

Surface Modification of Low-Density Polyethylene Films by a Novel Solution Base Chemical Process

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ABSTRACT: The surfaces of the film samples of low-density polyethylene (LDPE) were chemically modified with an aqueous solution of ammonium persulphate solution (0.1 M) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.2 M) heated to about 80°C for 2.5 h for which polar groups like $-\text{OH}$, $-\text{CO}$, $-\text{COOH}$, etc., were generated on the surface of the LDPE films. The modified films were analyzed by Infrared (IR) spectroscopy, Scanning Electron Microscopy (SEM), and Electron Spectroscopy for Chemical Analysis (ESCA). New surface of LDPE produced

by this modification, demonstrated reasonable oxygen incorporation on the surface of polymer films through chemical bonding, which is essential for adhesion processes. For these chemical changes the extent of printability and adhesion. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3046–3051, 2004

Key words: LDPE; chemical modification; oxygen incorporation; printability; adhesion

INTRODUCTION

Polyethylenes are widely used in various industries because of its abundant supply, good processibility, and low energy demand for processing, low cost, and high chemical stability. In the packaging industry it is widely used directly or in the form of laminates with aluminum foil, paper, or other polymeric materials.¹ In the leather industry it is used widely as shoe-shoal.²

Surface topography and presence of polar groups on the surface play a crucial role for obtaining good adhesion, as adhesion occurs through chemical interactions as well as mechanical interlocking between the surface and adhesive. Among the polyethylenes, low-density polyethylenes (LDPE) are used widely for its high specific modulus and strength. But it exhibits poor adhesion property due to its smooth and nonpolar nature of its surface. Moreover, the printability on the LDPE surface is also poor for the same reason. Any change of the chemical composition and morphology of the surface may enhance the adhesion property^{3,4} and printability of LDPE film. Various attempts have been made to improve the adhesion properties of polyethylenes, such as corona discharge,^{5,6} plasma treatment,^{7–10} chemical etching,^{11–16} to improve the surface characteristics.

To improve these properties, recently fuming nitric acid^{17,18} chromic acid,¹⁹ and nickel-salt in the presence of persulphate²⁰ are used to etch the LDPE films to

improve the performance of the films in various applications.

We report here the results of our attempts to modify the surfaces of LDPE films by an aqueous solution of Fe^{3+} ion salt with ammonium persulphate at 60°C and above. The spectroscopic analysis by IR, SEM, and XPS has characterized polar groups. Generated on the surface of the films through the chemical treatment. The printability and adhesion property of the modified surface with commercial epoxy resin have been evaluated. Results of these studies are presented in this communication.

EXPERIMENTAL

Materials

LDPE, grade FS 300 (IPCL, Baroda) was blown onto smooth films of approx. 2 mm and 0.1 mm thick by the usual extrusion film blowing technique. Ammonium persulphate (MERCK India Ltd), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (BDH), $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ (S.D. Fine Chem, India) were used as the reagents.

Surface modification

LDPE film was cut into sizes of 10 × 5 cm and the film samples were washed with hydrochloric acid (HCl), acetone, and distilled water and finely dried in oven at about 60°C. Then the dried films were dipped in the aqueous solution of ammonium persulphate and $\text{Fe}(\text{NO}_3)_3$ in an appropriate molar ratio, at a desired temperature for a different periods of immersion placed in a temperature bath. After the treatment, the

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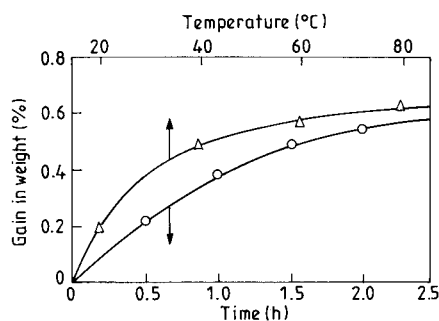


Figure 1 The variation of percentage weight gain of persulphate-treated LDPE film with time of treatment (at 70°C) and temperature (for 3 h).

film was dipped in deionized water, then washed and dried at 50°C under vacuum.

Characterization

Weight and thickness measurement

Analytical balance and Baker Mercer thickness measuring instrument were used for the measuring of weight and thickness, respectively.

SEM analysis

Surface morphology of the persulphate-treated and untreated LDPE film was examined with a Cam Scan Series II Scanning electron Microscope.

IR analysis

The IR absorption spectra of persulphate-treated and untreated film (thickness 0.1 mm) were recorded with a Shimadzu-470 IR spectrophotometer in a range of 400–4000 cm^{-1} .

