

Fabrication of a Novel Polyethylene/Starch Blend Through Mediation of a High-Energy Ball Milling Process: Mechanical Properties and Formation Mechanism

Alireza Sharif,* Jamal Aalaie, Homeira Shariatpanahi, Homayoon Hosseinkhanli, Alireza Khoshniyat

Polymer Engineering Group, Department of Chemical Engineering, Tarbiat Modares University, Tehran, Iran

Correspondence to: A. Sharif (E-mail: sharif.a1355@gmail.com and asharif@modares.ac.ir)

ABSTRACT: High-energy ball milling (HEBM) was performed before melt mixing to fabricate a novel blend containing 85 wt % of a high density polyethylene (HDPE) and 15 wt % of a maize starch, using neither compatibilizer nor plasticizer materials in the blend formulation. Scanning electron microscopy and rheometry results revealed a strong interface between the two phases of the blend. Formation of the interface with high strength was ascribed to the grafting reactions, taking place between the phases during the HEBM process, and corroborated by Fourier transform infrared characterizations. A possible formation mechanism for the starch-grafted polyethylene was proposed based on the measurements and comprehensive analysis. Interestingly enough, when compared to HDPE mixtures which contained the same amount of the starch, but were made only by conventional melt blending, the ball mill-mediated sample showed superior mechanical and biodegradation properties. These properties enhancements were related to both the HDPE/starch strong interface and the damaged starch originated by the mechanical action of the milling process. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polyethylene; starch; ball milling; mechanical properties; biodegradation

Received 7 February 2012; accepted 31 May 2012; published online

DOI: 10.1002/app.38155

INTRODUCTION

With the growing environmental awareness and shortage of natural resources, there is a strong demand for biodegradable polymers as an ultimate solution to the problems caused by disposal of nonbiodegradable plastic wastes.¹ Among different kinds of biodegradable polymers, starch is the most promising with immense potential and low price. However, the applications of pure starch materials have been limited due to their water sensitivity and brittle properties.²

To overcome these drawbacks, starch is usually modified (physically or chemically) or melt blended with other synthetic polymers. Unfortunately, these strategies tend to shift rather than alleviate the problem and therefore, have not so far led to commercially acceptable starch-based products. For example, chemical modifications, including esterification, etherification, cross-linking, oxidation, carboxymethylation, benzoylation, and so on, generally make starch more brittle and stiff due to the associated degradation reactions.^{3,4} Although plasticization of starch with glycerol [to obtain the so-called thermoplastic starch

(TPS)] increased its flexibility, it has been shown that the plasticizer could leach out of starch matrix after a short period of time, and thus the material still showed a brittle behavior.⁴ In addition, high amounts of wastewater or organic solvents, used in the traditional process of the above starch modifications, can result in serious environmental pollution problems.⁴

Besides, to achieve synthetic polymer/starch blends with desirable physical and mechanical properties, the high interfacial tension between the nonpolar synthetic polymers and the highly polar starch must be overcome.⁵ For instance, in preparation of blends from polyethylene (the most widely used polyolefin around the world) and starch, it would be unavoidable to use appropriate amounts of various chemical compatibilizers such as poly(ethylene-co-glycidyl methacrylate) and poly(ethylene-g-maleic anhydride) (PE-g-MA) copolymers in the blends formulation.⁶ Because most of the compatibilizers are toxic^{7,8} and harmful materials to human health, the aforementioned blends have missed the opportunities to meet the challenging demands of the growing market of food and hygienic products packaging

*Present address: Department of Chemical Engineering, Polymer Engineering Group, Tarbiat Modares University, Tehran, Iran..

according to the international health standards.⁹ On the other hand, many researchers, for example, in Refs. 10 and 11, have proposed the use of the TPS, instead of dry starch, in blends with polyethylene, as a solution to the problem of the low mechanical properties of the prepared blends. Nevertheless, using the TPS would limit the starch content, deteriorating the biodegradability of the final blend.¹²

In an attempt to investigate whether nanoparticles could replace chemical compatibilizers in polyethylene/starch blends, recently Sharif et al.¹³ compared the physical and mechanical properties of compatibilized and uncompatibilized melt-blended polyethylene/starch/organoclay mixtures. It was shown that although the incorporation of the nanoclays enhanced the nanocomposites biodegradability, the presence of a PE-g-MA, as a compatibilizer, was necessary for achieving composites of relatively high tensile strength and elongation at break. The results of this study corroborate previous findings^{6,14–16} suggesting that regardless of how the starch granules and synthetic polymers have been modified, melt mixing methods are unable to provide a high-strength interface between the two components without an aid of a chemical compatibilizer.

Therefore, developing alternative methods of preparing compatibilizer-free polyethylene/starch blends, possessing desirable physical and mechanical properties, are highly in demand for food and drug packaging, disposable devices, and many others.¹³

In this work, we demonstrated the potential of a solid-state method, high-energy ball milling (HEBM), in combination with melt mixing, for production of a compatibilizer-free high density polyethylene (HDPE)/dry-starch blend, containing 15 wt % of the starch, with acceptable mechanical and biodegradation properties. It is important to note that the HEBM, although may seem as a time-consuming and laborious method in a first approximation, enables one to obtain novel polymer mixtures with new characteristics, difficult to obtain by other conventional techniques.^{17,18}

The properties of the prepared blend were discussed in terms of the formation of a strong interface between the ball-milled polyethylene and starch components, as deduced from morphological and rheological studies. Furthermore, polyethylene/starch as well as polyethylene/starch/PE-g-MA blends with the same starch content were prepared only by the melt mixing and their mechanical and biodegradation properties reported, for comparison.

