Interfacial Adhesion Reaction of Polyethylene and Starch Blends Using Maleated Polyethylene Reactive Compatibilizer

SEONG IK YOO,[1] TAE YEON LEE,[1] JIN-SAN YOON,[2] IK-MO LEE,[3] MAL-NAM KIM,[4] HAN SUP LEE[1]

[1] Department of Textile Engineering, INHA University, 402-751 Inchon, Korea

[2] Department of Polymer Science, INHA University, 402-751 Inchon, Korea

[3] Department of Chemistry, INHA University, 402-751 Inchon, Korea

[4] Department of Biology, Sangmyung University, 110-743 Seoul, Korea

ABSTRACT: The interfacial reaction of the polyethylene (PE)/starch blend system containing the reactive compatibilizer maleated polyethylene (m-PE) was directly characterized by Fourier transform infrared (FTIR) spectroscopy. A significant amount of anhydride groups on m-PE existed as hydrolyzed forms, resulting in a large amount of carboxyl groups. Using a vacuum-heating-cell designed in the laboratory, the carboxyl groups were successfully transformed into the dehydrolyzed state (i.e., anhydride group). This result enabled the direct spectroscopic observation of chemical reaction occurring at the interface. For the PE/starch blend system containing m-PE, the chemical reaction at the interface was verified by the evolution of ester and carboxyl groups in the FTIR spectra. The effect of the reactive compatibilizer on the interfacial morphology was also examined by scanning electron micrography (SEM). Enhanced interfacial adhesion was clearly observed for the blend system containing reactive compatibilizer. Tensile strengths of blend systems containing m-PE also increased noticeably compared with the corresponding system without compatibilizer. A similar observation was made for the breaking elongation data. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 767–776, 2002

Key words: maleated polyethylene (m-PE); interfacial adhesion; polyethylene; starch; maleic anhydride

INTRODUCTION

Recently, a great deal of attention has been paid to the application of biodegradable polymers, such as starch, lignin, cellulose, gluten, and chitin, and its derivatives to replace the conventional petro-

leum-based plastics that cause significant environmental problem because of their nonbiodegradability.[1] Because polyethylene (PE) is one of the most extensively produced nondegradable polymer and various types of PEs are used extensively in many fields, including agricultural and food-packaging films,[2] there has been an increased interest in enhancing the biodegradability of PEs by blending them with a cheap natural biopolymer.[3]

Starch that shows a high biodegradation rate is a blend of amylose and amylopectin, both of which are polysaccharides composed of α-D-glucopyranosyl units, $(C_6H_{10}O_5)_x$.[4] Ever since Griffin[5–7] used granular starch as a filler in PE to enhance the biodegradability of the PE blend system, many studies have been focused on the increase of the mechanical properties and processibility of the starch/polyolefin blend system. On adding hydrophilic starch, tensile strength and breaking elongation of the PE blend decreases significantly because of poor interfacial adhesion strength. The processibility of PE/starch blend also deteriorates. These problems have been somewhat resolved by adding a compatibilizer, which strengthens the interfacial adhesion by reacting with the granular starch.

Using poly(ethylene-co-acrylic acid) (EAA) as compatibilizer in the presence of urea and hydroxide, Otey and Westoff[8–10] obtained a PE/starch blend film containing a high amount of starch (40–50%). The carboxyl group on EAA was known to form hydrogen bonding with the hydroxyl group on starch, resulting in helical V-type complexes.[11–13] However, those blend systems require high amounts of EAA to achieve reasonable mechanical properties and the biodegradation rate was known to decrease noticeably.[14] According to the work of Panayiotou,[15] compatibility between low-density polyethylene (LDPE) and plasticized starch could be increased with a relatively small amount of maleated polyethylene (m-PE), and the resultant blend system still showed good biodegradability. However, there are still limited number of studies to clarify the exact nature of interfacial adhesion mechanism of PE/starch blend system containing m-PE as a reactive compatibilizer.

In this work, direct observation of the interfacial reaction was made by Fourier transform infrared (FTIR) spectroscopy for the PE/starch blend system containing m-PE as a compatibilizer. The morphology and mechanical properties of the blend system used were correlated with the FTIR spectroscopy results.