XPS analysis

XPS (ESCA) spectra were obtained using a V.G. Scientific ESCA Lab MK II Spectrometer using AlK_{α} (1489.6 eV) radiation. X-ray radiation was operated at 240 W (12 kV and 20 mA). The analyzer chamber pressure was maintained at about 10^{-9} Torr.

Laminate preparation

A commercial resin and its room temperature hardener (Araldite, Grade 150GY, Ciba-Geigy Ltd, India) were mixed well and sandwiched between two similar samples (modified/unmodified film) and cured under pressure 49 N for 24 h at room temperature. The experiment was repeated separately for the unmodified film.

Printability test

The test of printability was performed at Coates of India. Ltd, Calcutta, using Brightflex blue 20 with Gravure R.K. print coat instrument, UK. The ink was placed on the top of the eight-step printing plate and different screens. The film was attached to the rubber role that was drawn on the said printing plate. Thus, the film was coated with the ink having eight different shades of the same ink. Then the film was air dried with hot air ($\approx 70^{\circ}\text{C}$). The nail scratch test and adhesion tests 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.

Adhesion testing

The strengths of adhesion of the virgin and chemically modified films were measured by a Zwick Universal Testing Machine (UTM 1445) at room temperature.

RESULT AND DISCUSSION

Weight and thickness measurement

Figures 1 and 2 show the variation in the weight percent and thickness for the persulphate/ Fe^{+3} -treated LDPE film. From the figures it is evident that gradually the weight and the thickness of the film increase with the increase of treatment time at a constant temperature (80°C). At a constant treatment time (2.5 h), the weight of the film increases with temperature. However, both the increase in weight and the thickness of chemically modified films become asymptotic after some time. The gain of weight and thickness is measured by the equations

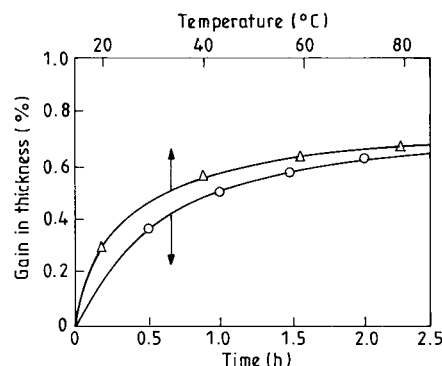


Figure 2 The variation of percentage thickness gain of persulphate-treated LDPE film with time of treatment (at 70°C) and temperature (for 3 h).

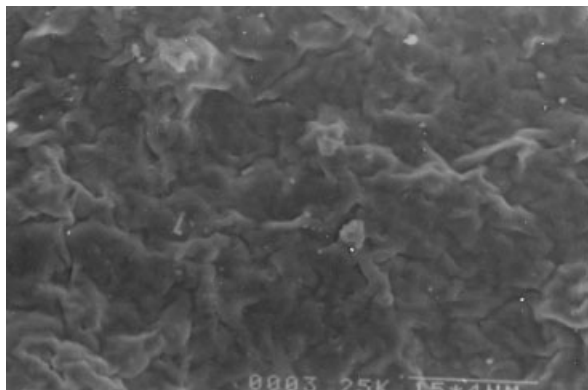


Figure 3 Scanning electron micrographs of virgin LDPE film.

$$\frac{(wt_2 - wt_1)}{wt_1} \times 100$$

and

$$\frac{(d_2 - d_1)}{d_1} \times 100$$

respectively. Suffix "1" and suffix "2" represent the initial and final value, respectively. As the boundary between modified and unmodified is not physically distinct, the thickness is measured approximately. All the data give rough idea about the effect of chemical process.

SEM analysis

The surface modifications as well as the change in topography and morphology of surface have been studied by SEM analysis. The SEM micrograph of persulphate treated and untreated LDPE films are shown in Figures 3 and 4. Pitting and surface roughing has been observed for the modified films. The

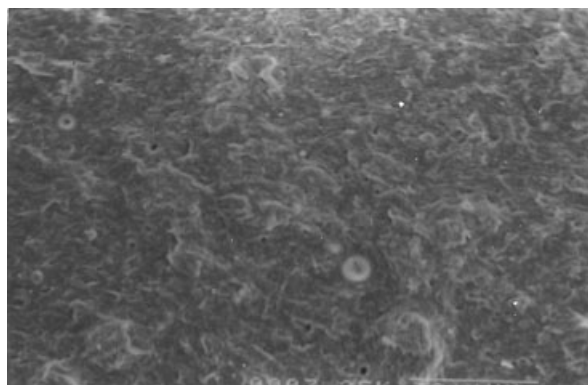


Figure 4 Scanning electron micrographs of modified (at 70°C for 3 h) LDPE film.