EXPERIMENTAL

Materials

The HDPE powder, with density of 0.95 (g/cm³) and melt flow index of 0.35 (g/10 min) at 190°C, was supplied by Bandar Imam Petrochemical Company, Bandar Imam, Iran (Poliran HB0035). The weight-average molecular weight and Poly Dispersion Index (PDI) were obtained by gel permeation chromatography as 225,000 (g/mol) and 20.5, respectively.¹⁹ The maize starch (C*GEL 03401, 26% amylose), with density of 0.54 (g/cm³), was purchased from Cargill Deutschland GmbH, Krefeld, Germany. The polyethylene (PE) copolymer grafted with maleic

anhydride (PE-g-MA), OPTIM E-118, with density of 0.93 (g/cm³), and melt flow index of 0.56 (g/10 min) at 190°C, was obtained from Pluss Polymer (India).

Sample Preparation

HDPE (12.5 g) and starch (12.5 g), in powder form, were milled in the presence of 190 g of alumina balls with 20 mm of diameter in a Pulverisette-5 (Fritsch, Germany) planetary ball mill. Milling was conducted for 15 h at ambient temperature and at the rotation speed of 350 rpm. To avoid excessive heating of the apparatus as well as of the milled powders, every 15 min of active milling action was followed by 5 min of resting. Following this procedure, chain scission seems to be neglectable.¹⁸ The resultant mixture, (HD/S)_b, was then melt blended with additional HDPE powder in a Brabender internal mixer (Brabender PL 2000 OHG, Duisburg, Germany) at 190°C, 60 rpm for 15 min, to obtain the final blend, containing 15 wt % of the starch. The final blend was labeled as HD-(HD/S)_b in this article. Also, the HDPE and starch, without and with the PE-g-MA, were mixed only in the internal mixer at 190°C, 60 rpm for 15 min to obtain the uncompatibilized, HD/S, and compatibilized, HD/S/MA, melt-blended samples, respectively, containing 15 wt % of the starch. Each of the molten samples was compression molded into sheets with a thickness of about 1 mm using a hydraulic press at 190°C and 150 bar for 3 min. The material was subsequently cooled under pressure to 30°C, which took ~10 min. It should be noted that, after molding, all the samples were immediately sealed in a polyethylene bag and placed in a vacuum desiccator for a minimum of 72 h before all the following measurements.

Tensile Properties

Tensile properties were measured according to ASTM D638 using rectangular sheets (1 mm thick) of the prepared specimens on a Zwick Z030 universal testing machine at a crosshead speed of 50 mm/min. Young's modulus (*E*) was calculated from the slope of the low strain region of the tensile curve. Average values from five experiments were determined.

Microscopy

Scanning electron microscopy (SEM, Philips XL30) images were used to study the phase morphology of the samples. The samples were cryogenically fractured in liquid nitrogen before imaging. Then the samples were sputter coated with a thin layer of gold.

Rheological Measurements

The melt-state linear viscoelastic properties of the samples were studied using a rheometrics mechanical spectrometer (Paar Physica MCR501) equipped with parallel plate geometry. All measurements were performed under nitrogen atmosphere in the frequency range of 0.01–100 s⁻¹ with strain amplitude of 1% at 190°C.

Fourier Transform Infrared

Fourier transform infrared (FTIR) measurements were carried out on the neat materials (HDPE and starch) as well as on the (HD/S)_b mixture to determine whether there has been any chemical reaction between polyethylene and starch during the milling process. FTIR spectra of the samples were recorded on a Bruker IFS 88 FTIR spectrophotometer at a resolution of 2

Table I. Mechanical Properties of the Studied Samples

Sample	Modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
HDPE	1.5 ± 0.07	27.0 ± 1.4	600 ± 25
HD/S	1.8 ± 0.09	26.0 ± 1.3	20.1 ± 1.2
HD/S/MA	1.7 ± 0.08	26.4 ± 1.3	33.2 ± 1.6
HD-(HD/S) _b	1.7 ± 0.08	30.1 ± 1.5	150.7 ± 7.5

cm⁻¹. The transmission mode was used on finely powdered samples prepared as KBr pellets. It is important to note that the (HD/S)_b mixture (3 g) was passed through a Soxhlet extractor before FTIR measurements to remove unreacted starch molecules from the sample. Hot water (90°C) was used as the extraction solvent and the extraction process was lasted for 72 h. At the end of the process, there was 1.9 g of (HD/S)_b mixture remained in the Soxhlet extractor. Therefore, we could calculate the fraction of starch bonded to the HDPE as 27%, assuming that all the unreacted starch molecules had been removed from the sample.

