Chemical Modification of LDPE Film

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ABSTRACT: Low-density polyethylene (LDPE) film was chemically modified by chromic acid treatment to generate polar groups on the surface. The film samples were etched by chromic acid with variation of temperature at a constant time (30 min) and variation of time at a constant temperature (room temperature = 26° C). The variation of weight and thickness of the film samples before and after etching was measured. The surface morphology of the etched films was studied by Scanning Electron Microscopy (SEM). IR and XPS analysis revealed the introduction of polar groups like —COOH, \rangle C==O, —SO₃H on the etched LDPE film surface, which exhibited improved printability. Etching also enhanced adhesion with epoxy resin. The mechanical properties of the laminates of the two specimens of the same film sample with epoxy resin were also measured. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1041–1048, 1999

Key words: low-density polyethylene; chromic acid; etching; XPS; printability

INTRODUCTION

Low-density polyethylene (LDPE) is widely used in diverse applications due to abundant supply, low cost, good processability, low energy demand for processing, and resistance to chemicals and harsh environments. Packaging industry demands mostly LDPE because of its high specific modulus and strength where it is used directly or in the form of laminates with aluminium foil, paper, etc. However, LDPE exhibits poor adhesion property due to its nonpolar nature, which results in poor mechanical properties of these laminates. Moreover, the printability on the LDPE surface is also poor. Modification of the LDPE surface is, therefore, necessary to impart good adhesion, better strength of the prepared laminates, and also superior printability on its surface. A number of methods have been utilized to modify the LDPE surface such as corona discharge,^{1,2} plasma treatment,^{3–7} and chemical etching.^{8–14}

Fuming nitric acid has been used to etch the LDPE film in our earlier reports.^{15,16} The printability on the etched film surface was better. The mechanical performance of the laminates of the etched films with epoxy resin was also improved. This is possible due to the surface roughening and formation of reactive functional groups on the surface by etching with HNO₃, which enhance the adhesion property and the mechanical performance of the film/matrix interface through chemical interaction as well as mechanical interlocking. In continuation of the investigation, the LDPE film has been treated by chromic acid. The printability of the modified surface and also the mechanical properties of the laminates of the etched films with a commercial epoxy resin have been evaluated. Results of these studies have been the subject matter of this communication.

EXPERIMENTAL

Materials

LDPE, grade FS-300 (IPCL, Baroda) was blown into smooth films by the usual extrusion film-

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blowing technique. Chromic acid was freshly prepared by dissolving potassium dichromate (AR Grade, S.D. Fine Chem.) in hot concentrated sulfuric acid (98%) (S.D. Fine Chem.) prior to use. Brightflex Blue 20 was used without further purification.

Surface Modification

LDPE (FS-300, IPCL) film was cut into sizes of 12 \times 6 cm and the film samples were washed with acetone and distilled water, and finally dried. The dried films were then etched by chromic acid at desired temperatures for different periods of immersion in a bath. The desired temperature in the bath was maintained using a temperature controller operating within ±2°C. After acid treatment the films were immediately washed with deionized water and dried at 50°C under vacuum.

Characterization

Weight and Thickness Measurement

The weights of the films before and after etching by chromic acid were measured with the help of an analytical balance. Similarly, the thicknesses of the samples before and after the chromic acid treatment were measured with the help of a Baker Mercer thickness measuring instrument.

SEM Analysis

Surface morphology of the etched and unetched LDPE films was examined with a Cam-Scan Series II Scanning Electron Microscope.

IR Analysis

The IR spectra for virgin and chromic acidtreated films were recorded with a Shimadzu 470 IR spectrophotometer.

XPS Analysis

XPS (ESCA) spectra were obtained using a V.G. Scientific ESCA Lab MK II spectrometer using AlK_{α} (148.6 eV) radiation. X-ray radiation was operating at 240 W (12 kV and 20 mA). The analyzer chamber pressure was 10^{-9} Torr.

Printability Test

The printability test was performed at Coates of India Limited, Calcutta. The ink used was Brightflex Blue 20. The printability test was carried with Gravure RK Print Coat instrument, UK. The ink was placed on the top of the eight-step printing plate of different screens. The film was attached to the rubber roll that was drawn on the said printing plate. Thus, the film was coated with the ink having eight different shades of the same ink. The film thus printed was air dried with hot air ($\sim 60^{\circ}$ C). The nail-scratch test and adhesion test with a scotch tape were carried out immediately after drying. The shade of the printed film was compared by naked eye with a standard corona-treated LDPE film printed by the same technique to determine the stability rating of the printability of the film.