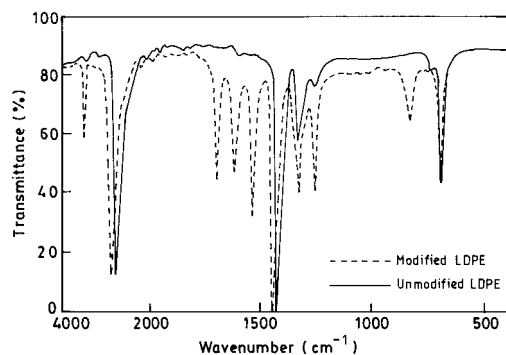


Figure 5 Infrared spectra of virgin (—) and 3 h persulphate-treated (---) LDPE film.

adhesion and printability of the polymer films are improved with an increase in the roughness of its surfaces.²¹ Therefore, the pitting and surface roughnesses are expected to help adhesion due to increase in surface area for bonding and by mechanical anchoring the substrate.

IR analysis

The absorption IR spectra of modified LDPE films (thickness 0.1 mm) is shown in Figure 5. Strong bands at 1697–1700 cm^{-1} confirm the presence of >C=O of the —COOH group. At 1620–1622 cm^{-1} , this corresponds to the >C=O group adjacent to an olefinic double bond or enolic >C=O group. A strong band at 3540–3590 cm^{-1} is due to —O—H stretching. At 782–790 cm^{-1} , this corresponds to C–H bending vibration of alkenes activated due to chemical modification of the surface. At 1308–1314 cm^{-1} , this corresponds to O–H bending of the carboxylic acid group. All these absorption peaks were absent in the unmodified sample. The absorption intensities of different groups are plotted against treatment time and temperature of chemical treatment (as shown in Fig. 6). Intensities of these absorption peaks increase with the increase in the treatment times and temperatures. This indicates that the number of functional groups gradually increases with the increase in the extent of the chemical treatment.

It is known²² that the persulphate ion attacks the double bond producing the epoxy or idol group. However, destructive oxidation of saturated hydrocarbon changes to carboxylic acids. The destructive oxidation is possible in the presence of Fe (III) ion in the presence of a strong oxidant.²³ The probable mechanism of chemical treatment can be presented as follows: $\text{Fe}^{3+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{FeO}^{2+} + \text{SO}_4^{2-}$.

Persulphate oxidizes Fe^{3+} ion to FeO^{2+} and the generated FeO^{2+} ion oxidizes carbon chain on the surface introducing all the polar groups like >C=O , —COOH , etc. It has been observed that only persul-

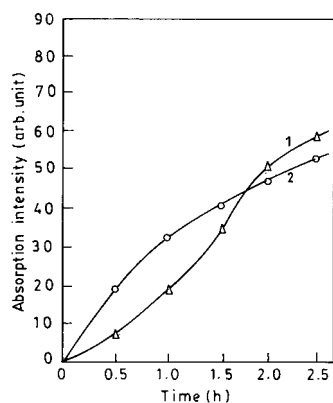


Figure 6 Variation of absorption peak intensities of different polar groups (1. —COOH and >C=O group) with time of per-sulphate treatment at 80°C .

phate does not produce any chemical changes under the above-mentioned conditions.

XPS analysis

Through the formation of some polar groups at the surface of persulphate-treated LDPE films identified by IR spectroscopy, it is difficult to analyze modification in the surface by IR studies, because of deep penetration (approx. $10\ \mu\text{m}$) of internal reflection of IR spectroscopy. Hence, chemical changes in a thin film surface may be identified by XPS- (ESCA) having shallow penetration (approx. $1\ \text{nm}$), which enhances its sensitivity to chemical composition of the surface of modified film. So by XPS spectra of films (persulphate treated and untreated), it can help to identify the presence of different functional groups in the polar surface semiquantitatively. XPS spectra of modified and unmodified films are shown in Figure 7. The deconvoluted XPS spectra of C_{1s} and O_{1s} for persulphate-treated film are shown in Figure 8(a) and (b), respectively. The unmodified film indicates a low level of oxygenated species. But O_{1s} signals of modified films indicate the presence of polar groups containing oxygen on the LDPE surface. It is observed that the O/C ratio is greater in the treated film than those of untreated films. It gradually increases with treatment time (Fig. 9), and become asymptotic after some time.

