

Surface Modification of LDPE Film by Chemical Processes with Ni²⁺ and Ammonium Persulfate

D. BANDOPADHAY, A. B. PANDA, P. PRAMANIK

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

Received 5 June 2000; accepted 22 November 2000

ABSTRACT: Chemical modification of the surface of low-density polyethylene (LDPE) film was performed with an aqueous solution of ammoniacal ammonium persulfate in the presence of Ni²⁺ ions, where the polar groups were generated on the surface of the LDPE film. The surface of the LDPE film was modified chemically with an ammoniacal solution of ammonium persulfate (1.1M) and Ni(SO₄)₂ (0.02M) heated at about 70°C for 3 h. The morphologies of the surfaces were studied with scanning electron microscopy and infrared spectroscopy; electron spectroscopy for chemical analysis revealed the introduction of polar groups on the surface, which improved printability and adhesion properties. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 406–415, 2001

Key words: low-density polyethylene; surface modification; chemical modification; nickel ion and persulfate; adhesion

INTRODUCTION

From the mid-20th century, different types of polymers have been widely used in our daily lives. Among the different types of polymers, polyethylene (PE) is used widely for its abundant supply, good chemical resistance, good processability, low-energy demand for processing, and low cost. In the packaging industries,¹ it is widely used because of its high specific modulus and strength. In the form of laminates, it is widely used in the lather industry,² where its contribution to adhesion is greatly needed.

Generally, the presence of polar groups and the surface topography of the substrate play a crucial role in obtaining good adhesion and, hence, good mechanical performances of laminates. However, low-density polyethylene (LDPE) has limitations in its adhesion properties because of its own non-

polar nature. To improve its surface nature, it is essential to generate polar groups on its surface. Different attempts have been made, such as plasma treatment,^{3–7} corona discharge,^{8–9} and chemical etching,^{10–15} to improve its surface characteristics. Changes in chemical composition and also the morphology of the surface by chemical treatments enhance its adhesion properties^{16,17} and mechanical properties and the mechanical performance of the film matrix interface through chemical interaction and a mechanical interlocking mechanism.

Recently, fuming nitric acid has been used as an etchant for ultra-high-molecular-weight polyethylene fibers to prepare composites with epoxy resin.¹⁸

In this article, we present our studies on the modification of the surface of LDPE films through immersion in a water bath (at ca. 70°C) with an aqueous solution of ammoniacal ammonium persulfate and Ni²⁺ ion salt. The introduction of polar groups was characterized by infrared (IR) spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). The print-

Correspondence to: P. Pramanik (pramanik@hijli.iirkgp.ernet.in).

Journal of Applied Polymer Science, Vol. 82, 406–415 (2001)
© 2001 John Wiley & Sons, Inc.

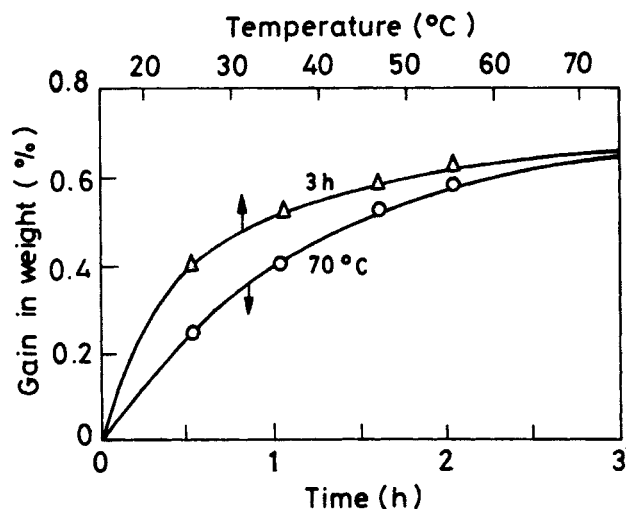


Figure 1 Variation of percent weight gain of persulfate-treated LDPE film with the time of treatment (at 70°C) and temperature (for 3 h).

ability of the modified surface and the mechanical properties of the laminate-modified surface with commercial epoxy resin were evaluated. Results of these studies are presented.

EXPERIMENTAL

Materials

LDPE, grade FS300 (IPCL, Baroda, India), was blown into smooth films with the usual extrusion-film blowing technique. Ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$; MERCK India Ltd., ammonia (S. D. Fine Chem, India), and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (BDH, India) were used in this investigation. Brightflex Blue 20 was used without further purification in the test of printability.

Surface Modification

The LDPE film was cut into 12×6 cm pieces that were 1-mm thick, and the film samples were washed with acetone and then with distilled water and dried in an oven at 50°C. The dried films were then treated with an ammonium persulfate and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ solution in the appropriate molar ratio at the desired temperature for different periods of immersion in a water bath. After chemical treatment, the films were washed with deionized water and dried at 50°C under vacuum.

Characterization

Weight and Thickness Measurements

The weights of the films were measured with an analytical balance. The thicknesses of the films

were measured with the help of a Baker Mercer thickness-measuring instrument.

SEM Analysis

The surface morphologies of the modified and unmodified LDPE films were examined with a Cam-Scan series II scanning electron microscope.