Laminate Preparation

From the acid-treated and untreated films, specimens of 8–10 cm length and 1 cm width were cut. Two of such specimens were laminated using commercial epoxy resin [Araldite, Standard (twopack), Ciba-Geigy Ltd., India] with its room temperature hardener and cured under 49 N pressure for 24 h.

Mechanical Testing

Tensile strength of the virgin LDPE film and the laminates was measured by an Instron 4204 universal testing machine at room temperature at a crosshead speed of 20 mm/min.

RESULTS AND DISCUSSION

Weight and Thickness Measurements

The variation of percentage weight and thickness for the chromic acid-treated LDPE film is shown in Figures 1 and 2. At a constant temperature $(26^{\circ}C)$ the weight of the film increases with time of etching. Also at constant time (30 min) of immersion in chromic acid, the weight of the film increases with temperature. The percentage increase in thickness of the film also increases similarly with the etching time and temperature. However, both the increases in the weight and the thickness of etched films level off after some time.

SEM Analysis

The SEM micrographs of chromic acid-treated and untreated LDPE films are shown in Figure 3. Pitting and surface roughening are observed for the treated films. The improvement of wettability and adhesion of a polymer is often attributed to



Figure 1 The variation of percentage weight gain of LDPE film with time (at 26°C) and temperature (for 30 min) of chromic acid treatment.

the increased roughness of its surface.¹⁷ Therefore, the pitting and surface roughness are expected to help adhesion due to increased surface area for bonding and mechanical interlocking and, hence, better mechanical performance of the laminates.

IR Analysis

IR spectroscopy has been used to study the changes occurring upon chemical modification and/or oxidation of LDPE film. The IR spectra of chromic acid-treated and untreated LDPE films are shown in Figure 4. From the IR analysis of the chromic acid-treated LDPE films, the appearance of strong bands at $1700-1712 \text{ cm}^{-1}$ confirms the presence of C=O of -COOH group. A band at 1620–1627 cm⁻¹ corresponds to C = 0 group adjacent to an olefinic double bond or enolic)C=O group. A strong band at 3580-3590 cm⁻¹ is due to the O—H stretching. The appearance of a strong band at $1170-1180 \text{ cm}^{-1}$ is assigned to the S= $\overline{0}$ group of sulfonic acid. All these absorption peaks were absent in the virgin LDPE film. The absorption intensities of different groups are plotted against the time and temperature of etching (Fig. 5). The intensity of these absorption peaks increases with an increase of the time and temperature of etching with chromic acid. This indicates that the number of functional groups increases with the extent of etching.

XPS Analysis

Formation of some polar groups in the chromic acid-treated LDPE films is observed by IR spectroscopy. However, it is difficult to analyze the surfaces by IR study because of deep penetration (approximately 10 μ m) of internal reflection IR spectroscopy. But recent advances in XPS (ESCA) with shallow penetration (approximately 1 nm) greatly enhance its sensitivity for surface analysis. The XPS spectra of the virgin and chromic acid-treated LDPE films are shown in Figure 6. The XPS spectrum of the virgin film indicates a low level of oxygenated species and complete absence of sulfonated species. But O_{1s} and S_{2p} signals of the chromic acid-treated films indicate the presence of polar groups containing oxygen and sulfur on the LDPE surface. Table I shows the O/C and the S/C atomic ratios of untreated and treated films. It was observed that the O/C and the S/C ratios were greater in the treated films than those in the untreated film.

The deconvoluted XPS spectra of C_{1s} , O_{1s} , and S_{2p} for the chromic acid-treated film are shown in Figure 7. The binding energies, areas, and full widths at half maxima (FWHM) calculated from the deconvoluted XPS spectra are presented in Table I. The C_{1s} spectra of chromic acid-treated films show peaks at 285.0, 286.7, 287.8, and 289.2 eV, which can be assigned to $-CH_2$, $-CH_2O-$ (e.g., ether, alcohol, ester, or hydroperoxide), C=O (e.g., aldehyde or ketone) and -COO-(e.g., carboxylic acid or ester), respectively.¹⁸ The deconvolution of the C_{1s} peak of the unetched film shows a single peak at 285.0 eV, indicating the presence of only C-C bonds in the films.

