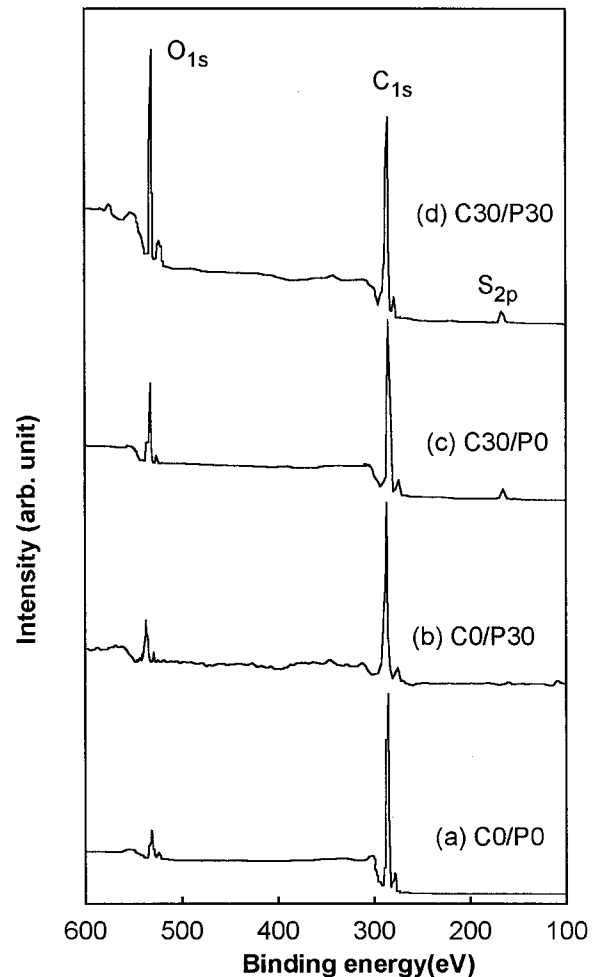


Figure 3 The ESCA spectra of (a) control, (b) C30/P0, (c) C30/P30, and (d) C30/P90 LDPE films.