IR Analysis

The IR analyses of the modified and unmodified films were performed from 400 to 4000 cm^{-1} with a Shimadzu-470 IR spectrophotometer.

XPS Analysis

XPS [electron spectroscopy for chemical analysis (ESCA)] spectra were obtained with a V. G. Scientific ESCA Lab MK II spectrometer with $\text{AlK}\alpha$ (148.6 eV) radiation. X-ray radiation was at 240 W (12 kV and 20 mA). The analyzer chamber pressure was 10^{-9} Torr.

Laminate Preparation

Specimens 8–10 cm in length, 1 cm wide, and 1 mm thick were cut from the chemically treated films. Two of these specimens were laminated with commercial epoxy resin [Araldite, standard (two pack), Ciba-Geigy Ltd., India] and hardened at room temperature. IT was cured under 49 N pressure for 24 h at room temperature. The ex-

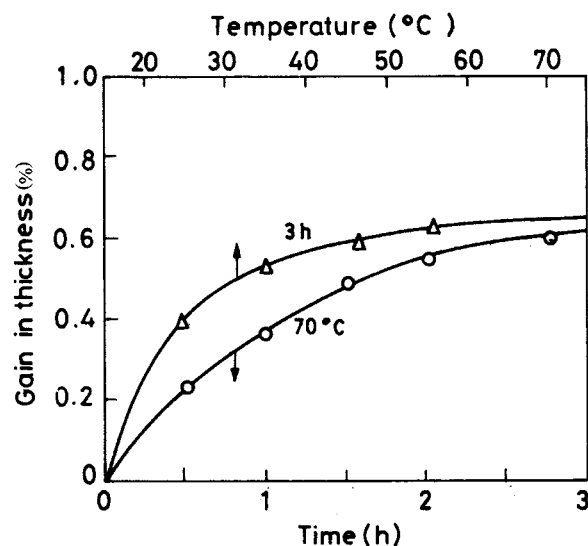
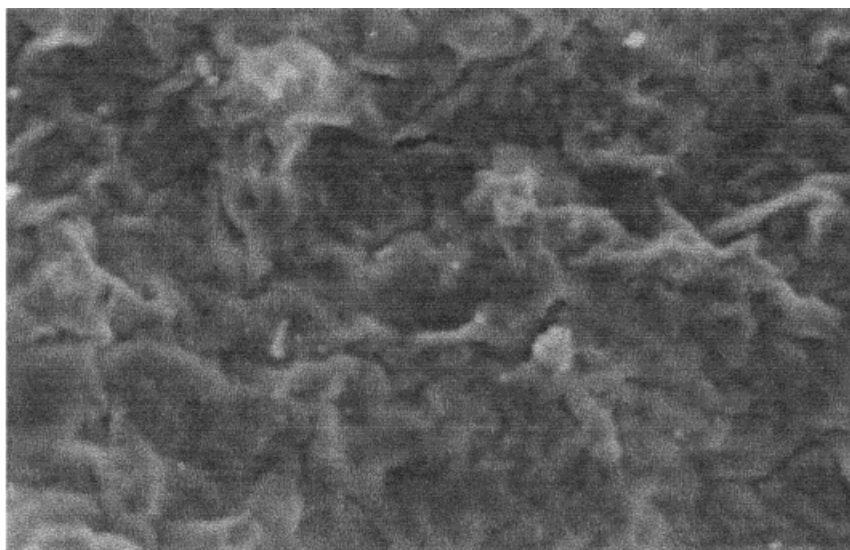
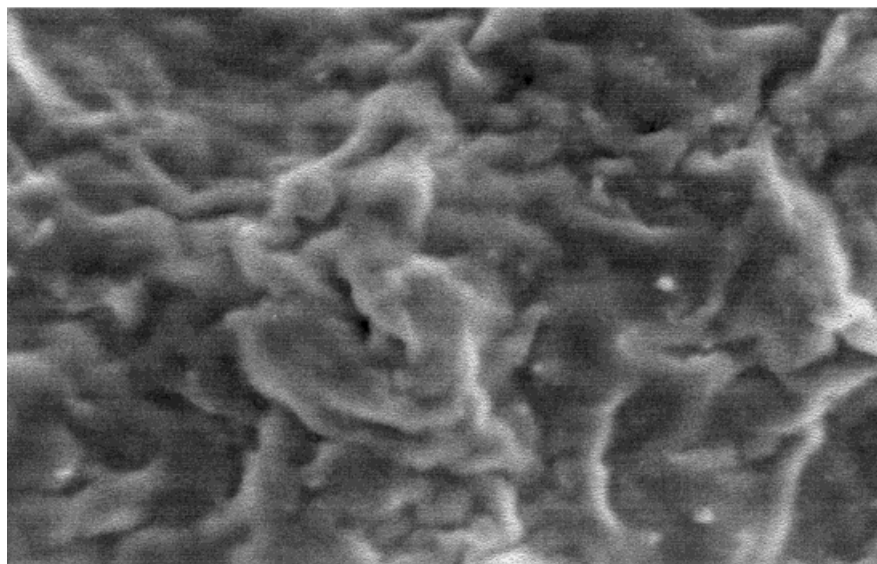


Figure 2 Variation of percent thickness gain of persulfate-treated LDPE film with the time of treatment (at 70°C) and temperature (for 3 h).



