Novel Surface Modification of High-Density Polyethylene Films by Using Enzymatic Catalysis

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ABSTRACT: The surface of high-density polyethylene (HDPE) films was modified by an enzyme, soybean peroxidase (SBP). The enzymatic surface modification was performed using a peroxidase as catalyst and hydrogen peroxide as oxidizing agent. The chemical composition and morphology of HDPE surfaces were characterized by X-ray photoelectron spectroscopy, infrared spectroscopy, and scanning electron microscopy. Results showed that after enzymatic treatment, the O/C atomic ratio of HDPE surfaces increased, and new functional groups such as –CO– appeared. Moreover, the surface of treated HDPE films became rougher than untreated surfaces. The hydrophilicity of treated and untreated HDPE films was analyzed by UV–vis spectroscopy and contact angle measurements. The decreased contact angle of the HDPE with water and increased adsorption ability of the surface to a water-soluble dye clearly indicated that enzymatic treatment can significantly increase the hydrophilicity of the surfaces of HDPE films. The catalytic mechanism of SBP was also discussed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3673–3678, 2004

Key words: enzymatic treatment; films; peroxidase; surfaces; modification

INTRODUCTION

From the mid-twentieth century, different types of polymers have been widely used in our daily lives. Among the different types of polymers, polyethylene (PE) is widely used for its abundant supply, good chemical resistance, good process ability, low-energy demand for processing, and low cost. However, PE has very poor adhesion to other materials because of PE's low surface energy, which limits its applications in some fields such as gluing, painting, and printing. To improve the surface properties of PE, it is necessary to modify the surface of PE. A number of surface-modification techniques such as plasma, corona discharge, radiation treatments, ion-beam treatment, flame treatment,[1–4] and chemical treatments[5–7] have been used to modify polymer surfaces. One of the most commons techniques is to introduce polar groups on the polymer surface by oxidation. Most of the conventional methods described in the literature, used to alter the polymer surface, require strong chemical agents. As a consequence enormous quantities of environmentally hostile chemicals used daily in wet polymer processing at the industrial level contribute to increasingly grave concerns about the ecological impact of industrial wastes and their treatment. Conversely, to lower the hazardous use of harsh chemicals and their environmental impact, biotechnological techniques must be applied to polymer processing.

Enzymatic surface treatments provide a new method of modification. The application of enzymes to modify the surface of natural polymers, such as wool, has been widely researched by industry.[8] Textile processing areas, such as deseizing, scouring, and bleaching of cellulose and woolen fabrics are some examples of successful biotreatments of textiles. The use of enzymes not only may remove unwanted adsorbed material but also may chemically modify the fiber surface. Besides defurring and antifouling treatments of wool, the so-called biopolishing of cotton fabrics and garments to obtain the stonewashing effect is a good example. Celluloses are commonly used industrial enzymes to finish cotton and wool fabrics leading to improvements in softness, good performance, and enhanced comfort effect. The use of enzymes may reduce chlorine consumption for fabric's descaling down to 5%. Enzymatic catalysis surface modification thus far provides information only about nitrile hydrase (member of the class of nitrile-converting enzymes) treatment of acrylonitrile fibers.[9] Polyacrylonitrile (PAN) was selectively modified by enzymatic attack, which led to the hydrolysis of the CN groups into the corresponding amides. Unlike other enzymatic modifications of natural fibers, this reaction was performed on the synthetic polymeric materials

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with the intention of obtaining a specific chemical species.

Peroxidase (donor: hydrogen peroxide oxidoreductase) is a widely distributed group of enzymes that oxidize a variety of substrates at the expense of hydrogen peroxide. Although the peroxidase-catalyzed homopolymerizations of various phenols and aniline derivatives were investigated by several groups,[10–14] relatively little information has been available about the copolymerization of phenol mixtures.[15–18] However, to the best of our knowledge, no reports have appeared on peroxidase treatments on the synthetic polymer surface. In this article, we were encouraged to investigate biotechnological techniques that exploit enzymatic catalysis. Enzymatic catalysis was been used to oxidize the surface of polyethylene. The enzyme used was soybean peroxidase (SBP). This surface modification was performed using a peroxidase as catalyst and hydrogen peroxide as oxidizing agent. The introduction of polar groups was characterized by infrared (IR) spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials

High-density polyethylene (HDPE) films (thickness 0.07 mm) were obtained from Hai Hong Polymer Manufactory (China).