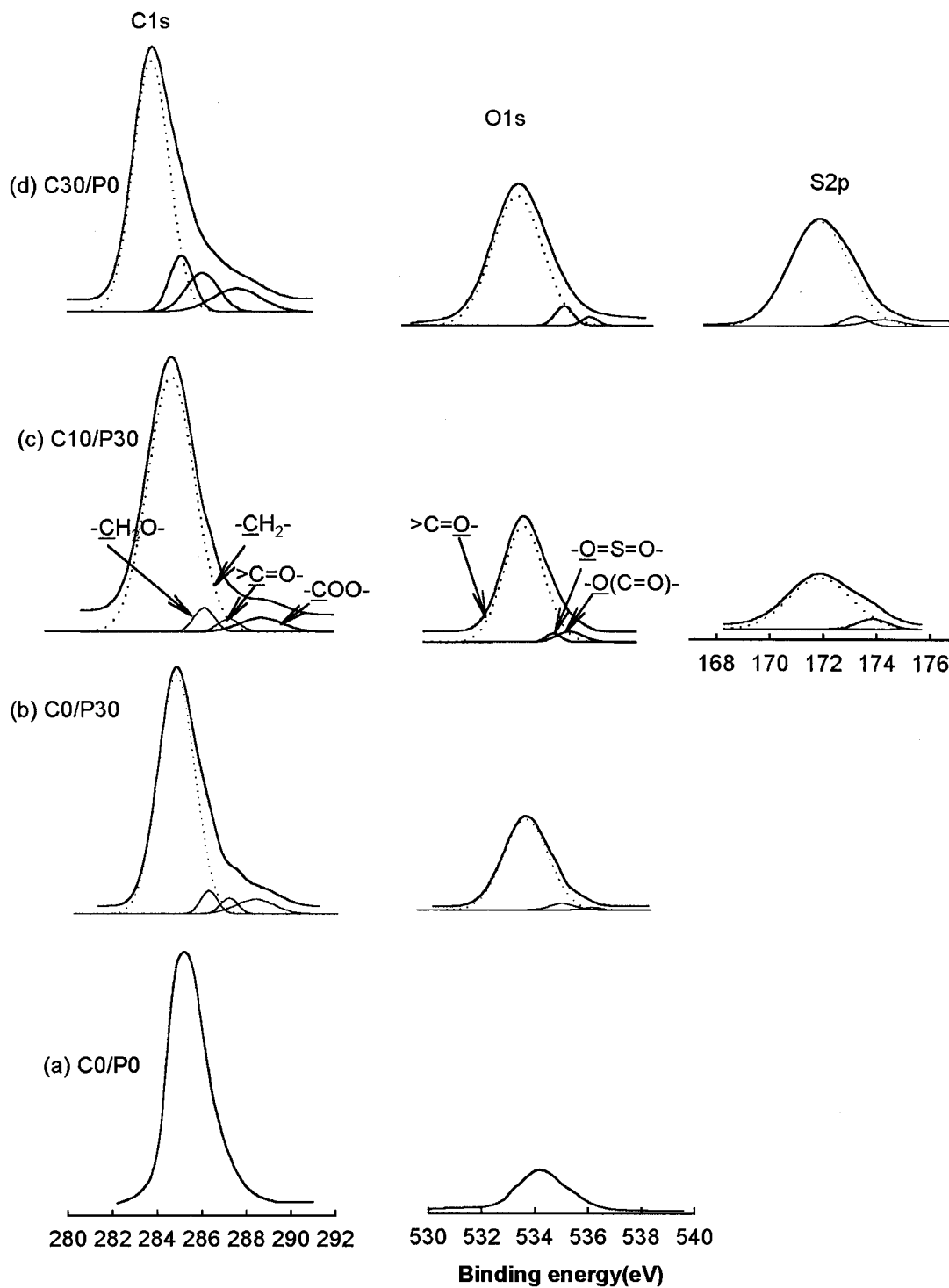


Figure 4 High-resolution C1s, O1s, and S2p ESCA spectra for samples (a) C0/P0, (b) C0/P30, (c) C10/P30, and (d) C30/P0 LDPE.

ened after 30 min. The improvement of the wettability and adhesion of a polymer is often attributed to increased surface roughness.¹⁴ Therefore,

the pitting was expected to promote adhesion because of an increased surface area for bonding and mechanical interlocking and, hence, better

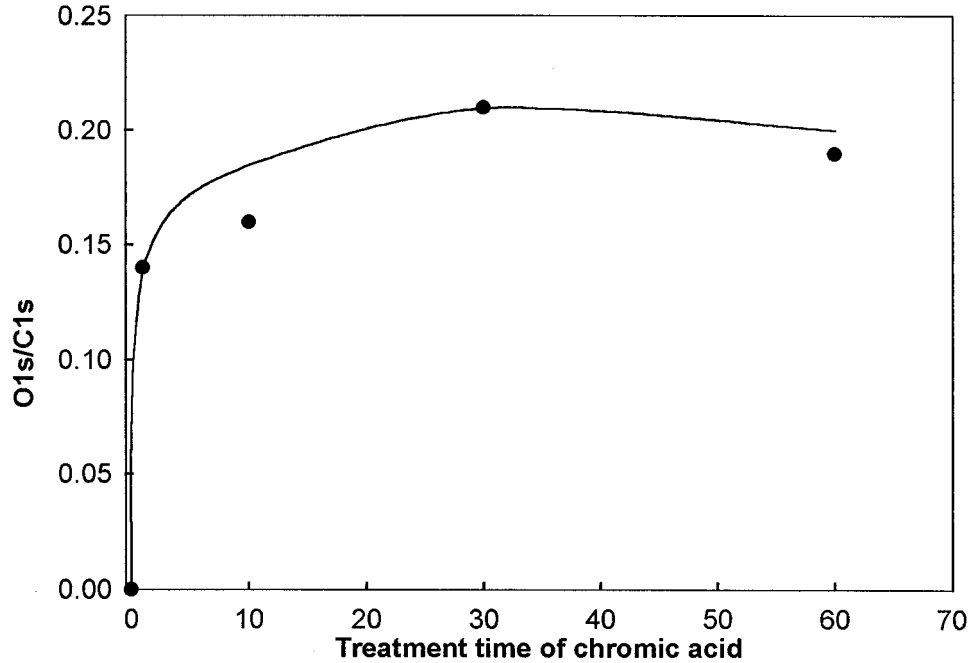


Figure 5 The effect of chromic acid treatment on the O1s/C1s values for samples C30/P0, C1/P0, C10/P0, C30/P0, and C60/P0.

interfacial adhesion between Cu and LDPE. However, we found that too many big pits in the LDPE surface hindered the interfacial adhe-

sion between copper and LDPE and also markedly decreased the tensile strength of the LDPE film.