(a)



(b)

Figure 3 Scanning electron micrographs of (a) virgin and (b) persulfate-treated (at 70°C for 3 h) LDPE films.

periment was repeated separately for the unmodified films.

Printability Test

The test of printability was done at Coates of India Ltd. (Calcutta) with Brightflex Blue 20 and a Gravure R. K. print-coat instrument (United Kingdom). The ink was placed on the top of the eight-step printing plate and different screens. The film was attached to a rubber role that was

drawn on said printing plate. Thus, the film was coated with eight different shades of the same ink. The printed film was air-dried with hot air ($\approx 60^\circ\text{C}$). The nail scratch test and adhesion test with Scotch tape were carried out immediately after the film was dried. The shade of the printed film was compared by the 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.

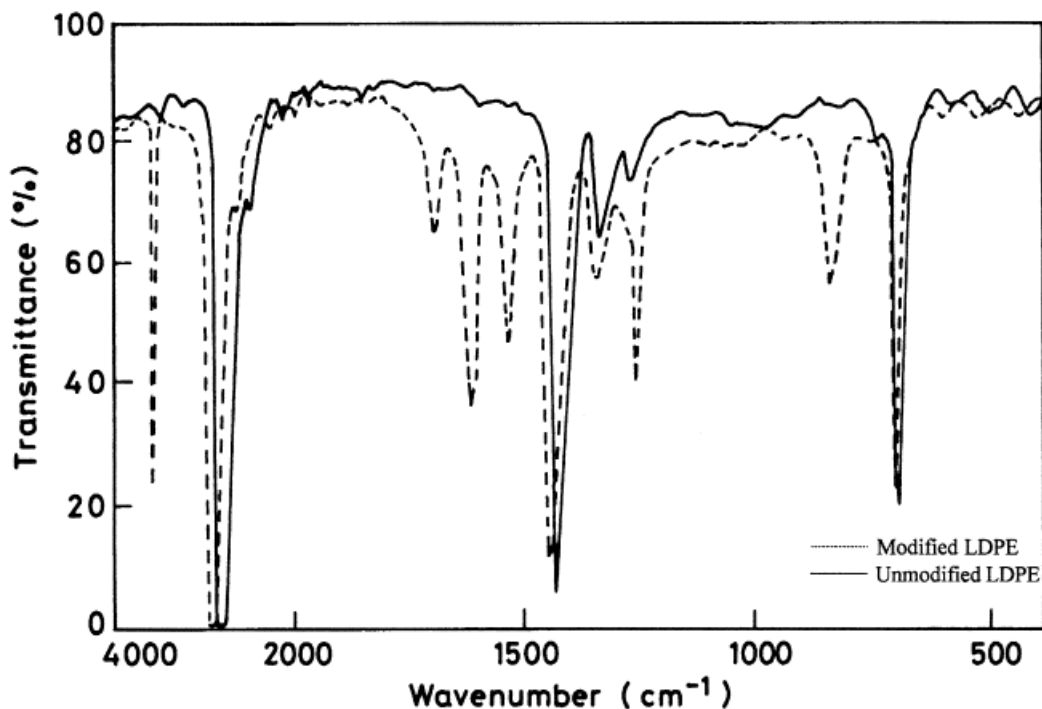


Figure 4 IR spectra of virgin (—) and 3-h persulfate-treated (· · ·) LDPE films.

Mechanical Testing

Tensile strengths (TSs) of the virgin LDPE and laminated films were measured by an Instron 4204 universal-testing machine at room temperature and a crash speed of 20 mm/min.

RESULTS AND DISCUSSION

Thickness Measurements

The variation in the weight percentage and thickness for the persulfate/ Ni^{2+} -treated LDPE film is shown in Figures 1 and 2. At a constant temperature (70°C), the weight of the film gradually increased with the increase of treatment time. Also, at a constant treatment time (3 h), the weight of the film increased with temperature. However, the increases in both the weight and thickness of the chemically modified films became asymptotic after some time. The gains in weight and thickness were measured by the equations $\frac{wt_2 - wt_1}{wt_1} \times 100$ and $\frac{d_2 - d_1}{d_1} \times 100$, respectively.

SEM Analysis

The changes in the topography and morphology of the film surfaces were studied with SEM. The

SEM micrographs of the modified and unmodified LDPE films are shown in Figure 3. Pitting and surface roughness were observed for the modified films. The adhesion of the polymer film was improved with an increase in the roughness of its surface.¹⁹ Therefore, the pitting and surface roughness were expected to help adhesion because of an increase in surface area for bonding and mechanical interlocking and, hence, better mechanical performance of the laminates.