Soybean peroxidase (SBP) was purchased from Shang Hai Bio-chemical Co. (China). The 1,4-benzenediol was a gift from Sheng Hai Chemical Co. (China).

The buffer and other chemical reagents used in this study were all of analytical grade.

Enzymatic modification of HDPE film surface

HDPE films were cut into rectangular pieces with a dimension of 120 × 30 × 0.1 mm (length × width × thickness). Before surface modification by enzyme, the sample pieces were washed with acetone and distilled water, then dried in a vacuum oven for 1 h at 85°C.

HDPE film (0.1 g) and 0.2 mg of SBP in 2.0 mL phosphate buffer (100 m*M*, pH 7.0) and 10 mL 1,4-benzenediol (5% acetone solution) were charged to a 50-mL flask. Hydrogen peroxide (10 mL, 3.0% aqueous solution) was then added dropwise to the mixture over 10 min at room temperature. After that, the mixture was maintained for another 5 min. The HDPE films were sequentially washed with water (three times), a mixture solvent of ethanol and water (1 : 1 v/v, three times), and acetone (three times), then dried under vacuum.

Staining reaction

The modified HDPE film was stained with methyl violet. The enzyme-treated HDPE film was suspended in a 50-mL flask with 30 mL methyl violet solution (5% aqueous solution) for 2 h at 60°C. Then the film was sequentially washed several times with water and acetone, and finally dried under reduced pressure.

Characterization

XPS measurements were carried out with a Philips XL ESCA XL20 spectrometer (Philips, The Netherlands) using Mg–K_α radiation, operated at 8 kV and 20 mA.

SEM micrographs were recorded using a Hitachi S-570 machine (Hitachi, Osaka, Japan), with an acceleration voltage of 15 kV. The surface of the PE sample was coated with gold by vacuum evaporation.

IR analyses of the PE sample films were performed from 400 to 4000 cm^{-1} with a Perkin–Elmer Spectrum 1000 IR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT).

UV–vis spectra were recorded on Perkin–Elmer Lambda 17 UV–vis spectrophotometer.

RESULTS AND DISCUSSION

IR analysis

The IR spectra of the modified and unmodified HDPE films are shown in Figure 1. Compared to the spectrum of untreated HDPE, the modified surface had several new peaks at 1650, 1625, and 3400 cm^{-1}, corresponding, respectively, to a –CO—R group adjacent to an olefin double bond, a Ph—CO—R group adjacent to an olefin double bond, and hydroxyl groups, suggesting that modified HDPE films had been modified. The absorption intensities of different groups were plotted against the concentration of H_2O_2. The absorption intensities increased with increased concentration of H_2O_2.

XPS analysis

To give further evidences of change in composition of treated HDPE film, XPS was performed to analyze the content of oxygen and carbon atoms, and the results are listed in Table I. The superficial oxygen content of the untreated HDPE film was 1.08%, attributed to the presence of the additive. The percentage of oxygen increased significantly in the sample treated with SBP, indicating that the surface of enzyme-treated HDPE was oxidized, consistent with the IR results as described above.