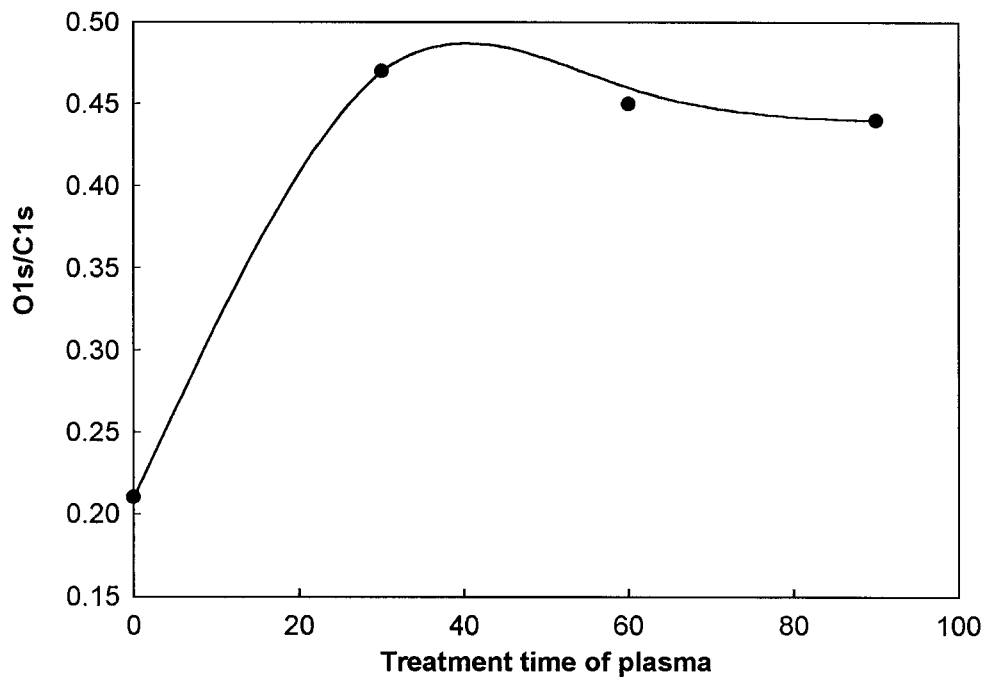
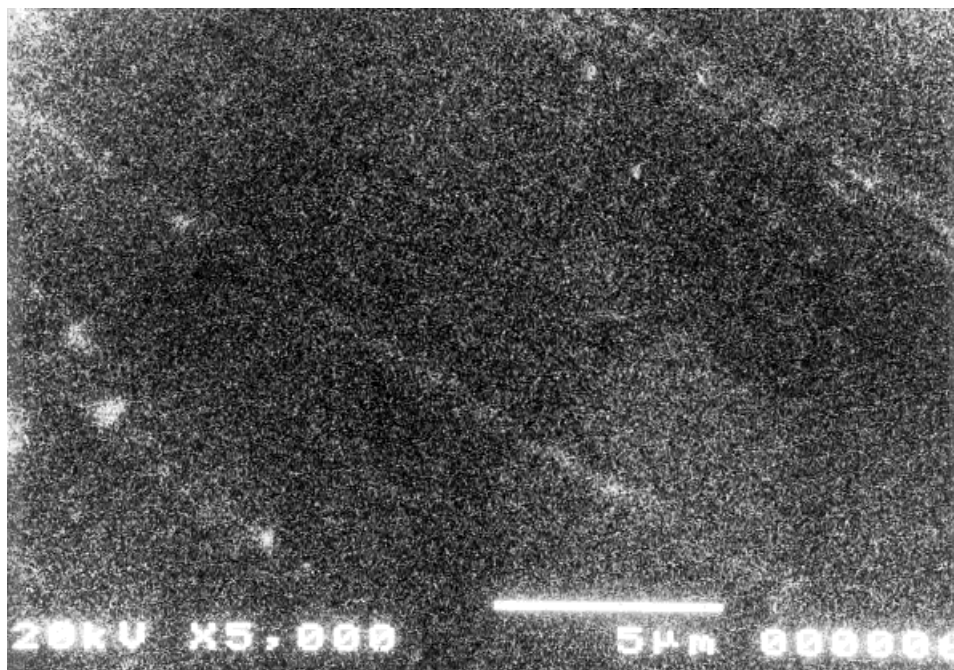
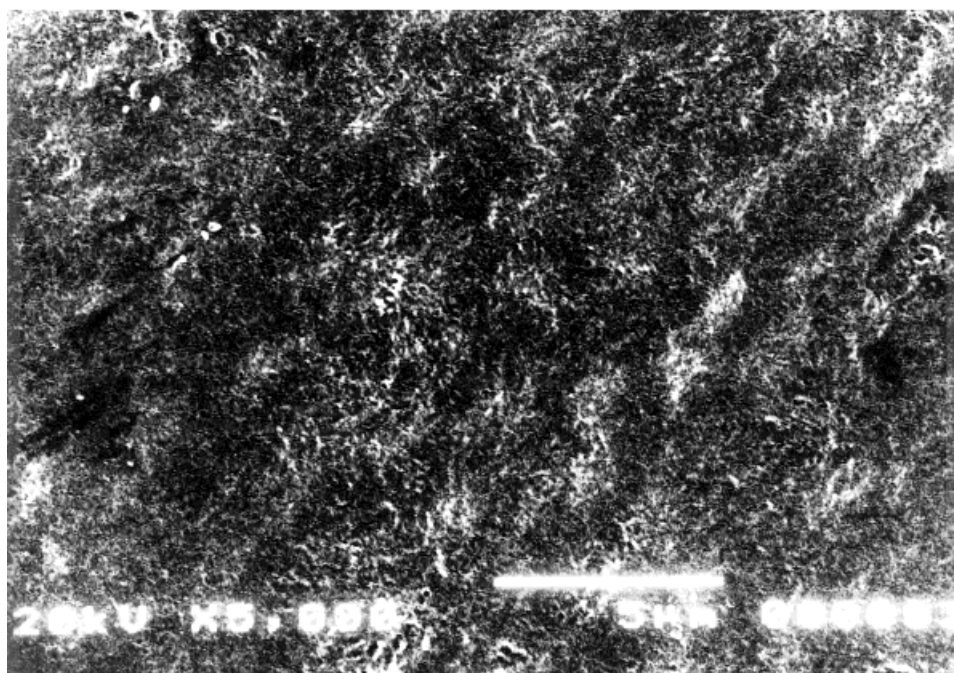


Figure 6 The effect of plasma treatment time on the O1s/C1s values for samples C30/P0, C30/P30, C30/P60, and C30/P90.