Biodegradation by Fungi

Different types of fungi including *Aspergillus niger* (DSM 63263), *Penicillium pinophilum* (DSM 1944), *Chaetomium globosum* (DSM 1962), *Trichoderma virens* (DSM 1963), and *Aureobasidium pullulans* (2404) were supplied by DSMZ (Germany) and used to investigate the resistance of the selected samples in this study to microorganisms, according to the ASTM G21 standard. Maintained cultures of these fungi were inoculated separately on Sabouraud dextrose agar (SDA) slopes. The cultures were grown in minimal medium containing (g/L): KH₂PO₄ 0.7; K₂HPO₄ 0.7; MgSO₄·7H₂O 0.7; NH₄NO₃ 1.0; NaCl 0.005; FeSO₄·7H₂O 0.002.; ZnSO₄·7H₂O 0.002.; MnSO₄·H₂O 0.001. The pH of the medium was adjusted to 7 and sterilized at 121°C for 20 min. The test samples (250 mg/50 mL) were surface sterilized with 70% ethanol for 2 h and added aseptically to the sterilized medium. The inoculum was prepared by suspending the spores from fully grown cultures on SDA slopes in 10 mL of sterile saline. This suspension (1.0 mL) was added to 50 mL of minimal medium in 250 mL Erlenmeyer conical flasks. Flasks were incubated at 30°C under stationary condition. After 3 months of biodegradation, the specimens were washed, dried, and weighed. The weight loss of the specimens (wt %) was measured according to the weight of specimens before (W_0) and after biodegradation (W_f):

$$W(\%) = \frac{W_0 - W_f}{W_0} \times 100 \quad (1)$$

Also, surfaces of biodegraded samples were observed using the Philips SEM.

RESULTS AND DISCUSSION

Mechanical Properties

Table I shows the mechanical properties of the various samples, fabricated in this work, along with those of the pure HDPE powder. According to nearly all studies that have previously

examined the mechanical properties of polyethylene/granular starch blends or composites,^{12,20–22} these blends exhibited an increase in Young's modulus but a decrease in tensile strength and elongation at break with increasing starch filler content. However, although the results regarding the present melt-blended samples were in harmony with the previous findings, interestingly enough the tensile strength of the HD-(HD/S)_b sample was higher than that of the HDPE. To our knowledge, this outcome, obtained via innovative method of polyethylene/dry-starch blend preparation, is unprecedented and has the potential to open a new fundamental understanding to bridge polymer morphology with the resultant mechanical properties. Moreover, elongation at break (a direct measure of impact strength²³) of the HD-(HD/S)_b sample, not only was higher than those of the HD/S and HD/S/MA ones, but also exceeded the values reported by other research groups^{20,24,25} for the ultimate elongation of HDPE mixtures containing as much as 15 wt % of starch.

Mechanism

To explain the mechanisms behind the increase in the mechanical properties of the HD-(HD/S)_b sample as compared to those of the melt-blended ones, SEM, rheometry, and FTIR spectroscopy techniques have been used for the assignment of the details of the samples morphologies.

Morphology. Figure 1 demonstrates the SEM micrographs of the as-received starch material and the neat starch after 10 h of ball milling. The as-received starch [Figure 1(a)] has a smooth and mirror-like surface, whereas there are scratches, abrasion, and voids on the surface of the ball-milled one [Figure 1(b)], originated from the mechanical action of the milling process. Also, it is obvious that the starch granule size was increased by ball milling.

The SEM micrographs of the fractured surfaces of the HD/S and HD-(HD/S)_b samples are shown in Figure 2. In accordance with the previous conclusions of different authors,^{20,21} the native starch preserved its original size and shape after melt processing [Figure 2(a)]. In addition, there is an obvious interface between the polyethylene and starch in the HD/S blend which indicates typical immiscibility of the two phases. On the other hand, the polyethylene/starch phase boundary became blurred in the HD-(HD/S)_b blend [Figure 2(b)]. Indeed, the interfacial adhesion between polyethylene and starch was enhanced without using any kind of external compatibilizer. However, we believe that the strong hydrogen bonds between starch molecules were broken under milling (some evidence will be presented later based on FTIR results, supporting this idea), rendering the molecules prone to more collisions with polyethylene chains. Also, damaged starch [Figure 1(a)], obtained during the HEBM process, could trap polyethylene chains into its surface cavities, providing intimate interfacial contacts between the two distinct phases. There is another interesting point regarding these results which deserves further attention. It is an accepted notion among researchers that, as the size of a polymer blend dispersed phase is being reduced, the blend miscibility and mechanical properties will be enhanced and vice versa.^{26–28} However, improvement in the mechanical properties of the HD-

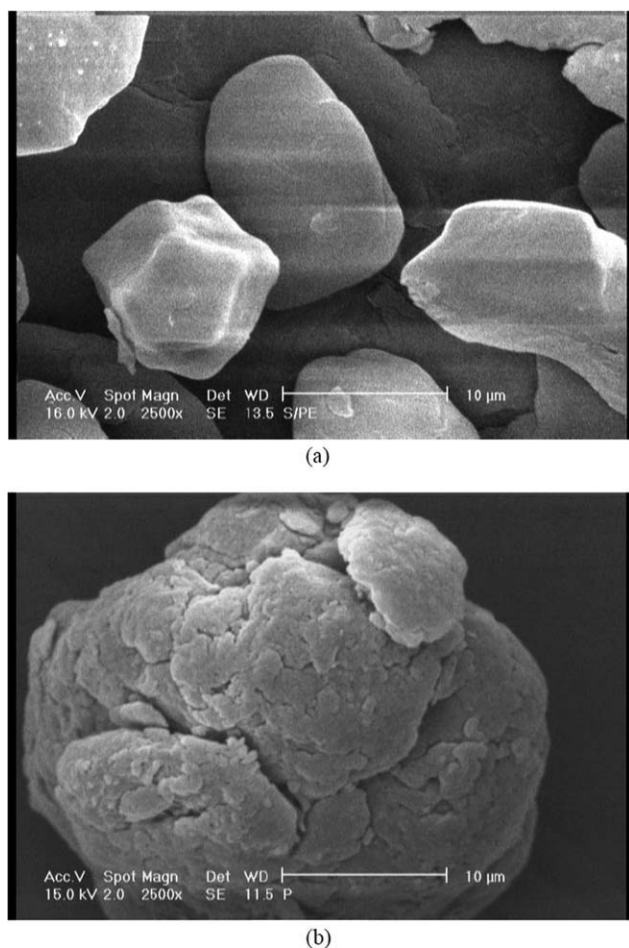


Figure 1. SEM micrographs (magnification: 2500 \times) of (a) the as-received starch material and (b) the neat starch after 10 h of ball milling.