IR Analysis

The IR spectra of the modified and unmodified LDPE films are shown in Figure 4. The strong band at $1697\text{--}1700\text{ cm}^{-1}$ confirms the presence of the $>\text{C}=\text{O}$ of the $-\text{COOH}$ group. The band at $1620\text{--}1622\text{ cm}^{-1}$ corresponds to a $>\text{C}=\text{O}$ group adjacent to an olefinic double bond or enolic $>\text{C}=\text{O}$ group. A strong band at $3540\text{--}3590\text{ cm}^{-1}$ was caused by $-\text{O}-\text{H}$ stretching. The band at $782\text{--}790\text{ cm}^{-1}$ corresponds to the $\text{C}-\text{H}$ bending vibration of alkenes activated by the chemical modification of the surface. The band at $1308\text{--}1314\text{ cm}^{-1}$ corresponds to $\text{O}-\text{H}$ bending of a carboxylic acid group. All these absorption peaks were absent in the unmodified sample. The absorption intensities of different groups were plotted against the treatment time and the tempera-

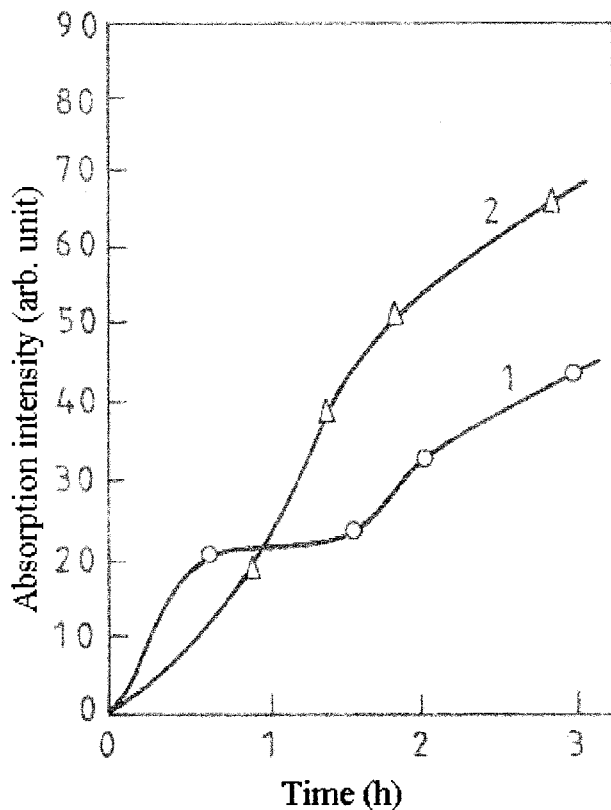
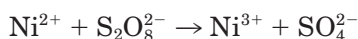


Figure 5 Variation of absorption peak intensities of different polar groups, (1) —COOH group and (2) >C=O group, with the time of persulfate treatment at 70°C.

ture of the chemical treatment (as shown in Fig. 5). The intensities of these absorption peaks increased with the increase in the treatment time and temperature. This indicates that the number of functional groups gradually increased with the increase in the extent of chemical treatment.

It is known²⁰ that the persulfate ion attacks the double-bond-producing epoxy or diol group. However, destructive oxidation of saturated hydrocarbons does not occur with persulfate alone. Destructive oxidation is possible in presence of the nickel(II) ion.²¹

The probable mechanism of chemical treatment can be presented as follows:



Persulfate oxidizes Ni^{2+} to Ni^{3+} , and the generated Ni^{3+} oxidizes the carbon chain on the surface, introducing all the polar groups, such as >C=O and —COOH.

XPS Analysis

Although the formation of some polar groups at the surface of the LDPE films was identified by IR spectroscopy, it was difficult to analyze the modification in the surface with IR spectroscopic study because of the deep penetration (ca. 10 μm) of internal reflection. However, chemical changes in a thin surface could be identified with XPS-(ESCA) with slow penetration (ca. 1 nm), which greatly enhanced its sensitivity to the chemical composition of the modified film surface. Thus, XPS could determine the presence of different functional groups at the surface quantitatively and qualitatively. XPS spectra of modified and unmodified films are shown in Figure 6(a,b). Figure 6(a,b) shows that the ratio of the areas of peak O_{1s} to peak C_{1s} is less in untreated film than in the treated film because of greater oxygenation in the chemically treated film. The O_{1s}