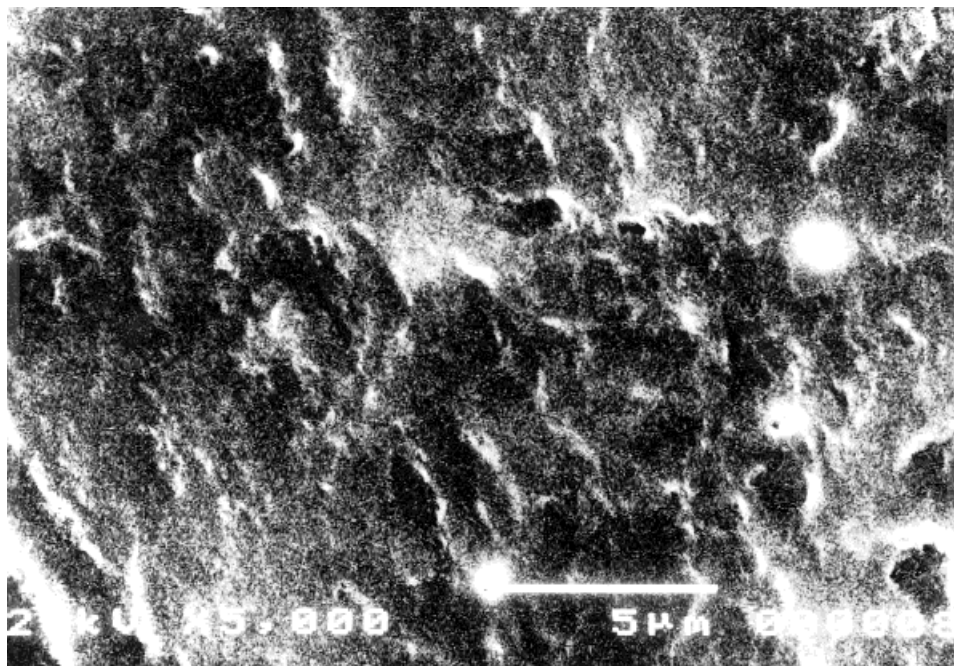


(a) C0/P0

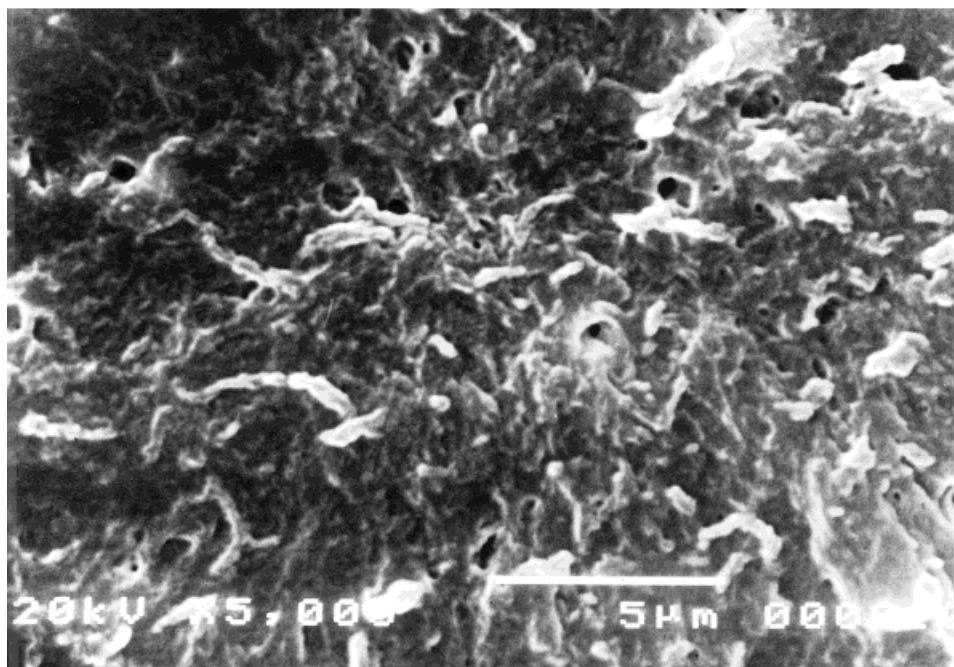


(b) C0/P90

Figure 7 Typical SEM microphotographs for samples (a) C0/P0, (b) C0/P90, (c) C1/P0, (d) C10/P0, (e) C30/P0, and (f) C60/P0.