EXPERIMENTAL

Sample

Commercial-grade polyethylene (PE) and corn starch were obtained from Han Yang Chemical Corp. (LLDPE, model 2558, MI; 5.0 g/10 min at
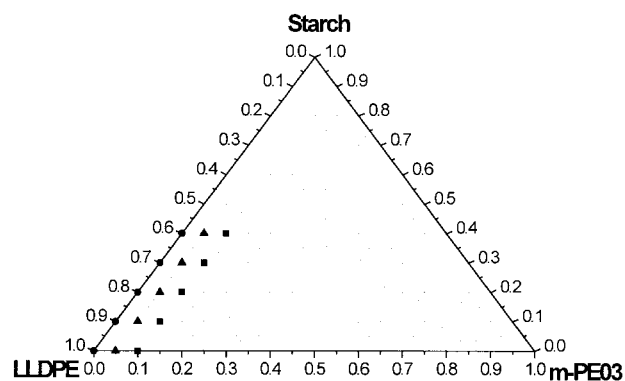

Figure 1 Composition diagram of PE/m-PE/starch blend samples. Key: (●) series one: (▲) series two; (■) series three.

190 °C) and Sam Yang Genex (model COO20) in Korea, respectively. Two different maleated polyethylenes, m-PE30 (Ho Nam Petrochemical Corp, model ES-300, MI; 0.3 g/10 min at 190 °C) and m-PE03 (Ho Nam Petrochemical Corp, model EM-510M, MI; 0.7 g/10 min at 190 °C), were used. m-PE03 contains 0.3 wt % maleic anhydride (MAH) on LLDPE and m-PE30 contains 3.0 wt % MAH on HDPE. Blend compositions of the samples used in this study are shown in Figure 1. Three different series of blend samples were prepared containing 0, 5, and 10 wt % m-PE03, respectively. Samples in series one (shown with circles in Figure 1) containing no compatibilizer were named LLDPE/starch samples, and those in series two and three (displayed with triangles and squares, respectively) were named LLDPE/m-PE (5 %)/starch and LLDPE/m-PE (10 %)/starch, respectively. In each series shown on the parallel line along the LLDPE/starch axis, starch contents were 0, 10, 20, 30, and 40 wt %.

Fourier Transform Infrared Spectroscopy (FTIR)

For FTIR spectroscopic measurement, m-PE was melt pressed into a thin film with a Carver Hot press (FRED S. CARVER Inc.; model 2697) at 170 °C. Thin films were then vacuum dried at 160 °C for ~60 min. Granular starch was initially dried in vacuum oven at 80 °C for >9 h to minimize the moisture contents. After initial drying, starch was then dissolved in purified water at 80 °C to form ~5 % solution, and the solution was cast onto a Teflon plate. The film was then dried in an oven heated at 80 °C. To analyze the chemical reaction at the interface with a FTIR spectroscope (Nicolet, model; 520p), two films (m-PE and
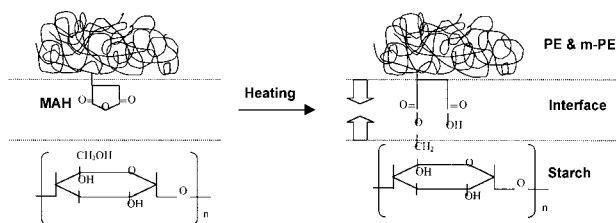
Figure 2 Interfacial chemical reaction of MAH and OH.

starch) are manually pressed to each other between two KBr windows.

The main purpose of the FTIR experiment was to measure the chemical reaction occurring at the interface between MAH groups on m-PE and hydroxyl groups on starch. Because any moisture in the spectrometer chamber may interfere with the chemical reaction, all FTIR experiments were done inside the vacuum-heating-cell that was specially designed for this experiment in this laboratory. With this vacuum-heating-cell, the samples could be heated with the built-in cartridge heaters while maintaining the vacuum state ($<10^{-3}$ Torr).

Morphology and Tensile Properties

All three components were vacuum dried at 90 °C for ~8 h before blending. Blend samples were prepared with Brabender (model Tlasti-Corder PLV151) and HAAKE Rheomixer (model 600p) at 180 °C at 60 rpm for 10 min. After blending, thick films of ~1-mm thickness were made by melt pressing with a hot press (FRED S. CARVER Inc.; model 2697) at 170 °C. To observe the interfacial morphology of blends, the specimen was frozen in liquid nitrogen and immediately fractured. Samples were coated with a gold/palladium alloy and the fracture surfaces were investigated by SEM (HITACHI; S-4200).