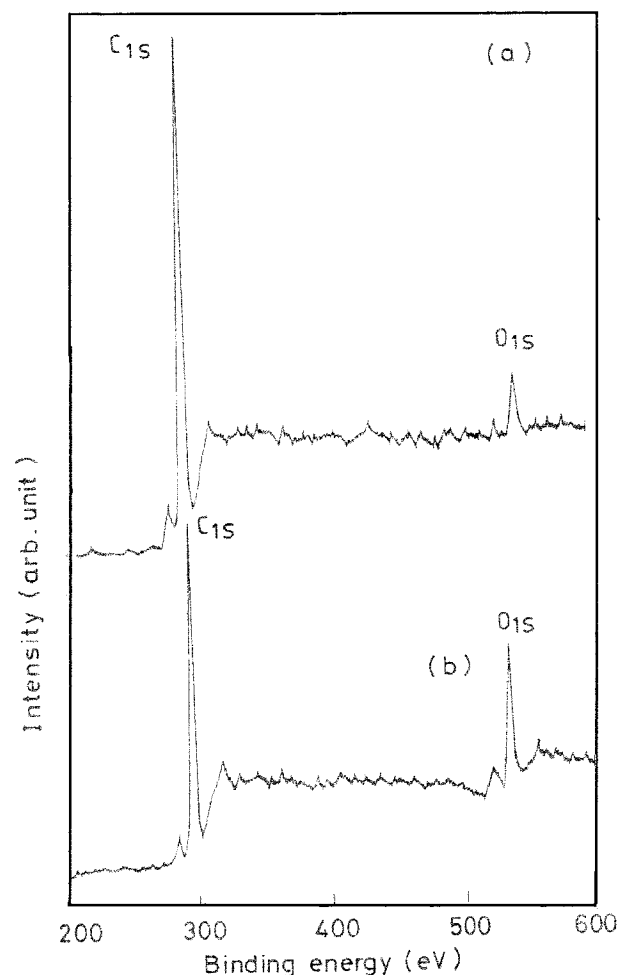
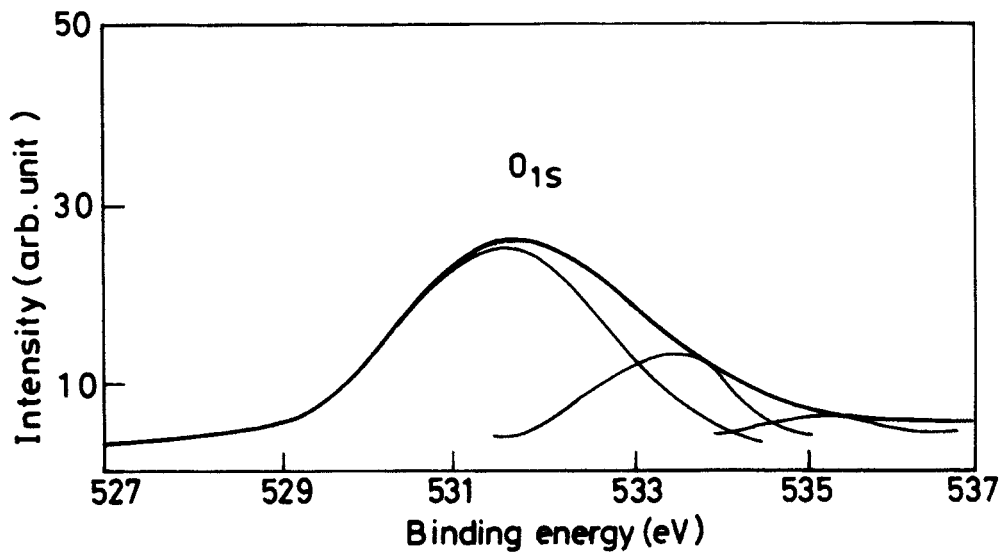
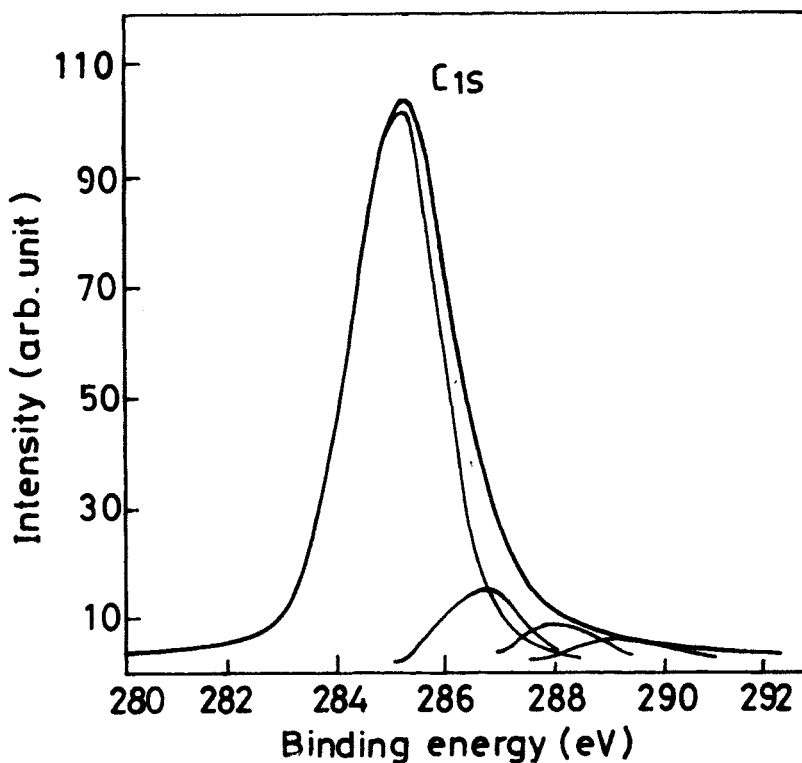


Figure 6 XPS spectra of (a) virgin and (b) persulfate-treated LDPE films.



(a)



(b)

Figure 7 Deconvoluted XPS spectra of (a) O_{1s} and (b) C_{1s} of modified LDPE film.

peak of the untreated film mostly came from a tribochemical process or a photochemical process during industrial processing. That is why the ratio of the areas of peak O_{1s} to peak C_{1s} is smaller in the untreated film than in the treated film. The signal of C_{1s} of the untreated film mostly came from CH₂.