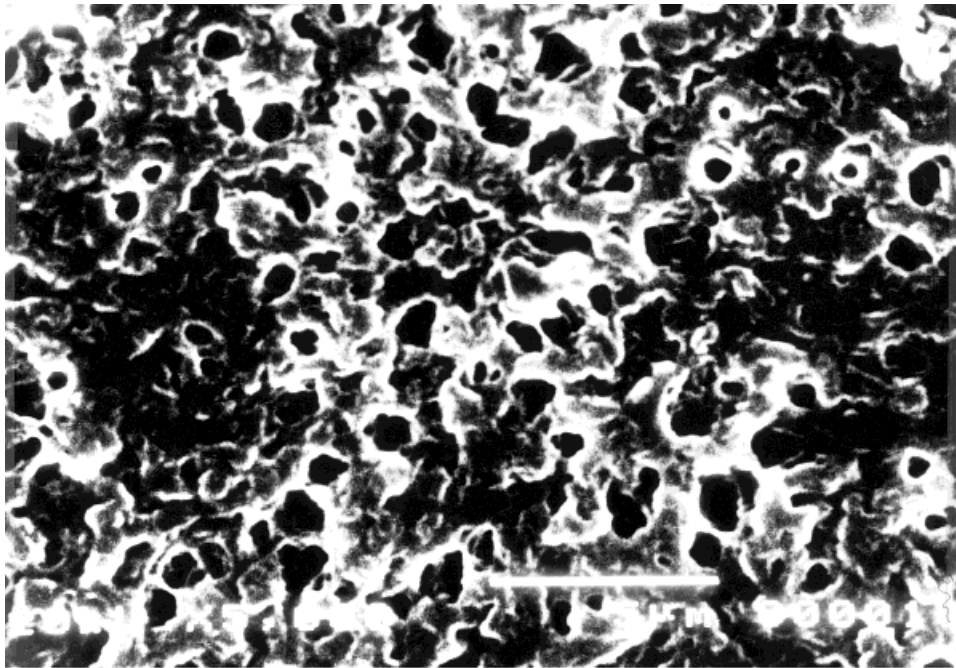


(c) C1/P0

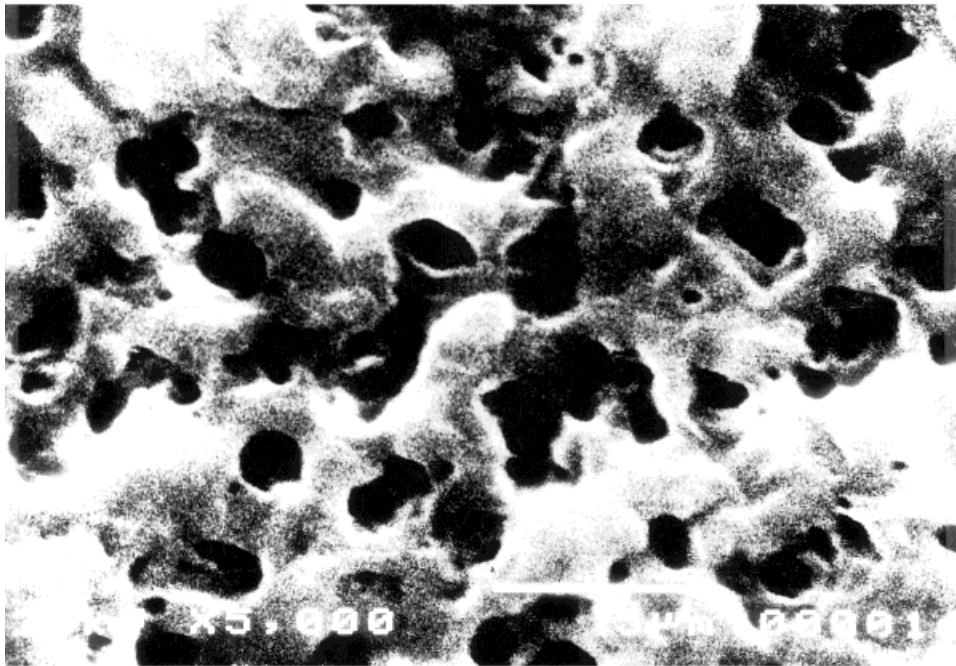


(d) C10/P0

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(e) C30/P0



(f) C60/P0

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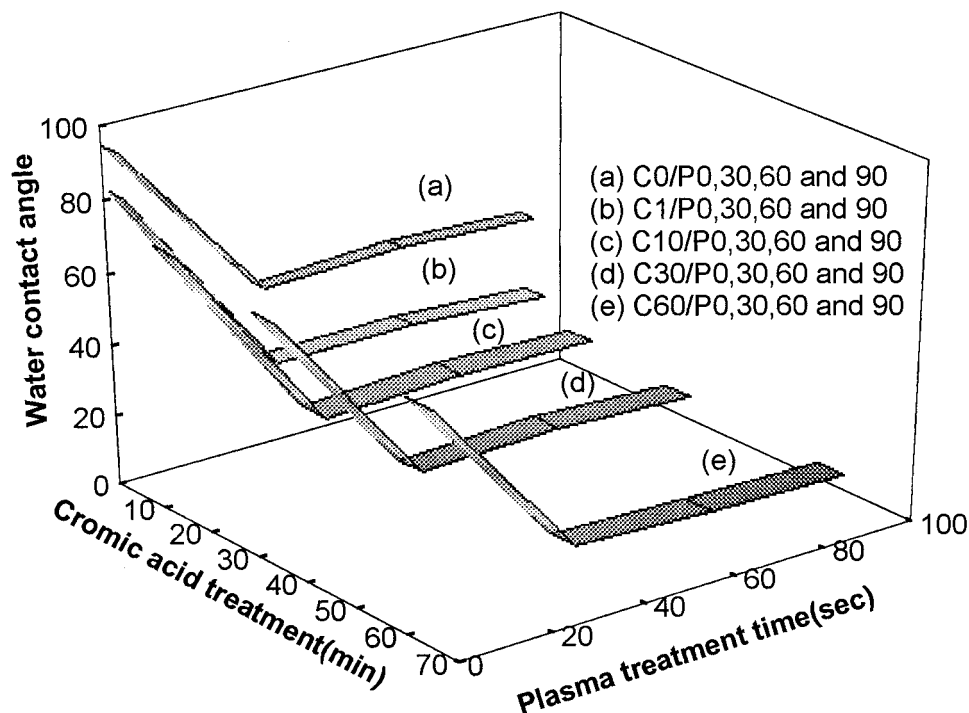


Figure 8 The effect of treatment times of chromic acid and oxygen plasma on the water contact angle.

The contact angle is a measure of surface hydrophilicity or wettability. Figure 8 and Table I show the relationship between treatment time and water contact angle. Water contact angle significantly decreased with increasing chromic acid and oxygen plasma treatment times (see Table I). A combination of oxygen plasma treatment with chromic acid treatment caused a drastic decrease in contact angle.

The typical stress-strain curves are shown in Figure 9. The tensile properties of untreated and chromic-acid-treated LDPE are shown in Table I. The effect of plasma on the tensile properties was negligible in this study. The tensile strengths of the LDPE films decreased with increasing chromic acid treatment time. These results seemed to be caused by the increase of polymer chain scission in the LDPE films by chromic acid treatment. It is generally accepted that about 10% strength reduction is allowable for chemical surface modification in various uses. When the treatment time of chromic acid at 70°C was within 30 min, the tensile strength reduction was below 10%.

Generally, it is known that complexes of the metal films to the oxygen-containing polar polymers are formed, and the presence of these com-

plexes correlates with the increase of adhesion strength. The polar groups formed on the LDPE film surface by treatment with chromic acid and then oxygen plasma may have contributed to improved adhesion between metal Cu and LDPE in this study. This was investigated with a scratch tester. Figure 10 shows the typical photomicrographs of Cu/LDPE film scratched by a stylus (diameter of diamond tip = 120 μ m) from 0 to 20 N. The critical load for Cu/LDPE system is shown in Table II. The adhesion strength between Cu metal and the modified LDPE films increased with an increasing treatment times of chromic acid and oxygen plasma up to 30 min and 30 sec, respectively, and decreased thereafter. The observed increase in adhesion may partly have been caused by the increase in the number polar groups on the surface of LDPE and partly caused by the increased roughness of the modified LDPE surface. It was concluded that a chromic acid treatment time of about 30 min at 70°C and a plasma treatment time of about 30 sec at room temperature was an optimum condition to improve the adhesion strength of thin Cu metal film to the surface modified LDPE film.