SEM analysis

The changes in the topography and morphology of treated and untreated film surfaces were studied by

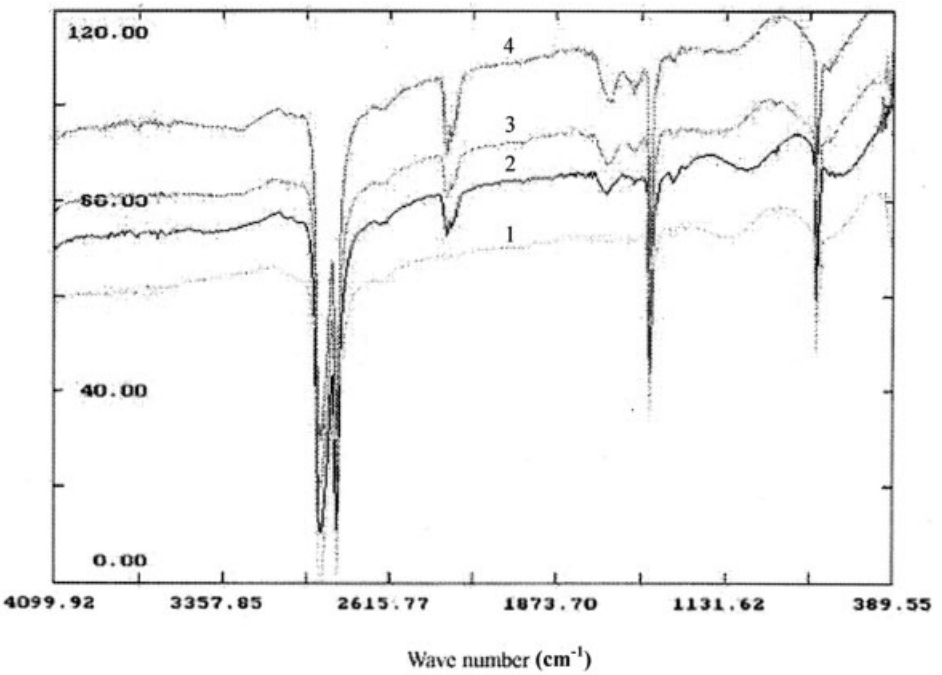


Figure 1 Infrared spectra of HDPE film: (1) untreated; (2) enzymatic modified (0.1% H_2O_2); (3) enzymatic modified (0.2% H_2O_2); (4) enzymatic modified (0.3% H_2O_2).

SEM as shown in Figure 2. Roughened, pitted surfaces were observed in the modified films. Some investigations proved that the adhesion of the polymer film to other materials was improved with an increase in the roughness of its surface attributed to an increase in surface area for bonding and mechanical interlocking[19,20]; thus the roughened surface with pitting in the enzyme-treated HDPE film was expected to improve the adhesion of HDPE film, thus leading to better mechanical performance of the laminates.

Wettability test

Measuring the contact angle of polymer surfaces permits a rapid and qualitative evaluation of polymer surface energy. The water contact angle of the untreated HDPE film was found to be 80°, implying that HDPE has a very low surface energy. Enzymatic modification decreased the contact angle of HDPE film, suggesting that the treated samples have higher surface energy and hence improved adhesion to other materials. It can be seen from Figure 3 that the degree of decrease is dependent on the treating time: the longer the treating time, the smaller the contact angle. For example, the contact angle of the treated surface decreased from 80 to 50° when the treating time was 10 min. However, when the exposed time was longer than 10 min, the contact angle remained constant, independent of the time.

TABLE I
Results of the XPS Analysis of HDPE Surface

	Atomic surface composition (%)	
Modification condition	O	C
Untreated	1.08	98.54
H_2O_2 treated	3.03	96.92
Enzymatic treated		
5 min	5.39	94.48
10 min	6.50	93.34

UV–vis analysis

Figure 4 shows the UV–vis spectra of various HDPE films after staining with methyl violet solution. The maximum absorption of methyl violet is at 560 nm. The untreated HDPE film shows the lowest degree of absorption, whereas the sample modified by H_2O_2 without enzyme has only slightly higher absorption than that of the untreated sample, indicating that the H_2O_2-treated samples did not undergo any significant chemical change on the surface. Note that the sample treated by enzymatic catalysis has an obviously higher degree of absorption than that without enzyme. Moreover, the longer exposure time promotes a higher degree of absorption. These results demonstrate that the enzyme accelerates the oxidation of H_2O_2, which is further explained in the next section.