The deconvoluted XPS spectra of C_{1s} and O_{1s} for persulfate-treated films are shown in Figure 7. In the untreated film, the spectrum indicates a low level of oxygenated species. However, O_{1s} signals of treated films indicate the presence of polar groups containing oxygen on the LDPE surface. The ob-

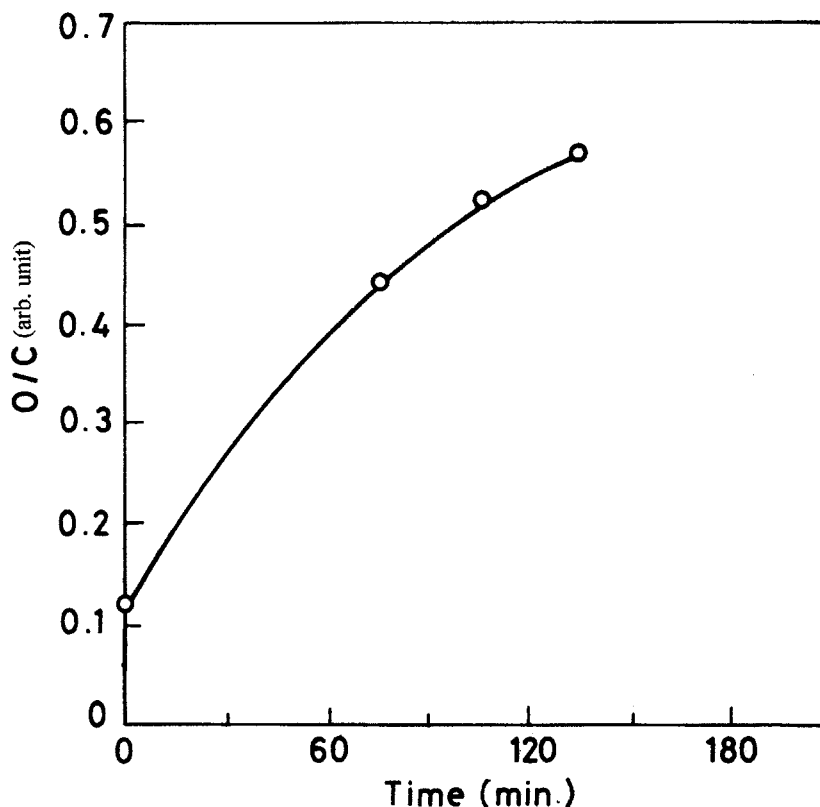


Figure 8 The variation of the O/C ratio of the XPS spectra of modified LDPE film with the time of treatment.

served O/C ratio was greater in the treated films than in untreated films, and it generally increased with the treatment time and became asymptotic after some time, which is evident from XPS spectra.

The binding energies, peak-areas, and full widths at half maxima of the deconvoluted XPS spectra (Fig. 7) of C_{1s} and O_{1s} of chemically treated LDPE films were calculated. The C_{1s} spectra for treated films showed peaks at 285.0, 286.5, 288.0, and 289.0 eV that could be assigned to $-\text{CH}_2$, $-\text{CH}_2\text{O}$ (ether, alcohol, ester), $>\text{C}=\text{O}$ (aldehyde, ketone), and COO^- (carboxylic acid, esters), respectively.²² Besides the peak of C_{1s} of the carboxylic acid group, the other peaks were weak. The deconvolution of the C_{1s} peak of the untreated film shows it to be a single peak, indicating the presence of only $-\text{CH}_2-\text{CH}_2-$ functionality in the film.

The shift of the O_{1s} peak (from 531.5 eV) of the modified films toward higher binding energies compared with that of unmodified films indicates that the relative concentration of oxygen connected with carbon having sp^2 hybridization in $-\text{COOH}$ increased. The deconvoluted O_{1s} spectra

of persulfate-treated film showed peaks at 532.2 and 535.3 eV that could be assigned to $\text{C}=\text{O}$ and $-\text{O}(\text{C}=\text{O})-$, respectively. The XPS spectra of the virgin LDPE film showed no peak in these regions, which indicates the absence of $-\text{COOH}$ and other oxygen-containing groups such as $>\text{C}=\text{O}$.

Mechanical Properties

Variations of TS of the films after chemical modification with treatment time and temperature are shown in Figure 9(a). The TS of the film increased initially in the same manner as the concentration of the polar groups increased on the surface. This indicates that the chemical interaction and hydrogen bonding caused by the generated polar groups on the surface of the chemically modified films resulted in a stronger adhesion process.