Tensile strength and strain were measured according to the ASTM D638 method using an universal testing machine (UTM; Hounsfield; model H10K-S). Measurements were done at a crosshead speed of 50 mm/min at room temperature with the initial grip distance of 20 mm. More than 10 measurements were conducted for each sample, and the results were averaged to obtain a mean value.

RESULTS AND DISCUSSION

The expected chemical reaction that might occur at the m-PE/starch interface is shown schemati-

cally in Figure 2. If a MAH group grafted on PE reacts with a hydroxyl group on starch, the anhydride group will become an ester linkage and carboxyl group. Even though many works have been reported on the improvement of interfacial adhesion of blend samples using reactive compatibilizer,[16–23] direct observations of the chemical reaction occurring at the interface have been scarcely reported.

The carbonyl stretching region of the FTIR spectrum of m-PE03 is shown in Figure 3(a). As expected, symmetrical and asymmetrical stretching vibration bands of anhydride groups are observed at 1865 and 1780 cm^{-1}, respectively.[24] However, a strong band at 1710 cm^{-1} is also observed. This band is believed to be due to the hydrolysis reaction of MAH group by H_2O molecules,[25,26] as shown schematically in Figure 3(b), during grafting of MAH onto PE or storage of m-PE. Each hydrolysis of MAH group with a H_2O will generate two carboxyl groups.[27]

The main purpose of this work is to verify the chemical reaction between the MAH group on m-PE and the hydroxyl group on starch at the interface, as shown in Figure 2. Because excess existence of the hydrolyzed state of MAH will hinder direct observation of the chemical reaction at the interface, it was necessary to dehydrolyze the carboxyl groups (hydrolyzed states of MAH groups) before the interfacial reaction.

To verify the dehydration process shown in Figure 3(b), m-PE30 film was initially heated to 160 °C and then maintained at that temperature for 60 min using the vacuum-heating-cell, which
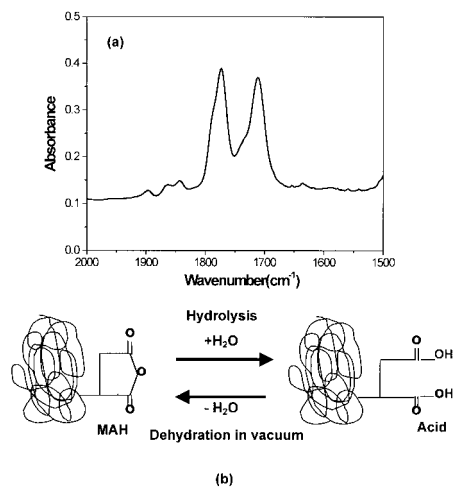
Figure 3 (a) FTIR spectrum of m-PE03 at room temperature. (b) Reversible chemical reaction process of MAH & acid.
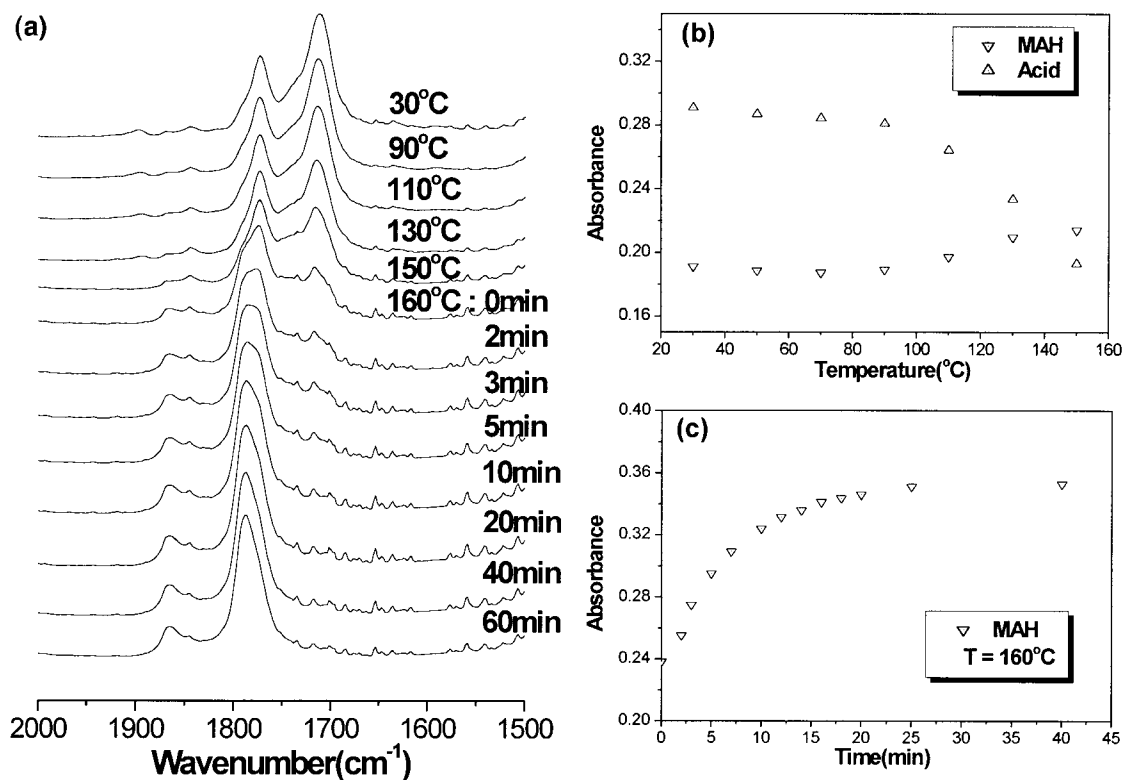
Figure 4 (a) FTIR spectra of m-PE30 as a function of temperature and time (Acid → MAH conversion). (b) Absorbance change of 1710 cm^{-1} (△) and 1780 cm^{-1}(▽) bands as a function of temperature. (c) Absorbance change of 1780 cm^{-1} band during isothermal treatment at 160 °C.