(HD/S)_b sample compared to the melt-blended ones, occurred simultaneously with an increase in the size of the starch minor phase [Figure 2(a, b)]. Therefore, we propose that mechanical properties enhancement of polymer blends should be mainly related to the improvement of interfacial adhesion between the blend phases rather than to diminishing the dispersed phase size.

Rheology. It has been shown that rheological measurements can be used as an original method for determining the interfacial adhesion strength between the components of polymer blends.²⁹

Storage modulus (G') and complex viscosity (η^*) of the prepared samples, as functions of angular frequency (ω), are shown in Figure 3. The HDPE shows the highest modulus and viscosity among the samples in entire studied frequency range. Addition of the starch to the HDPE, decreased its G' and η^* values in the whole frequency range, exhibiting the typical rheological behavior of polymer blends whose components are immiscible with each other. However, the decrease was much less pronounced in the case of the HD-(HD/S)_b sample as compared to the melt-blended ones (HD/S and HD/S/MA). These differences may be interpreted as coming from the enhanced interfacial strength between the HDPE and starch components in the sample pre-

pared via the HEBM process [Figure 2(b)]. Similar to the well-known Mullins effect in filled rubbers,^{13,28,30} it seems that the absence of polyethylene-starch binding in the HD/S blend [Figure 2(a)] caused the HDPE molecules to slip over the surface of the undamaged starch granules, leading to elasticity reduction (Figure 3). However, the slight enhancement of the rheological properties of the HD/S/MA, in comparison with those of the HD/S may be due to the limited reactions between the maleic anhydride of the PE-g-MA copolymer and the starch hydroxyl groups.¹²

Furthermore, a relaxation process of the dispersed droplets of minor phase in polymer blends, after their slight deformations, has been proposed to be responsible for the blends high elasticity.¹³ The occurrence of the relaxation process relies strongly on a key factor, namely, the good interaction at the interface of the minor and major phases. Therefore, the higher elasticity of the HD-(HD/S)_b sample, as compared to that of the HD/S and HD/S/MA ones, can also be ascribed to the starch relaxation

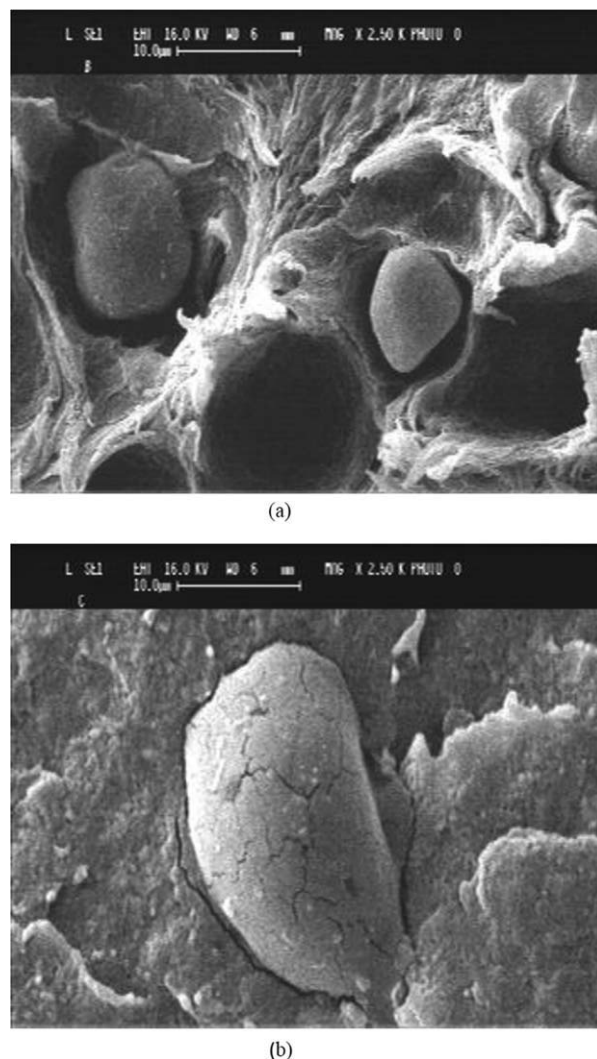


Figure 2. SEM micrographs (magnification: 2500 \times) of the fractured surfaces of (a) HD/S and (b) HD-(HD/S)_b samples.