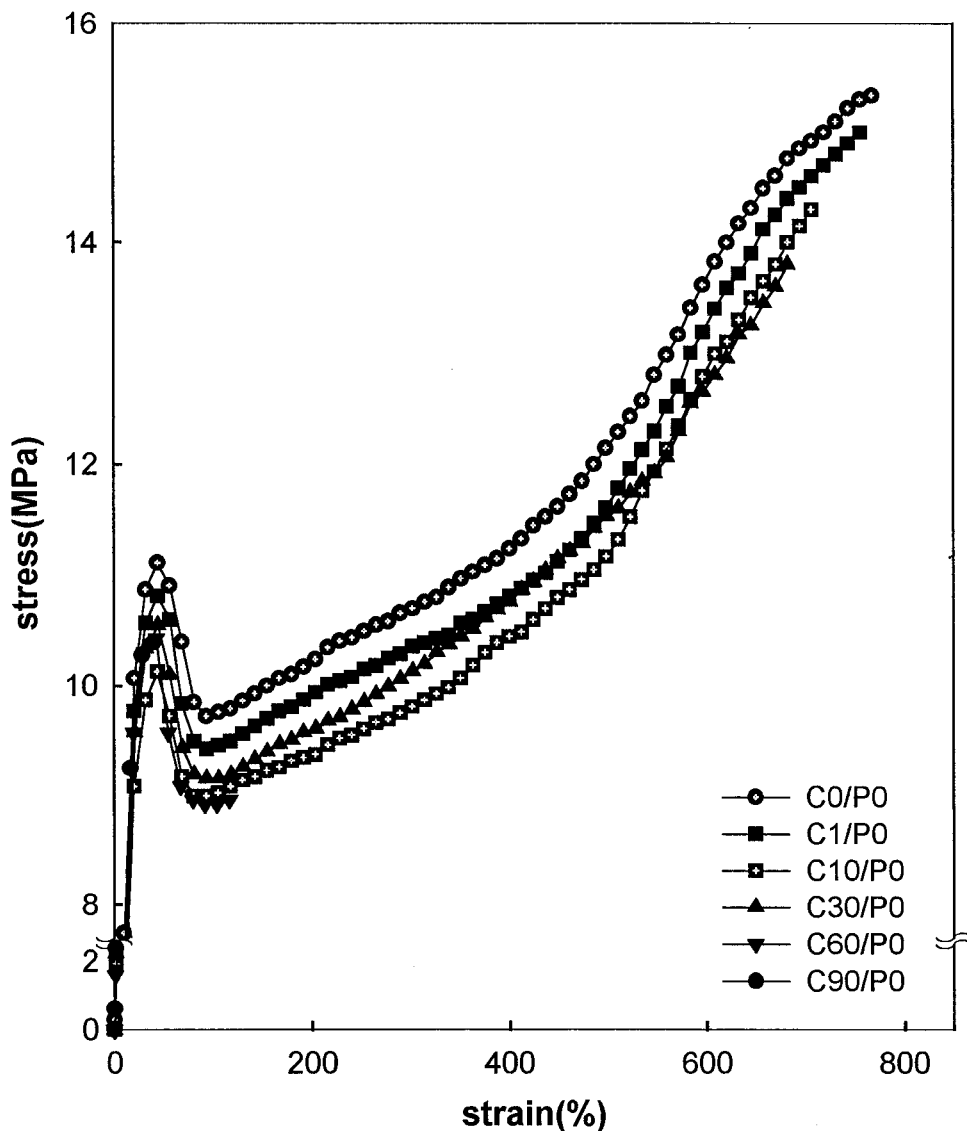


Figure 9 The stress-strain curves for film samples C0/P0, C1/P0, C10/P0, C30/P0, C60/P0, and C90/P0.

CONCLUSIONS

The LDPE film was surface modified by chromic acid [$K_2Cr_2O_7/H_2O/H_2SO_4$ (4.4/7.1/88.5)] treatment at 70°C with a subsequent oxygen plasma treatment to improve the interfacial adhesion between the evaporated copper film and the LDPE film. The effect of the treatment time on the surface chemistry and topography, mechanical properties of LDPE film, and adhesion strength of evaporated copper metal film on the LDPE film surface were investigated. It was demonstrated by ATR-FTIR and ESCA that the surface modifi-

cation with chromic acid and oxygen plasma was effective in introducing polar groups on the LDPE film. The number of polar groups and the surface roughness increased with increasing treatment time of chromic acid and plasma. Water contact angle significantly decreased with increasing treatment time of chromic acid and plasma, respectively. The combination treatment of oxygen plasma with chromic acid drastically decreased contact angle. When the treatment time of chromic acid and oxygen plasma was above 30 min and 30 sec, respectively, the contact angle was below 20°. With an increasing treatment time of