provided vacuum state ($<10^{-3}$ Torr) during the entire process. In Figure 4(a), carbonyl stretching regions of FTIR spectra obtained during heating and isothermal heat treatment processes are shown. Absorbance changes of asymmetric stretching vibration of MAH groups (1780 cm^{-1}) and of carboxyl groups as a function of temperature are shown in Figure 4(b). The absorbance change of the 1780 cm^{-1} band during isothermal treatment at 160 °C is shown in Figure 4(c) as a function of time.

It is clear from Figure 4(b) that the intensity of carboxyl groups decreases slowly up to ~110 °C and then is followed by the sudden decrease on further heating. The results in Figure 4 indicate that the dehydration process seems to be completed by vacuum drying at 160 °C for ~60 min. It is to be noted that the DSC thermogram of m-PE30 showed endothermic melting transition starting at ~110 °C (data not shown) This result indicates that the dehydration process can be significantly facilitated by the melting transition of the crystalline material. The sudden decrease of

carboxylic acid content may be interpreted in terms of two different reasons. The first reason is the melting transition of the crystalline region. Even though it is unreasonable to contain carboxyl groups in the crystalline lattice of PE by co-crystallization of ethylene and carboxyl groups, the carboxyl groups acting as points defects may be surrounded by the crystalline lattice. Because the dehydration process shown in Figure 3(b) should be accompanied by the removal of the water molecules out of the crystalline lattice, the dehydration process will be significantly hindered by the crystalline portions surrounding the lattice defects. A second possible reason for the sudden decrease of carboxylic acid content at ~110 °C is a viscosity decrease of the amorphous matrix. Decreased viscosity is expected to facilitate the diffusion of the water molecule out of the matrix. The exact contribution of two possible reasons is not clear at this stage. However, the sudden decrease at the starting of the melting transition seems to indicate that most of carboxyl groups are surrounded by the crystalline lattices. The viscos-

ity of amorphous matrix should decrease gradually on heating. If the viscosity decrease might be the major factor, the decrease of carboxylic acid content is expected to decrease linearly, not abruptly at a certain temperature.