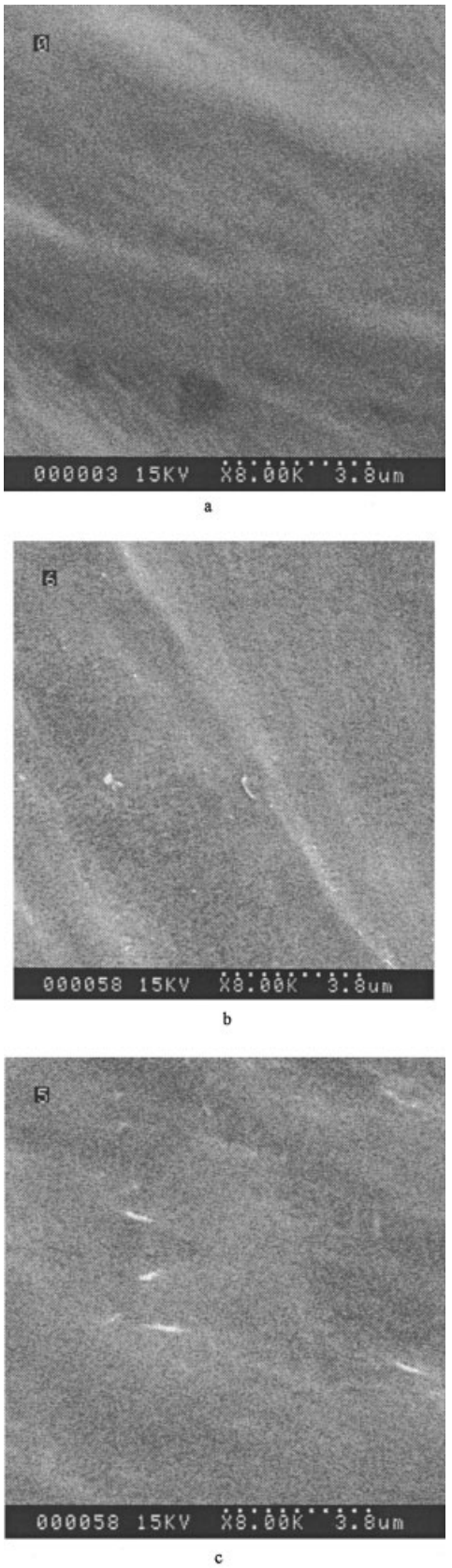


Figure 2 SEM micrographs of (a) untreated HDPE; (b) enzymatic-treated HDPE; (c) chemically treated HDPE (30% H_2O_2).

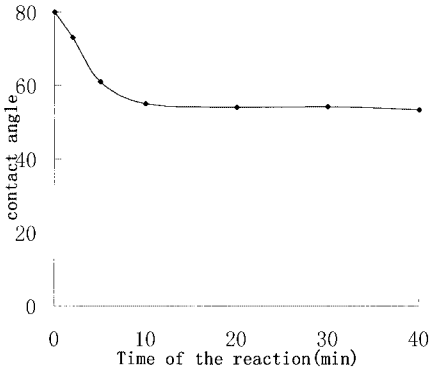


Figure 3 Effect of treatment time on the contact angle of HDPE film.

Mechanism of enzyme treatment of HDPE film surface

These investigations have demonstrated that SBP could accelerate the oxidation of HDPE by H_2O_2. Although no conclusive explanation can be given, two mechanisms are hypothesized to explain the oxidation process involved in this study based on previous researches and our investigations. Previous studies have found that the catalysis mechanism of most peroxidases is similar, containing three distinct steps.[21] In the catalytic cycle of this study, Fe(IV)═O, which has high-energy species, was generated and assumed to be used as an oxidizer to oxidize the HDPE film surface, as schematically described in pathway A (Scheme 1). Because free-radical species are generated as intermediates in many enzyme catalysis reactions,[22–24] it has been assumed that they could be used as primary radicals to initiate polyethylene free radicals. Therefore the secondary mechanism of surface oxidation of HDPE by enzyme might be described as follows. At the beginning of the reaction, phenols are preferentially oxidized and subsequently deproto-