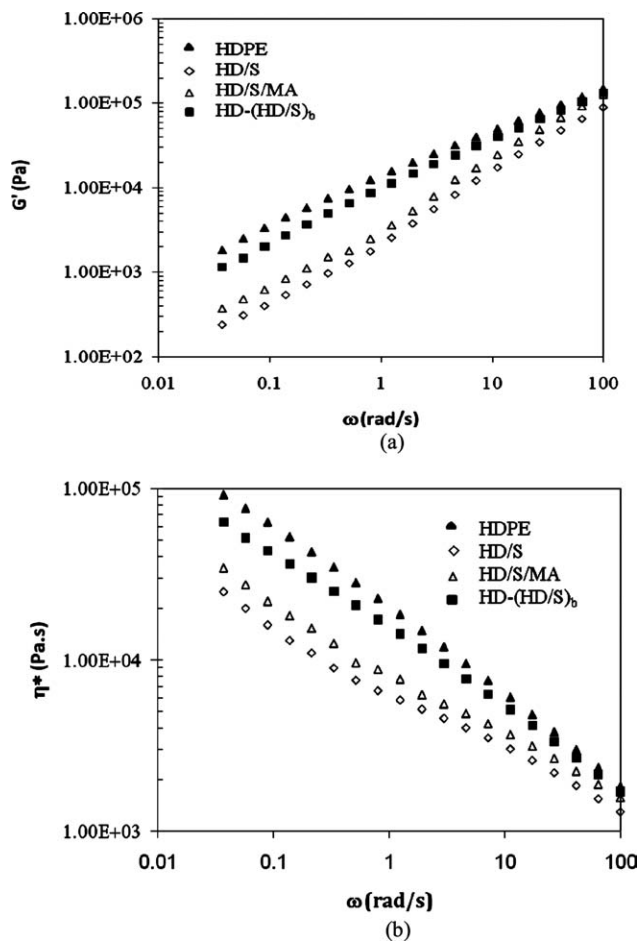


Figure 3. Rheological behaviors of the studied samples: (a) $G'(\omega)$ and (b) $\eta^*(\omega)$, measured at $T = 190^\circ\text{C}$ with 1% strain.

and deformation in the former, during the rheological measurements.

Fourier Transform Infrared. The FTIR spectra of the neat materials (HDPE and starch) can be seen in Figure 4, whereas Figure 5 displays those of the $(\text{HD/S})_b$ system. Figure 4(a) shows the well-defined characteristic peaks of the neat HDPE at 2917, 2849, 1473, and 719 cm^{-1} .³¹ In the spectrum of the starch [Figure 4(b)], the broad band at 3426 cm^{-1} , the sharp band at 2930 cm^{-1} , and the band at 1646 cm^{-1} correspond to the hydrogen-bonded hydroxyl groups, C—H stretches associated with the ring methane hydrogen atoms, and δ (O—H) bending of water, respectively. Also, the bands from 764 to 1157 cm^{-1} are attributed to the C—O bond stretching.²⁵

Inspection of the spectrum of the $(\text{HD/S})_b$ (Figure 5) reveals the presence of the main characteristics peaks of polyethylene at 2917, 2849, and 1473 cm^{-1} and of starch at 3390 and 1644 cm^{-1} . The most important characteristic peak in the $(\text{HD/S})_b$ spectrum, which cannot be seen in the spectra of the neat components (Figure 4) is the peak at 1200 cm^{-1} . We believe that this peak can be due to the formation of C—O—C bonds between the polyethylene and starch during the HEBM process. Also, the peak around 3400 cm^{-1} in the spectrum of the starch

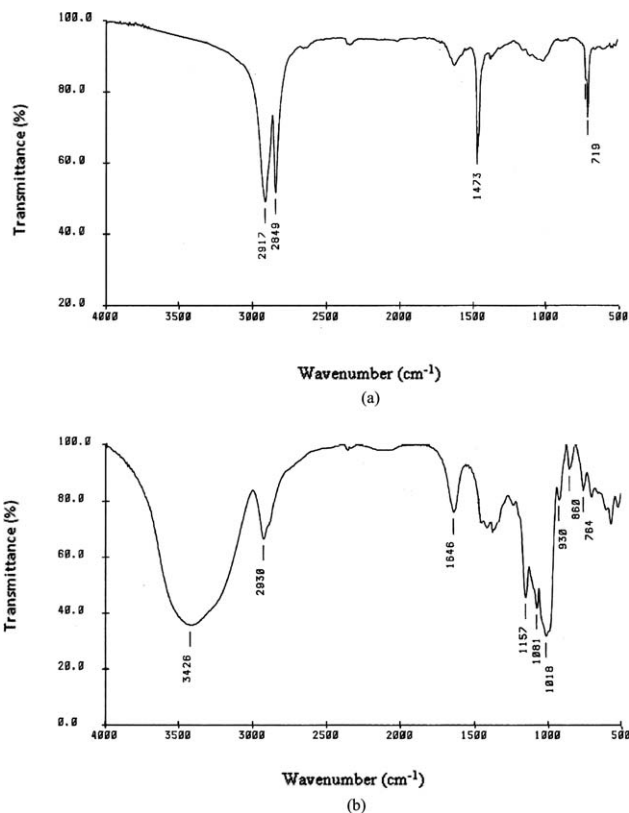


Figure 4. FTIR spectra of (a) HDPE and (b) starch materials.