Because almost all hydrolyzed states (carboxylic acid forms) of anhydride groups were verified to be converted into dehydrolyzed state (MAH forms) by thermal treatment under vacuum, it is now possible to check the chemical reaction between MAH on m-PE and hydroxyl groups on starch by the FTIR method. Before attempting to make direct observation of the reaction between m-PE and starch, two preliminary tests were performed.

The dehydrolyzed m-PE was heated again up to 170 °C and maintained at that temperature for ~1 h to check the chemical stability of the MAH group under the reaction condition that will be used for the interfacial reaction of m-PE with starch. FTIR spectra (not shown) obtained during heating under vacuum showed neither a carboxylic acid band near 1710 cm^{-1} nor an ester band at 1730 cm^{-1}. Furthermore, the carbonyl stretching region of the FTIR spectrum obtained at 170 °C under vacuum is practically identical with that of dehydrolyzed m-PE at room temperature. This result indicates that MAH groups retain their chemical structure in the temperature range studied if treated under vacuum. However, if the thermal treatment is performed at an atmospheric pressure, a significant amount of MAH groups were converted into carboxylic acid forms (data not shown).

The reactivity of MAH with hydroxyl group was initially measured with m-PE30 and hydroxyl-terminated poly(tetramethylene oxide) (PTMO) with molecular mass of 2500 g/mol. Because PTMO is low molecular mass material, the chemical reaction, if it occurs, could be observed within a relatively short period of reaction time because of the low viscosity of PTMO. Before using, it was vacuum dried at 80 °C for at least 12 h to remove water molecules dissolved in PTMO. Thin films of dehydrolyzed m-PE30 and PTMO were manually compressed to each other using two KBr plates, and the specimen was inserted into the vacuum-heating-cell.

In Figure 5, FTIR spectra obtained during heating from 30 to 170 °C (Figure 5(a)) and isothermal treatment at 170 °C (Figure 5(b)) are shown. It is noted that all spectra in Figure 5 were obtained under vacuum. With each set of FTIR spectra, the absorbance change of carbonyl

stretching band of MAH/ester groups are also shown either as a function of temperature (Figure 5(a)) or as a function of isothermal treatment time at 170 °C (Figure 5(b)). As expected from Figure 2, the chemical reaction between anhydride and hydroxyl group could be verified by the decrease of anhydride group content and also by the increase of ester and carboxylic acid content. On heating the m-PE30/PTMO two-layer film from 30 to ~120 °C under vacuum, the absorbance of carbonyl stretching band of MAH group at 1780 cm^{-1} seems to decrease slowly. Its decreasing rate is increased on further heating to 170 °C, as shown in the lower figure in Figure 5(a). However, the absorbances at 1730 and 1710 cm^{-1}, corresponding to carbonyl stretching band of ester and acid groups, respectively, is only observed through the slight increase of base line. In Figure 5(b), FTIR spectra obtained during isothermal heat treatment at 170 °C are plotted with the same base line to show clearly the absorbance change as a function of time. The absorbance of the 1730 cm^{-1} band is gradually increased at the expense of that at 1780 cm^{-1}. The absorbance change of those two bands appears to persist up to 2 h, as shown in the lower figure in Figure 5(b). This result undoubtedly shows that the interfacial reaction between anhydride and hydroxyl group can be directly observed by FTIR spectroscopy.

It is worth noting that the chemical reaction between m-PE and PTMO only shows appreciable increase of ester group absorbance at 1730 cm^{-1} without any significant increase of carboxyl group absorbance at 1710 cm^{-1}. By comparing two FTIR spectra in Figures 3 and 5(b), the difference between two (ester and acid) absorption frequencies might be easily noted. Reaction of an anhydride group with a hydroxyl group will form an ester and a carboxylic acid groups. Because the mobility of PTMO is relatively high, the carboxyl group formed appears to further react with the remaining hydroxyl group, resulting in the negligible absorbance around 1710 cm^{-1}. Based on these results, it can be concluded that the reactivity of MAH with hydroxyl groups is relatively high at ~170 °C, provided that the mobility of hydroxyl group is sufficient.