The bonding energies, peak area, and full widths at half maxima (FWHM) of the deconvoluted XPS spectra (Fig. 8) of C_{1s} and O_{1s} spectra for persulphate-treated LDPE films has been calculated. The C_{1s} spectra for treated films show peaks at 285.0, 285.5, 288.0, and 289.0 eV, which can assigned to $\text{—CH}_2\text{—}$, $\text{—CH}_2\text{OH}$ (methylene, alcohol), >C=O (aldehyde, ketone) and —COO— (carboxylic acid).²⁴ In contrast, the deconvolution of the C_{1s} peak of the unmodified film shows

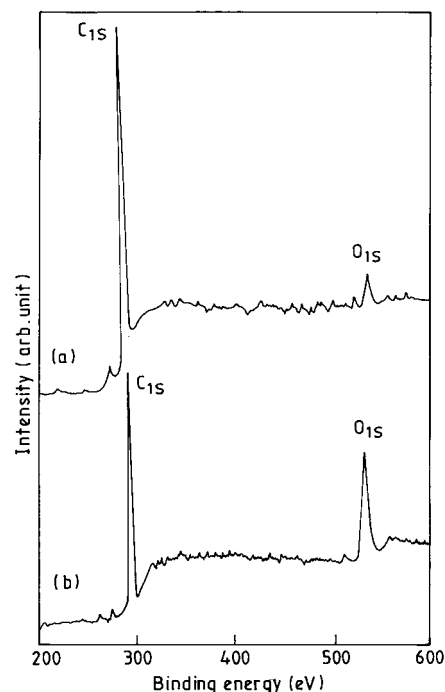


Figure 7 The XPS spectra of (a) modified and (b) unmodified LDPE film.

the single peak at 285.0 eV, indicating the presence of only one valency state C ($\text{—CH}_2\text{—}$) in the film.

The shift of the O_{1s} peak (from 531.5 eV) of the modified films towards higher binding energies com-

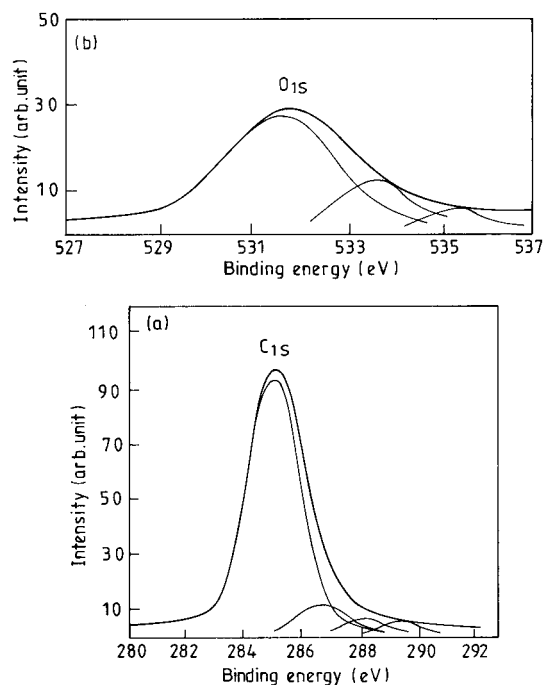


Figure 8 Deconvoluted XPS spectra of (a) C_{1s} (b) O_{1s} of modified film.

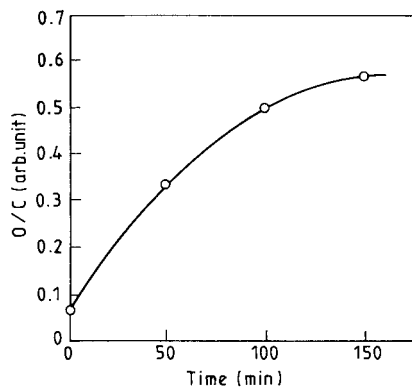


Figure 9 The variation of O/C ratio of XPS spectra of modified LDPE film with treatment time.

pared with that of unmodified films, indicates that the relative concentration of oxygen connected with carbon having sp^2 hybridization in $-\text{COOH}$ increases. The deconvoluted O_{1s} spectra of persulphate-treated film show peaks at 532.2 and 535.3 eV, which can be assigned to $\text{C}=\text{O}$ and $-\text{O}(\text{C}=\text{O})-$, respectively. The XPS spectra of the virgin LDPE film shows no peak at these regions, indicating the absence of $-\text{COOH}$ and other oxygen containing groups like $\text{>C}=\text{O}$.