[Figure 4(b)] is slightly wider, at all heights, than that in the $(\text{HD/S})_b$ spectrum (Figure 5), which points to the reduction of the hydrogen-bonded hydroxyl groups of the starch in the latter.³¹ In other words, the milling process emancipated some —OH groups from the H-bonding network, affording activated hydroxyl bonds to the starch molecules. Overall, the high mechanical energy of the milling process could abstract some hydrogen atoms from the HDPE molecules as well as from the activated OH groups of the starch molecules, leaving macroradical chains in the ball mill chamber. Subsequently, the active macroradicals interacted with each other and formed some new ether bonds, which caused the appearance of the aforementioned FTIR peak at 1200 cm^{-1} . Previously, Zhang et al.²³ reported the formation of ester bonds between maleic anhydride

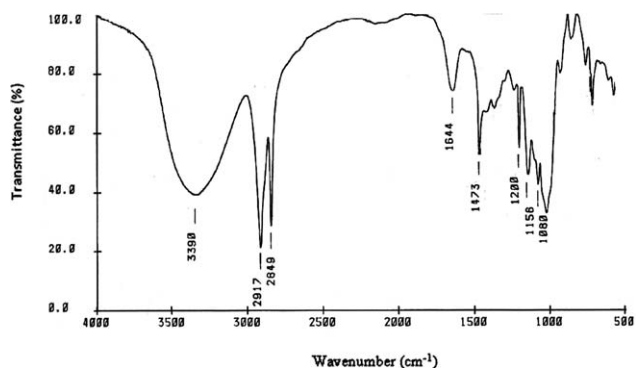
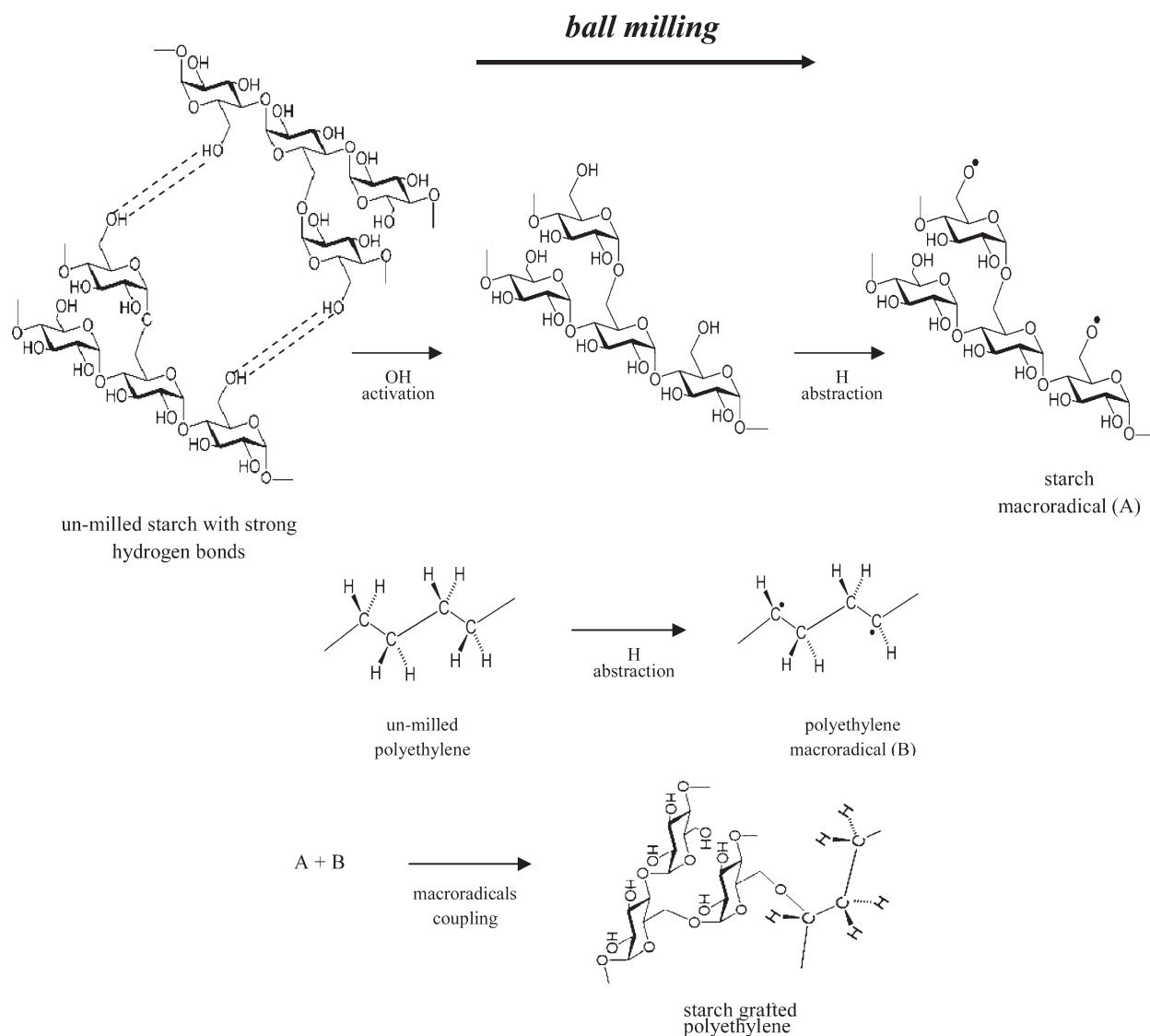


Figure 5. FTIR spectra of the $(\text{HD/S})_b$ mixture.



Scheme 1 . A suggested mechanism for starch grafting onto polyethylene during the HEBM process.

groups of a maleated polyethylene and hydroxyl groups of cellulose in a ball-milling process, although they did not offer any morphological support for the phenomenon. However, this is the first time that attempts have been made to investigate the possibility of reaction between a unfunctionalized polyethylene and a natural polymer. Scheme 1 demonstrates the suggested mechanism, leading to starch grafting onto polyethylene in the HEBM process.