Similarly, the virgin LDPE film shows only a single O_{1s} peak at 531.5 eV. The shift of O_{1s} peak of the chromic acid-treated films towards higher binding energies (>531.5 eV) indicates that the relative concentration of groups containing oxy-



Figure 2 The variation of percentage thickness gain of LDPE film with time (at 26°C) and temperature (for 30 min) of chromic acid treatment.



Figure 3 Scanning electron micrographs of (a) virgin and (b) chromic acid-treated (for 30 min at 45°C) LDPE films.

gen, mostly carboxyl groups, increases. The deconvoluted O_{1s} spectra of chromic acid-treated films show peaks at 532.2, 534.6, and 535.3 eV, which can be assigned to C=O, -(O=S=O)-, and -O(C=O)-, respectively.

The XPS spectrum of the virgin LDPE shows no peak at this region, indicating the absence of any sulfur containing groups on its surface. The S_{2p} spectrum of the chromic acid-treated films, on the other hand, shows peaks at 165.0, 167.8, and 169.1 eV, which can be assigned to sulfide, sulfoxide, and sulfone groups respectively.¹⁹

Mechanical Properties

Table II presents the mechanical properties of virgin and the chromic acid-treated LDPE film samples. Variation of tensile strength of the film with time and temperature of chromic acid treat-



Figure 4 Infrared spectra of virgin and chromic acidtreated LDPE films.

ment is shown in Figure 8. The tensile strength of the film increases initially in the same manner as the concentration of the polar groups increases on the surface (Fig. 5). This indicates the chemical interaction and also hydrogen bonding caused by the generated polar groups on the surface of the etched film. However, the lower tensile strength is observed for the film treated by chromic acid at 60°C, which may be due to chain degradation.

Table III represents the mechanical performance of the laminates made up of the chromic acid-treated LDPE films with epoxy resin (Araldite). It is observed that the tensile strength



Figure 5 The variation of IR absorption peak intensities of different polar groups $(1. -COOH, 2. -SO_3H)$ with time (at 26°C) and temperature (for 30 min) formed due to chromic acid treatment of LDPE films.



Figure 6 The XPS spectra of untreated and chromic acid-treated LDPE film.

of the laminates made up of the etched LDPE film samples is better than that of the virgin LDPE film laminate sample. The variation of tensile strength of the laminates prepared with etched films with time and temperature of the chromic



Figure 7 Deconvoluted XPS spectra of C_{1s} , O_{1s} , and S_{2p} of chromic acid-treated LDPE films.

acid treatment is shown in Figure 9. The tensile strength increases with time of etching at 26°C up to 12 h. It also initially increases with etching for 30 min with temperature higher than room temperature and reaches a maximum at 45°C and then decreases. The trend of increase of tensile

Film Code	Element	Peak Position (eV)	Area	FWHM	O/C	S/C
А	C_{1s}	285.0	260.3	_	0.063	_
	0_{1s}^{1s}	531.44	16.5	_	_	_
В	C_{1s}	285.0	943.2	2.400	0.517	0.042
	15	286.7	44.0	1.440		
		287.8	30.0	1.050		
		289.2	22.5	1.680		
	O_{1s}	532.2	552.0	3.600		
	15	534.6	15.6	1.800		
	S_{2n}	535.3	3.12	0.720		
	2p	165.0	318.0	2.760		
		167.8	9.72	0.720		
		169.1	6.24	0.600		

 Table I
 Binding Energies, Peak Areas, and Full Widths at Half Maxima (FWHM) Calculated from the Deconvoluted XPS Spectra

A, untreated LDPE film; B, chromic acid treated (12 h, 26°C) LDPE film.

Treatmen	t Conditions			
Time (h)	Temp. (°C)	$\begin{array}{c} \text{Thickness} \\ \text{(mm)} \times 10^2 \end{array}$	Elongation at Break (%)	
	_	5.2	148.5	
0.25	26	5.5	210.6	
3	26	6.2	176.2	
6	26	4.3	143.5	
12	26	6.2	157.3	
0.5	30	5.5	238.6	
0.5	45	6.0	189.7	
0.5	60	6.3	127.4	

Table IITensile Properties of Virgin andChromic Acid-Treated LDPE Films

strength is quite similar to the increase of absorption intensities of the polar groups (Fig. 5). It may be concluded that the formation of polar groups on the surface of the etched LDPE film is responsible for higher strength of the laminates through the chemical interactions with the epoxy resin. Also, surface roughening and pitting (as observed by SEM analysis, Fig. 3) due to the chromic acid treatment help improve the tensile strength through the mechanical interlocking.