Printability test

The permanent printing by polar printing ink on the nonpolar surface of LDPE films is very difficult. So for permanent printing on the LDPE surface some polar groups are required. The printing by Brightflex Blue 20 on modified (by persulphate) LDPE film shows that the printability grade increases appreciably. With the increase of persulphate treatment time, printability increases. The generation of some polar groups on the film surface of persulphate-treated films facilitates printability. The scratch/nail hardness value of the printability test indicates (which is given in Table I) the property of permanent printing on the persulphate-treated LDPE film surfaces.

Adhesion properties

The peel strength of the laminates are measured by a Zwick Universal Testing Machine (UTM 1445) at room

TABLE I
Printability of Persulphate-Treated LDPE Film Using Brightflex Blue 20

Type of LDPE film used	Time of persulphate treatment (h)	Printability	Scratch/nail hardness
Unmodified	—	5	1
Modified	1.5	7	4
Modified	2	8	3
Modified	2.5	10	1

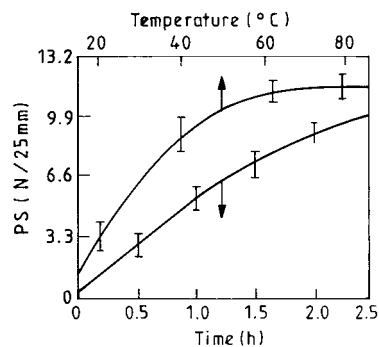


Figure 10 Variation of peel strength of epoxy resin-laminated LDPE films with time and temperature of persulphate treatment.

temperature. The laminates are produced by adhering modified surfaces of the two substrates (thickness 2 mm) having a width of 2.5 cm with epoxy resin (Araldite, Ciba-Geigy) cured under pressure 49 N for 24 h at room temperature. Variations of peel strength of the laminates after chemical modification with time of treatment and temperature is shown in the Figure 10. The adhesion strength of the film increases initially in the same manner as the concentration of the polar groups increases on the surface. This indicates that the chemical interaction and also hydrogen bonding caused by the generated polar groups on the surface of the chemically modified film result in the stronger adhesion process.

The trend of the increase in the adhesion strength is quite similar to the increase of absorption intensities of the polar groups (Fig. 6). It may be concluded that the formation of polar groups on the surface of the chemically treated LDPE film is responsible for higher strength of the laminates through the chemical interactions with the epoxy resins. Also, surface roughening and pitting (as observed by SEM analysis; Figs. 3 and 4) due to the persulphate treatment may help to improve the tensile strength through the mechanical interlocking.

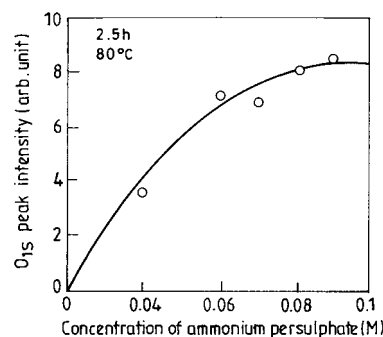


Figure 11 The variation of O_{1s} peak intensity with persulphate ion concentration.

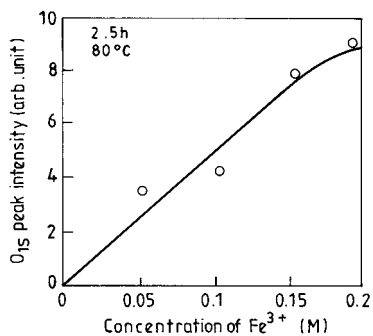


Figure 12 The variation of O_{1s} peak intensity with Fe³⁺ ion concentration.

We have maintained maximum concentration of Fe (III) ion (0.01 M) when the effects of persulphate ion become asymptotic. The concentrations of persulphate and Fe (III) ion are optimized to gate the maximum rate of oxidation without any iron oxide deposition. The optimum concentration of persulphate is 0.1 M and Fe (III) ion 0.2 M, which are evaluated from the intensity of O_{1s} peak of the oxidized film, which are shown in Figures 11 and 12. As per the Figures 11 and 12, we find from the intensities of O_{1s} peak in XPS that it reaches a maximum when ammonium persulphate concentration is 0.1 M and intensities of O_{1s} peak increases linearly that the concentration of Fe (NO₃)₃ but after 0.2 M state it start to deposit a basic ferric salt medium.