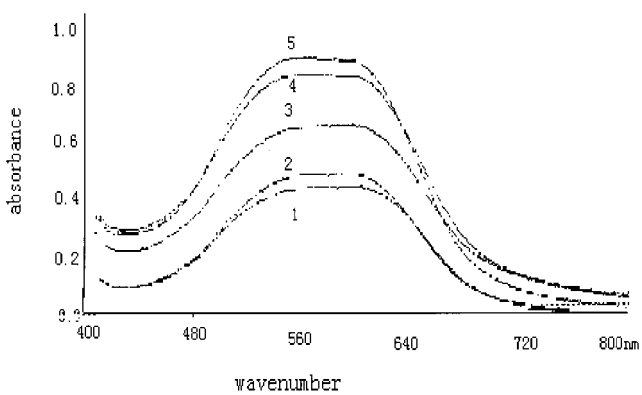
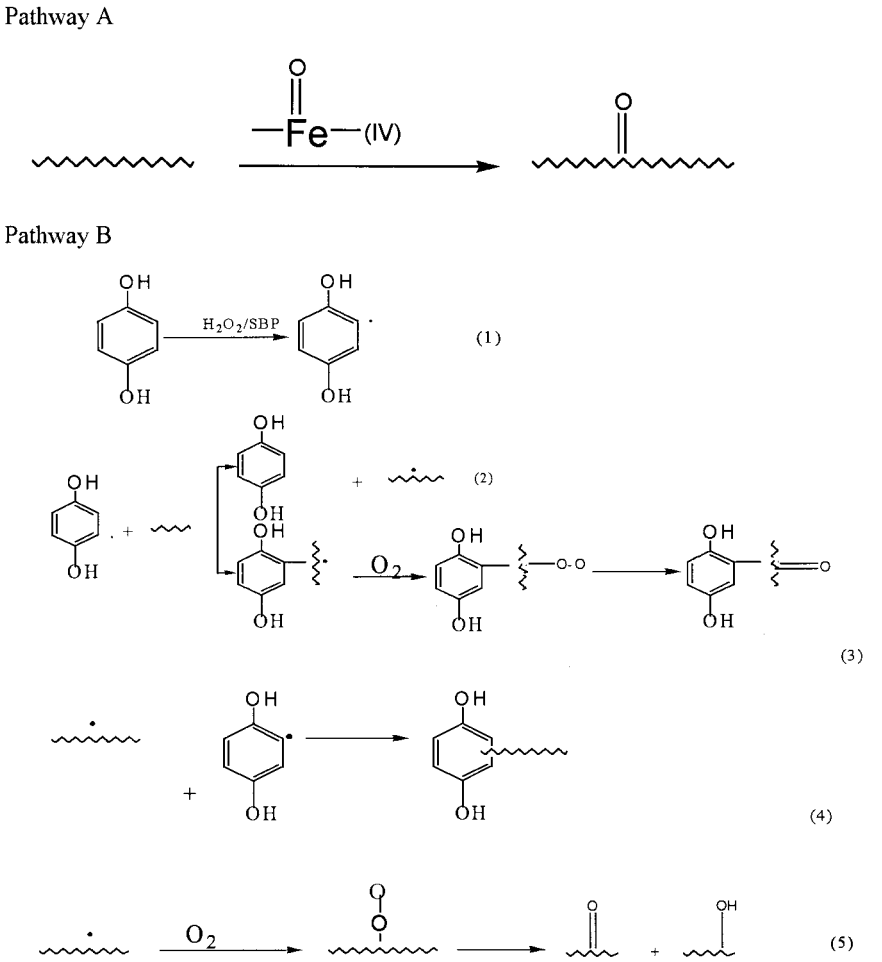


Figure 4 UV–vis spectra of enzymatic modification HDPE after being immersed in methyl violet solution: (1) unmodified; (2) H_2O_2 modified; (3) enzymatic treated (2 min); (4) enzymatic treated (5 min); (5) enzymatic treated (10 min).