The mechanical performance of the laminates made up of chemically modified LDPE films with epoxy resin (Araldite) was studied. The TS of the modified and laminated LDPE

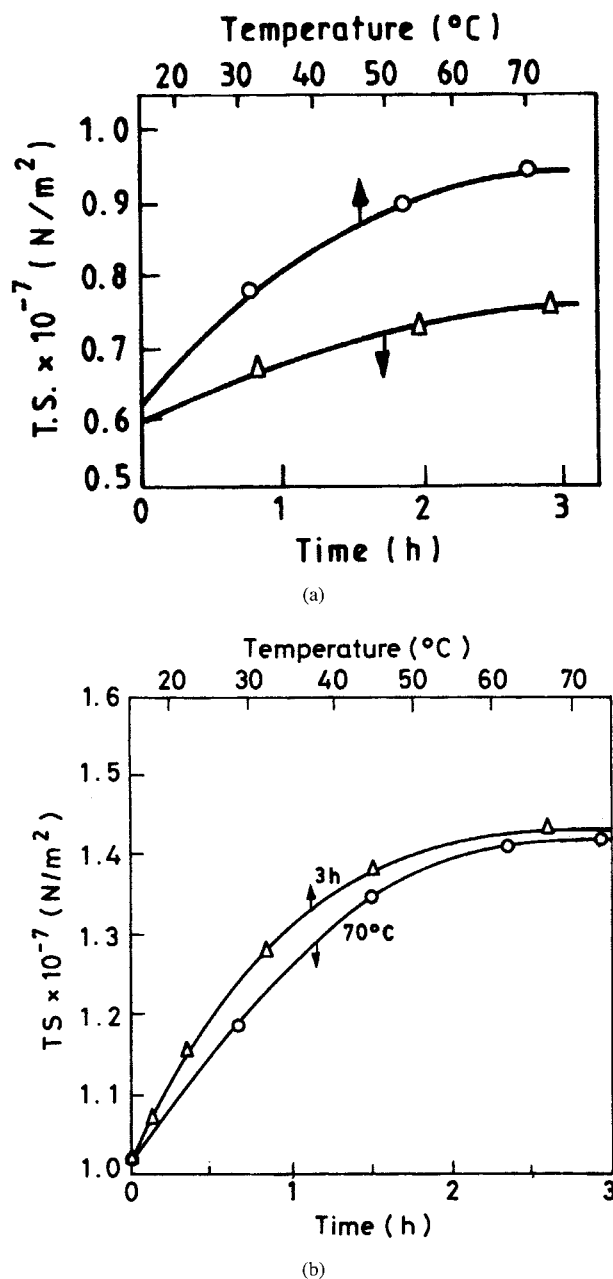


Figure 9 Variation of the TS of (a) modified and (b) epoxy-resin-laminated LDPE films with the time and temperature of persulfate treatment.

film was better than that of unmodified and laminated LDPE film. The variation in TS of the laminates prepared with chemically treated films with the time and temperature of the persulfate treatment is shown in Figure 9(b). The TS increased with the increase in the time of chemical treatment at 70°C up to 3 h. The trend of the increase in the TS was 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 chemically treated LDPE film was responsible for the higher strength of the laminates through the chemical interactions with the epoxy resins. Also, surface roughening and pitting (as observed by SEM analysis; Fig. 3) caused by the persulfate treatment helped to improve the TS through mechanical interlocking.

We maintained the maximum concentration of nickel ion (0.02M) when the effects of persulfate ion became asymptotic and did not produce any film of nickel oxide. The presence of ammonium salt also helped to retain the nickel ion in solution without any oxide deposition. The concentrations of persulfate and nickel ion were optimized to gain a maximum rate of oxidation without any nickel oxide deposition. The optimum concentrations were 1.1M for persulfate and 0.02M for nickel ion, which were evaluated from the intensity of the O_{1s} peaks of the oxidized film, shown in Figures 10 and 11. From Figures 10 and 11, we found that the rate of oxidation determined from the O_{1s} peak in XPS reached a maximum when the concentration of ammonium persulfate was 1.1 M; for $NiSO_4$, the peak of O_{1s} increased linearly with concentration. However, after 0.2 M was reached, a black film of NiO_2 appeared; for this reason, we tried to maintain the concentrations of ammonium persulfate and $NiSO_4$ at the previously mentioned levels. We preferred nickel sulfate for the inertness of its sulfate group. Moreover, persulfate also generated sulfate in the medium.

CONCLUSIONS

The modification of the LDPE film surface by an ammonium persulfate and $NiSO_4$ solution led to an improvement of the mechanical performance in its laminates with better adhesion with epoxy resin. Mechanical interlocking caused by surface roughening (as observed by SEM analysis) and chemical bonding with epoxy resin caused by the generation of active polar groups, such as $-COOH$ and $>C=O$ (as observed by IR and XPS analysis), on the surface of the modified LDPE films were responsible for the excellent TS of their laminates and improved printability. This may have been caused by the formation of chemical