In our earlier study, the optimum condition for etching with fuming nitric acid is 70°C and 25 min for LDPE and LDPE/LLDPE (50/50) films. However, longer exposure reduces mechanical properties of these laminates.¹⁶ LDPE films treated at 60°C for 30 min with fuming nitric acid do not show reduction in mechanical strength.¹⁵ Ultrahigh molecular weight polyethylene fibers on treatment with fuming nitric acid at 70°C for



Figure 8 The variation of tensile strength (TS) of virgin LDPE film with time and temperature of chromic acid treatment.

Table IIITensile Properties of the LaminatesMade Up of Chromic Acid-Treated LDPE Filmswith Epoxy Resin

Treatment	Conditions			
Time (h)	Temp. (°C)	$\begin{array}{c} Thickness \\ (mm) \times 10^2 \end{array}$	Elongation at Break (%)	
_	_	19.5	182.5	
0.25	26	21.5	141.3	
1	26	16.8	145.6	
3	26	18.2	159.9	
6	26	17.1	149.1	
12	26	17.6	157.6	
0.5	30	18.6	110.4	
0.5	45	16.9	139.3	
0.5	60	15.2	153.8	

30 min were reported to show lowering of mechanical strength due to chain degradation.¹⁴ On the other hand, LDPE films treated with chromic acid at 70°C become blackened after 30 min. This perhaps points out that chromic acid is a stronger oxidizing etchant than fuming nitric acid for polyethylene.

Printability Test

Polyethylene is nonpolar in nature, whereas printing inks are usually polar. So permanent printing on the polyethylene surface is very difficult. However, printability is expected to be improved by introducing polar groups onto the sur-



Figure 9 The variation of tensile strength (TS) of the epoxy resin-laminated LDPE film with time and temperature of chromic acid treatment.

	Treatment Conditions				Scratch/
Film	Time (h)	Temp. (°C)	Printability	Adhesion ^a	Hardness ^a
Untreated	_	_	7	0	0
Treated	1	26	10	8	0
Treated	12	26	10	9	2
Treated	0.5	30	8	8	2
Treated	0.5	45	8	9	2
Treated	0.5	60	9	9	3
Treated LDPE (Coates)	—	_	10	10	10

Table IVPrintability and Adhesion Analysis of Chromic Acid-Treated LDPE Film, Ink Used:Brightflex Blue 20

^a 0, poor; 10, excellent.

face. Table IV presents the result of printability and adhesion tests of the LDPE films. The printability grading is 7 for the virgin LDPE samples, which show little or no adhesion properties. However, on treating with chromic acid, both the printability and adhesion properties have improved appreciably. With the increase of etching time and temperature, both the printability and adhesion properties increase. The generation of some polar groups on the film surface due to etching with chromic acid facilitates printability and adhesion properties. The scratch/nail hardness value of the printability test indicates the property of permanent printing on the chromic acidtreated LDPE film surfaces.

In case of the fuming nitric acid (FNA)-treated LDPE films, printability property was also improved. But there was no improvement in adhesion property of the etched films. The scratch/nail hardness of such FNA treated LDPE films was found to be zero.¹⁵ This might be due to the low level of introduction of functional groups on the surface, or the nitrogen containing functional groups are not polar enough for printing by Brightflex Blue 20.

CONCLUSION

The surface treatment of LDPE film by chromic acid introduces polar groups like —COOH, — SO_3H , etc., onto the film surface. The mechanical performances of the laminates of chromic acid-treated LDPE film is improved due to better adhesion with epoxy resin. The excellent tensile strength of the laminates may be caused by the mechanical interlocking due to surface roughening (as observed by SEM analysis), as well as chemical interaction or bonding with epoxy resin due to generation of active polar groups on the film surface. Improved printability of the chromic acid-treated LDPE films may be due to the formation of chemical bonds between the ink and the generated functional groups on the surface. As an etchant for LDPE, chromic acid appears to be better than fuming nitric acid.

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