Scheme 1 Proposed mechanism of the enzymatic modification of HDPE film.

nated to corresponding phenoxy radicals [reaction (1)]. The phenoxy radical abstracts hydrogen from the polyethylene chain and forms a surface radical on the HDPE chain [reaction (2)]. The formed radicals (polyethylene radical), when contacted with air, are rapidly transferred into peroxides. Then the polar groups were introduced to the HDPE film by peroxidized decomposition [reaction (5)].

CONCLUSIONS

We investigated the surface modification of HDPE film by using an enzyme as a catalyst and H_2O_2 as an oxidizer. Characterizations of modified HDPE film showed that hydrophilic groups such as –OH and C═O are introduced on the treated HDPE surface, causing a change in morphology of the modified HDPE surface to that of a roughened surface with pits. The modified HDPE film was characterized by greatly improved hydrophilicity and higher surface energy, and was thus expected to have improved adhesion to other materials.

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References

1. Foerch, R.; McIntyre, N. S.; Hunter, D. H. J Polym Sci Part A: Polym Chem 1990, 28, 803.
2. Shard, A. G.; Radyal, J. P. S. Macromolecules 1992, 25, 2053.
3. Nakada, S.; Sawatari, C.; Tamura, K.; Yagi, T. Colloid Polym Sci 2001, 279, 754.
4. Lu, Q.-H.; Li, M.; Yin, J.; Zhu, Z.-K.; Wang, Z.-G. J Appl Polym Sci 2001, 82, 2739.
5. Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. Langmuir 1998, 4, 912.
6. Idage, S. B.; Badrinaryanan, S.; Vernkar, S. P.; Sivaram, S. Langmuir 1996, 12, 1018.
7. Bandopdhay, D.; Panda, A. T.; Pramanik, P. J Appl Polym Sci 2001, 82, 406.
8. Cegarra, J. J Soc Dyers Colour 1996, 112, 326.
9. Battistel, E.; Morra, M.; Marinetti, M. Appl Surf Sci 2001, 177, 32.
10. Dordick, J. S.; Marletta, M. A.; Klibanov, A. M. Biotechnol Bioeng 1987, 30, 31.
11. Akkara, J. A.; Senecal, K. J.; Kaplan, D. L. J Polym Sci Part A: Polym Chem 1991, 29, 1561.
12. Uyama, H.; Kurioka, H.; Sugihara, J.; Kobayashi, S. Bull Chem Soc Jpn 1996, 69, 189.

13. Goretzki, C.; Ritter, H. Macromol Chem Phys 1998, 199, 1019.
14. Ichinose, D.; Muranaka, T.; Sasaki, T.; Kobayashi, M.; Kise, H. J Polym Sci Part A: Polym Chem 1998, 36, 2593.
15. Blinkovsky, A. M.; Dordick, J. S. J Polym Sci Part A: Polym Chem 1993, 31, 1839.
16. Reihmann, M. H.; Ritter, H. Macromol Chem Phys 2000, 201, 798.
17. Reihmann, M. H.; Ritter, H. Macromol Biosci 2001, 185.
18. Pasta, P.; Carrea, G.; Monzani, E.; Gaggero, N.; Colonna, S. Biotechnol Bioeng 1999, 62, 489.
19. Wrobel, A. M.; Kryszewski, M.; Rakowski, W.; Okoniewski, M.; Kubacki, Z. Polymer 1978, 9, 908.
20. Hiner, A. N. P.; Hernandez-Ruiz, J.; Arnao, M. B.; Garcia-Canovas, F.; Acosta, M. Biotechnol Bioeng 1996, 50, 655.
21. Gold, H.; Wariishi, M. H.; Valli, K. ACS Symp Ser 1989, 389, 127.
22. Tien, M.; Kirk, T. K.; Bwll, C. J Biol Chem 1986, 261, 1687.
23. Tuor, U.; Wariishi, H.; Schoemaker, H. W. Biochemistry 1992, 31, 4986.
24. Halliwell, B.; Gutteridge, J. M. C. Free Radicals in Biology and Medicine; Clarendon Press: Oxford, UK, 1989.