It is worth noting here that the aforementioned unusual improvements in the tensile strength, elongation at break, interfacial adhesion, and rheological properties of the HD-(HD/S)_b blend can be explained to be due to the presence of the (HD/S)_b system which acted as an efficient and nontoxic compatibilizer between the polyethylene and starch phases.

Biodegradation. Table II shows the final weight losses of the prepared samples in the biodegradation test. These losses of weights correspond directly to the extent of biodegradation by

the fungi. The HDPE, as an essentially nonbiodegradable material, exhibited only 0.50 wt % of weight loss, whereas the HD/S, HD/S/MA, and HD-(HD/S)_b samples showed 2.00, 4.00, and 7.00 wt % loss of weights, respectively.

The higher degradability of the HD/S/MA than the HD/S (Table II) may be due to the reaction of anhydride groups of the PE-g-MA with hydroxyl groups of the starch, forming ester groups

Table II. Final Weight Losses of the Selected Samples after 3 Months of Biodegradation by the Fungi

Sample	Weight loss (wt %)
HDPE	0.50
HD/S	2.00
HD/S/MA	4.00
HD-(HD/S) _b	7.00

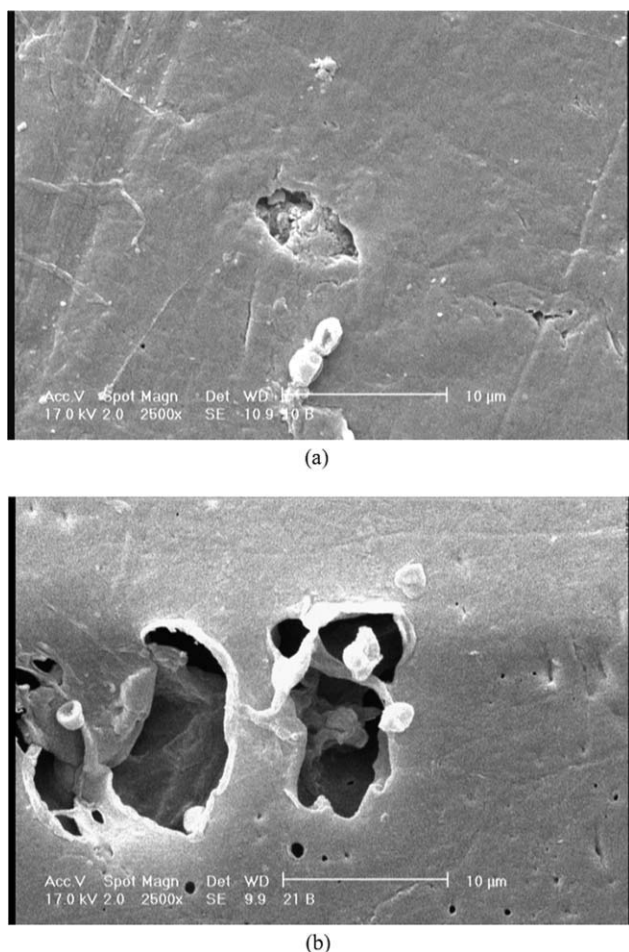


Figure 6. SEM micrographs (magnification: 2500 \times) of (a) HD/S and (b) HD-(HD/S)_b samples after 3 months of exposing to the fungi.

that can be more readily accessed by the fungi.³² However, the shape and morphology of the damaged starch could be the reason behind the fact that the HD-(HD/S)_b had the best biodegradability among the studied samples. As discussed based on the FTIR results, given in the previous section, the ball-milled starch had more free hydroxyl groups than the as-received and melt-processed ones. Therefore, these active hydroxyl groups had more chance to interact with the hydrogen atoms of water molecules which were available in the process of biodegradation. Regarding the fact that composites with a higher affinity to water are usually more prone to organism attack,¹³ the HD-(HD/S)_b degraded more than the HD/S when exposed to the fungi.

SEM micrographs of the HD/S and HD-(HD/S)_b samples after 3 months of exposure to the fungi are demonstrated in Figure 6. The observed holes and cracks on the surfaces can be considered as signs of the samples biodegradation. It should be noted that the surfaces of the above samples were very smooth before degradation (SEMs are not shown here for brevity). It is seen that the HD-(HD/S)_b sample had more and larger crack and holes, emanating from its higher biodegradability. These observations are in accordance with the results of Table II.

CONCLUSIONS

An innovative procedure for producing a HDPE/starch blend in the absence of any external compatibilizer agent was presented. The procedure consisted in the first step of mixing the HDPE and pristine starch in solid states by HEBM process, to obtain the (HD-S)_b mixture. Subsequently, a certain amount of the mixture was melt blended with the pure HDPE, until the HD/(HD-S)_b blend containing 85 wt % of the HDPE and 15 wt % of the starch was achieved. The HD/(HD-S)_b showed enhanced mechanical and biodegradation properties as compared with HD/S as well as HD/S/MA blends, containing the same starch loadings, but prepared only by melt-mixing method. The properties of the HD/(HD-S)_b blend were discussed in terms of the formation of a strong interface between the ball-milled polyethylene and starch components, as inferred from the SEM micrographs, rheological studies, and FTIR characterizations. Furthermore, a mechanism was proposed to explain the formation of the starch-grafted polyethylene during the HEBM process. The polyethylene/starch blend, fabricated through mediation of the HEBM process, would have a great potential to be the first choice for food and hygienic products packaging due to the absence of any toxic or hazardous materials in its formulation. Finally, this study opens new avenues for *in situ* compatibilization of immiscible HDPE–starch blends, simultaneously with improving their biodegradability.