The reactivity of anhydride group grafted on m-PE03 and the hydroxyl group on starch was also characterized by FTIR spectroscopy. Three FTIR spectra are shown in Figure 6. The FTIR spectrum of dehydrated m-PE03, shown in Figure 6(a), shows very low absorbance of the ester band
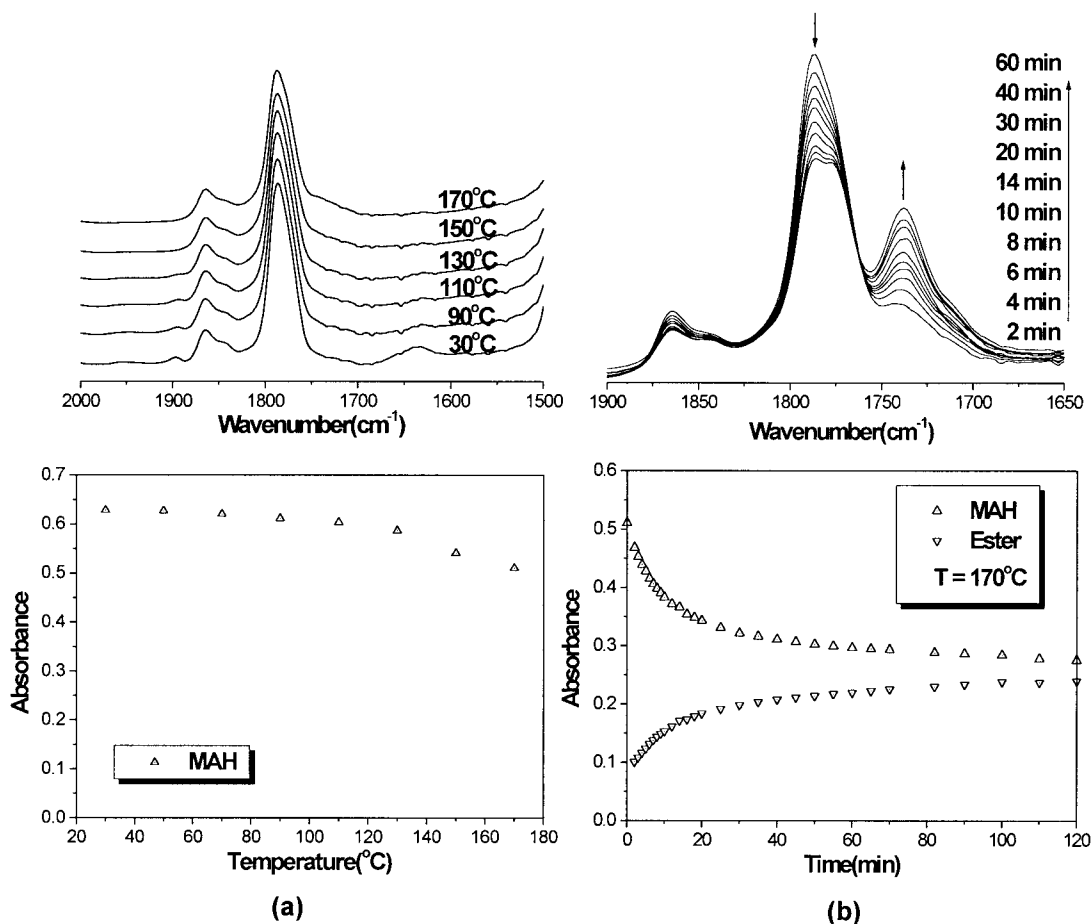
Figure 5 FTIR spectra of m-PE30/PTMO two-layer film as a function of (a) temperature and (b) isothermal heat treatment time at 170 °C.

and negligible absorbance of the carboxylic acid band. After FTIR measurement, the same m-PE03 film was placed on top of a thin film of starch and compressed manually between two KBr plates. The two-layer specimen was then heated treated at 160 °C under vacuum. Figures 6(b) and (c) are FTIR spectra obtained after 2 and 3 h of isothermal heat treatment, respectively. Even though the absorbances of ester and acid bands at 1730 and 1710 cm^{-1}, respectively, are not very high, the two absorbances are noticeably increased compared with those in the spectrum shown in Figure 6(a). It is to be noted that starch does not show any absorption band at those frequency ranges. Therefore, any absorbance increases at 1730 and 1710 cm^{-1} should be indicative of the chemical reaction between anhydride on m-PE and hydroxyl groups on starch. The fact that the absorbances of the 1780 cm^{-1} band of the spectra in Figures 6(b) and 6(c) are appreciably lower than the corresponding one of Figure 6(a)

further confirms the occurrence of the interfacial adhesion reaction.