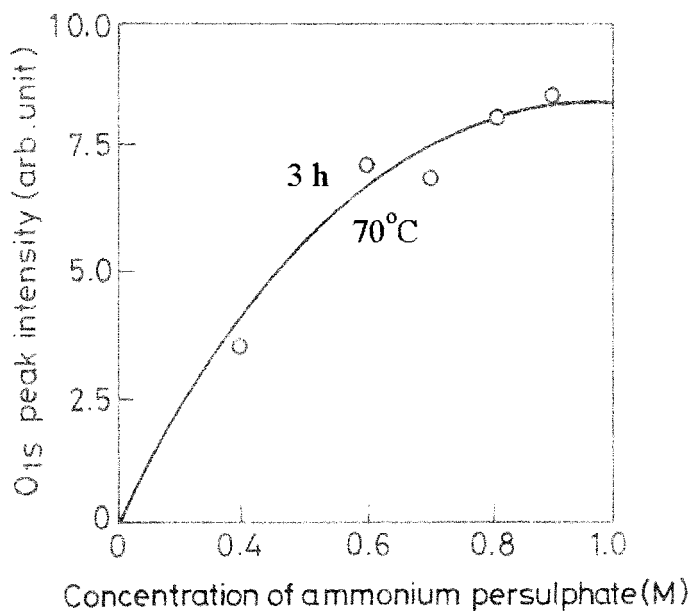


Figure 10 Variation of O_{1s} peak intensity with persulfate ion concentration.

bonding between the ink and the newly generated functional groups on the surface. Surface modification of LDPE films by this process appears to be better than other chemical process because of its easy handling.

The authors thank the Indian Institute of Technology (Kharagpur, India) for providing facilities and varied

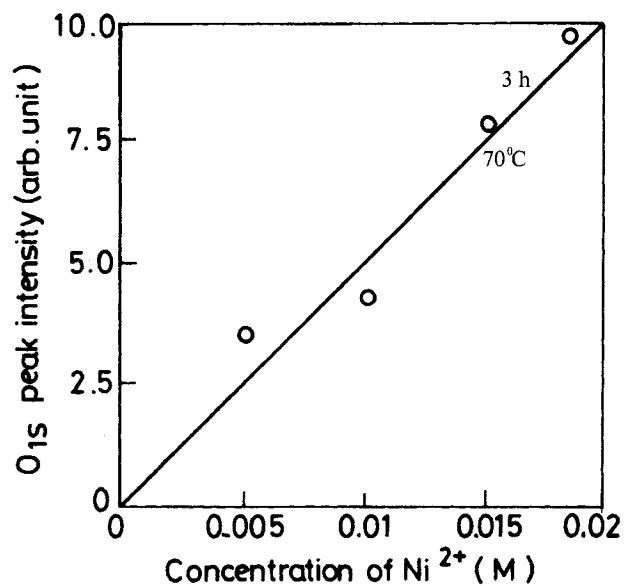


Figure 11 Variation of O_{1s} peak intensity with nickel ion concentration.

support for this investigation. The authors also acknowledge the valuable contributions made by Dr. A. Pathak, Mr. R. K. Pati, and Ms. A. Sen to this research.

REFERENCES

1. Brody, A. L.; Marsh, K. S. *The Wiley Encyclopedia of Packaging Technology*, 2nd ed.; Wiley: New York, 1997; p 752-758.
2. *Technical Literature*; Bata India, 1980.
3. Foerch, R.; McIntyre, N. S.; Hunter, D. H. *J Polym Sci Part A: Polym Chem* 1990, 28, 803.
4. Ladizesky, N. H.; Ward, I. M. *J Mater Sci* 1983, 18, 533.
5. Shard, A. G.; Radyal, J. P. S. *Macromolecules* 1992, 25, 2053.
6. Yasuda, H.; Marsh, H. C.; Brandt, S.; Reily, C. N. *J Polym Sci Polym Chem Ed* 1977, 15, 991.
7. Clark, D. T.; Wilson, R. *J Polym Sci Polym Chem Ed* 1983, 21, 837.
8. Bezigian, T. *Tappi J* 1992, 75, 139.
9. Kaplan, S. L.; Rose, P. W.; Nguyen, H. X. *Chang, H. W. SAMPE Q* 1998, July, 55.
10. Eriksson, J. G.; Golander, C. G.; Baszkin, A.; Ter-Minassian-Saraga, L. J. *Colloid Interface Sci* 1984, 100, 381.
11. Blais, P.; Carisson, D. J.; Csullog, G. W.; Wiles, D. M. *J Colloid Interface Sci* 1974, 47, 636.
12. Postema, A. R.; Doornkamp, A. T.; Meijer, J. G.; Vlekkert, H. V. D.; Pennings, A. *Polym Bull* 1986, 16, 1.

13. Ward, I. M.; Ladizesky, N. H. *Pure Appl Chem* 1985, 57, 1641.
14. Packhan D. E.; Bright, K.; Malpass, B. W. *J Appl Polym Sci* 1974, 18, 3237.
15. Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *J Am Chem Soc* 1977, 99, 4746.
16. Clark, D. T.; Feast, W. Y. *Adhesion in Polymer Surface*; Wiley, 1978; pp 213–232.
17. Souheng, W. U. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982; pp 279–359.
18. Taboudoucht, T.; Opalco, R.; Ishida, H. *Polym Compos* 1992, 13, 81.
19. Wrobel, A. M.; Kryszewski, M.; Rakowski, W.; Okoniewski, M.; Kubacki, Z. *Polymer* 1978, 9, 908.
20. Hains, A. H. *Method for the Oxidation of Organic Compounds*; Academic: London, 1974; p 174.
21. Pramanik, P. Unpublished work.
22. Briggs, D.; Brewis, D. M.; Konieczko, M. B. *J Mater Sci* 1976, 11, 1270.