For verification of any role of NO₃⁻ the experiments were conducted with Fe₂(SO₄)₃·5H₂O in place of Fe(NO₃)₃. It is observed that there is no significant change of effect of oxidants in the surface oxidation process. The choice of Fe (NO₃)₃ is advantages because it does not produce easily any precipitate of basic iron salt.

The material after oxidation was soaked with C₆H₆ for 8 h. The benzene extract was analyzed with HPLC (Agilent, 1100 Series) to detect low molecular weight components. There was no materials having molecular weight less than 10⁵ D. the average molecular weight of original materials was 6–7 × 10⁵ D.

CONCLUSIONS

Modification the of surface by ammonium persulphate solution and Fe(NO₃)₃ of LDPE films leads to improvement of mechanical performance of its laminates for better adhesion with epoxy resin. Mechanical interlocking due to surface roughening (as observed

by SEM analysis) and chemical bonding with epoxy resin due to generation of active polar groups like —COOH, >C=O, etc. (as observed by IR and XPS analysis) on the surface of the modified LDPE film are responsible for the excellent tensile strength of their laminates. It has improved printability of the modified LDPE film due to the formation of the chemical bonding between the ink and newly generated functional groups on the surface. Surface modification of LDPE film by this process appears to be simple and environment friendly.

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References

1. Brody, A. L.; Marsh, K. S. *The Wiley Encyclopedia of Packaging Technology*; Wiley: New York, 1997, p. 752, 2nd ed.
2. *Technical Literature*. India Ltd: Bata, 1980.
3. Clark, D. T.; Feast, W. Y. *Adhesion in Polymer Surface*: John Wiley & Sons: New York, 1978, p. 213.
4. Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *J Am Chem Soc* 1977, 99, 4746.
5. Bezigian, T. *Tappi J* 1992, 75, 139.
6. Foerch, R.; McIntyre, N. S.; Hunter, D. H. *J Polym Sci Chem* 1990, 28, 803.
7. Ladizesky, N. H.; Ward, I. M. *J Mater Sci* 1983, 18, 533.
8. Shard, A. G.; Radyal, J. P. S. *Macromolecules* 1992, 25, 2053.
9. Yasuda, H.; Marsh, H. C.; Brandt, S.; Reily, C. N. *J Polym Sci Chem* 1977, 15, 991.
10. Clark, D. T.; Wilson, R. J. *Polym Sci Chem* 1983, 21, 837.
11. Kaplan, S. L.; Rose, P. W.; Nguyen, H. X.; Chang, H. W. *SAMPE Q*. 1998, July, 55.
12. Eriksson, J. G.; Golander, C. G.; Baszkin, A.; Ter-Minassian-Saraga, L. *J Colloid Interface Sci* 1984, 100, 381.
13. Blais, P.; Carisson, D. J.; Csullog, G. W.; Wiles, D. M. *J Colloid Interface Sci* 1974, 47, 636.
14. Postema, A. R.; Doornkamp, A. T.; Meijer, J. G.; Vlekkert, H. V. D.; Pennings, A. *Polym Bull* 1985, 16, 1.
15. Ward, I. M.; Ladizesky, N. H. *Pure Appl Chem* 1985, 57, 1641.
16. Packhan, D. E.; Bright, K.; Malpass, B. W. *J Appl Polym Sci* 1974, 18, 3237.
17. Taboudoucht, T.; Opalko, R.; Ishida, H. *Polym Comp* 1992, 13, 81.
18. Bag, D. S.; Ghosh, S. N.; Maiti, S. *Eur Polym J* 1998, 34, 855.
19. Bag, D. S.; Kumar, V. P.; Maiti, S. *J Appl Polym Sci* 1999, 71, 1041.
20. Bandopadhyay, D.; Panda, A. P.; Pramanik, P. *J Appl Polym Sci* 2001, 82, 406.
21. Wrobel, A. M.; Kryszewski, M.; Rakowski, W.; Okoniewski, M.; Kubacki, Z. *Polymer* 1978, 9, 908.
22. Hains, A. H. *Method for the Oxidation of Organic Compounds*; Academic Press: London, 1974, p. 174.
23. Pramanik, P. Unpublished work.
24. Briggs, D.; Brewis, D. M.; Konieczko, M. B. *J Mater Sci* 1976, 11, 1270.