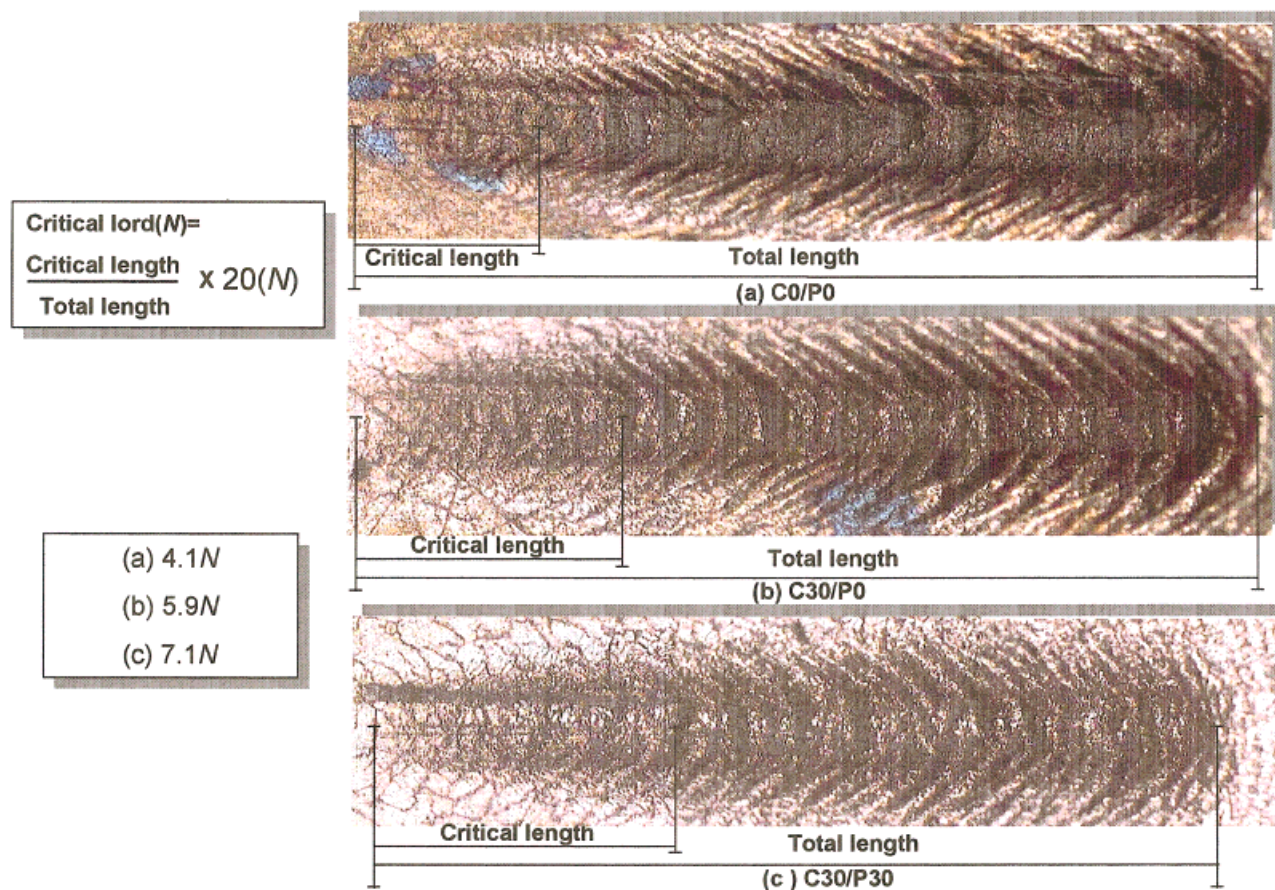


Figure 10 Electron micrographs of scratch channels of Cu/LDPE specimens: (a) C0/P0, (b) C30/P0, and (c) C30/P30. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

chromic acid, the tensile strength of LDPE film decreased remarkably, and the film color changed after about 10 min and then blackened after 30

Table II Scratch Test Results for LDPE Films Treated With Chromic Acid and Oxygen Plasma

Sample Code	Critical Length ^a (μm)	Total Length (μm)	Critical Load ^b (N)
C0/P0	335	1635	4.10
C0/P30	408	1657	4.92
C10/P0	412	1617	5.09
C10/P30	426	1592	5.85
C30/P0	480	1640	5.35
C30/P30	545	1530	7.12

^a Length from starting point to a point of periodic fold.

^b Critical load = critical length/total length × total load (20 N).

min. With the scratch test, the adhesion between copper and LDPE was found to increase with increasing treatment times of chromic acid and oxygen plasma up to 30 min and 30 sec, respectively. From these results, we concluded that the optimum treatment times with chromic acid and oxygen plasma were about 30 min and 30 sec, respectively, to improve the adhesion of copper/LDPE system.

REFERENCES

1. Bag, D. S.; Kumar, V. P.; Maiti, S. *J Appl Polym Sci* 1999, 71, 1041.
2. Bag, D. S.; Ghosh, S. N.; Maiti, S. *Eur Polym J* 1998, 34, 855.
3. Blais, P.; Carlsson, D. J.; Csullog, G. W.; Wiles, D. M. *J Colloid Interface Sci* 1974, 47, 36.

4. Bezigian, T. *Tappi J* 1992, 75, 139.
5. Shard, A. G.; Badyal, J. P. S. *Macromolecules* 1992, 25, 2053.
6. Foerch, R.; McIntyre, N. S.; Hunter, D. H. *J Polym Sci Part A: Polym Chem* 1990, 28, 803.
7. Ladizesky, N. H.; Ward, I. M. *J Mater Sci* 1983, 18, 533.
8. Nuzzo, R. G.; Smolinsky, G. *Macromolecules* 1984, 17, 1013.
9. Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. *J Am Chem Soc* 1977, 99, 4736.
10. *Plasma Surface Modification of Polymers: Relevance to Adhesion*; Strobel, M.; Lyons, C. S.; Mittal, K. L., Eds.; Utrecht, The Netherlands: VSP, 1994.
11. Gerenser, L. J. *J Vac Sci Technol A* 1988, 6, 2897.
12. *Metallized Plastic 5 & 6: Fundamental and Applied Aspects*; K. L. Mittal, Ed.; Utrecht, The Netherlands: VSP, 1998.
13. Mittal, K. L. *J Vac Sci Technol* 1976, 13, 19.
14. Wrobel, A. M.; Kryszewski, M.; Rakowski, W.; Okoniewski, M.; Kubacki, Z. *Polymer* 1978, 19, 908.