ACKNOWLEDGMENTS

The authors would like to place on record their appreciation for the support rendered by the Research and Technology Directorate/National Iranian Oil Company, for the research leading to the present article. Special thanks are also given to Mrs. Chitsazian from Industrial and Environmental Protection Division at RIPI, for her help with the biodegradation experiments.

REFERENCES

1. Wang, X.; Hu, Y.; Song, L.; Xuan, S.; Xing, W.; Bal, Z.; Lu, H. *Ind. Eng. Chem. Res.* **2011**, *50*, 713.
2. Zhang, Q.; Yu, Z.; Xie, X.; Naito, K.; Kagawa, Y. *Polymer* **2007**, *48*, 7193.
3. Glenn, G. M.; Orts, W. J.; Nobes, G. A. R.; Gray, G. M. *Ind. Crops. Prod.* **2001**, *14*, 125.
4. Wu, Q.; Chen, X.; Zhang, Y.; Wu, Z.; Huang, Y. *Ind. Eng. Chem. Res.* **2011**, *50*, 2008.
5. Yu, L.; Dean, K.; Li, L. *Prog. Polym. Sci.* **2006**, *3*, 576.
6. Taguet, A.; Huneault, M.; Favis, B. D. *Polymer* **2009**, *50*, 5733.
7. Varela, C.; Rosales, C.; Perera, R.; Matos, M.; Poirier, T.; Blunda, J.; Rojas H. *Polym. Compos.* **2006**, *27*, 451.
8. Hippi, U. Ph.D. Thesis, Helsinki University of Technology, **2005**.
9. Aznar, M.; Vera, P.; Canellas, E.; Nerin, C.; Mercea, P.; Stormer, A. *J. Mater. Chem.* **2011**, *21*, 4358.
10. Shujun, W.; Jiugao, Y.; Jinglin, Y. *J. Polym. Environ.* **2006**, *14*, 65.

11. Matzinos, P.; Tserki, V.; Gianikouris, C.; Pavlidou, E.; Panayiotou, C. *Eur. Polym. J.* **2002**, *38*, 1713.
12. Ruiz, H.; Martin Martinez, E.; Mendez, M. A. *Starch/Starke* **2011**, *63*, 42.
13. Sharif, A.; Aalaie, J.; Shariatpanahi, H.; Hosseinkhanli, H.; Khoshniyat, A. *J. Polym. Res.* **2011**, *18*, 1955.
14. Bikiaris, D.; Panayiotou, C. *J. Appl. Polym. Sci.* **1998**, *70*, 1503.
15. Huang, C.; Roan, M.; Kuo, M.; Lu, W. *Polym. Degrad. Stab.* **2005**, *90*, 95.
16. Gupta, A. P.; Sharma, M. *J. Polym. Environ.* **2010**, *18*, 492.
17. Vertuccio, L.; Gorrasi, G.; Sorrentino, A.; Vittoria, V. *Carbohyd. Polym.* **2009**, *75*, 172.
18. Olmos, D.; Dominguez, C.; Castrillo, P. D.; Gonzalez-Benito, J. *Polymer* **2009**, *50*, 1732.
19. Sharif, A.; Mohammadi, N.; Ghaffarian, S. R. *J. Appl. Polym. Sci.* **2009**, *112*, 3249.
20. Nakamura, E. M.; Cordi, L.; Almeida, G. S.; Duran N.; Mei, L. H. I. *J. Mater. Process Technol.* **2005**, *162*, 236.
21. Pedroso, A. G.; Rosa, D. S. *Polym. Adv. Technol.* **2005**, *16*, 310.
22. Walker, A. M.; Tao, Y.; Torkelson, J. M. *Polymer* **2007**, *48*, 1066.
23. Zhang, F.; Qiu, W.; Yang, L.; Endo, T.; Hirotsu, T. *J. Mater. Chem.* **2002**, *12*, 24.
24. Sailaja, R. R. N.; Chanda, M. *J. Appl. Polym. Sci.* **2001**, *80*, 863.
25. Kang, B. G.; Yoon, S. H.; Lee, S. H.; Yie, J. E.; Yoon, B. S.; Suh, M. H. *J. Appl. Polym. Sci.* **1996**, *60*, 1977.
26. Fenouillot, F.; Cassagnau, P.; Majeste, J. C. *Polymer* **2009**, *50*, 1.
27. Jafari, S. H.; Yavari, A.; Asadinezhad, A.; Khonakdar, H. A.; Bohme, F. *Polymer* **2005**, *46*, 5082.
28. Santos, J.; Guthrie, J. *J. Mater. Chem.* **2006**, *16*, 237.
29. Chen, Y.; Li, H. *Polymer* **2009**, *46*, 7707.
30. Mullins, L. *Rubber Chem. Technol.* **1969**, *42*, 339.
31. Stuart, B.; George, B.; McIntyre, P. *Modern Infrared Spectroscopy*; Wiley: New York, **2008**.
32. Shang, X.; Fu, X.; Chen, X.; Yang, L. *J. Appl. Polym. Sci.* **2009**, *114*, 3574.