Comparing the results in Figure 6 with those in Figure 5, two main differences can be easily observed. Even though interfacial reaction between m-PE and PTMO tends to generate ester functional group without any significant content of carboxyl groups, the corresponding one between m-PE and starch seems to make a similar amount of ester and carboxyl groups. Furthermore, the interfacial reaction with starch appears to take a longer time than that with PTMO. Both differences might be understood in terms of the viscosity difference between PTMO and starch. At the isothermal reaction temperature, low molecular weight PTMO is virtually a viscose liquid, whereas starch remains as a solid state. Because of the high mobility of PTMO in the viscose liquid state, the carboxyl groups formed from reaction of anhydride group with hydroxyl group of PTMO have enough chance to further react with the
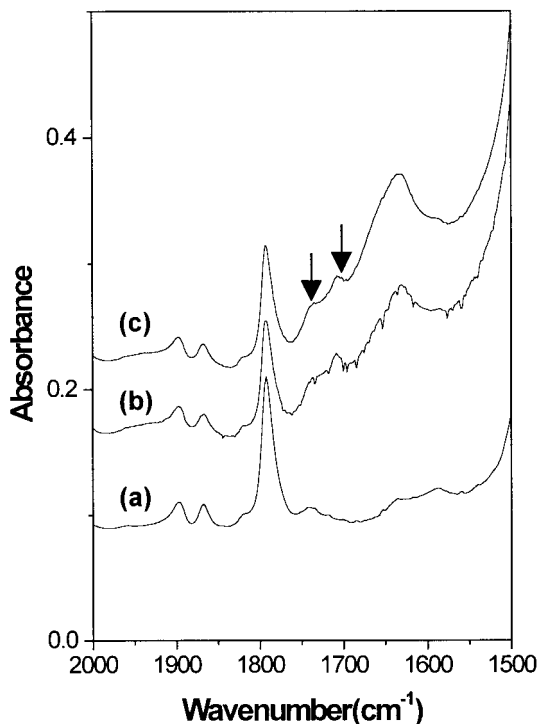
Figure 6 FTIR spectra of (a) m-PE03 after the dehydration process and (b) and (c) m-PE03/starch two-layer film after heat treatment for 2 and 3 h, respectively.

remaining hydroxyl groups to form another ester linkage.

Bikiaris and Panayiotou[28] also studied the interfacial chemical reaction between MAH on m-PE and hydroxyl groups in plasticized starch (granular starch + glycerol; PLST) by FTIR spectroscopy. Using LDPE/m-PE/PLST blends, they observed one broad carbonyl stretching IR band, which seems to be an overlapping band of 1728 and 1709 cm^{-1} bands. Based on that result, they reported the formation of the ester and carboxyl groups through the interfacial reaction between MAH of m-PE and hydroxyl groups on PLST. As pointed out in Figures 5 and 6, the chemical reaction of MAH on m-PE with hydroxyl group was significantly facilitated if the viscosity of one component is low. Because the PLST has hydroxyl-group-containing glycerol component of very low viscosity, the chemical reaction between MAH and hydroxyl groups appeared to have occurred mainly through glycerol, not through starch.

It is important to characterize the interfacial morphology to understand the mechanical properties for the immiscible blend systems.[29] For the blend system used in this study, the major component will be the PE matrix and the minor component will form dispersed phases. To see the interfacial structure between the matrix and dispersed phase, SEM microphotographs of fracture surface were obtained and are presented in Figure 7. Figures 7(a) and (b) are, respectively, SEM micrographs of LLDPE (80 wt %)/starch (20 wt %) blend and LLDPE (90 wt %)/starch (10 wt %) blend containing no reactive compatibilizer. As seen from Figure 7(a), many dispersed starch phases were removed from the fracture surface, presumably because of the weak interfacial adhesion between the matrix and dispersed phases. For most of the starch particles still remaining at the fracture surface, the starch phases appear to be practically separated from the matrix, as shown in the enlarged figure, Figure 7(b). The fracture surface of LLDPE (60 wt %)/m-PE03 (30 wt %)/starch (10 wt %) in Figure 7(c) shows no sign of interfacial failure. Almost all starch particles remain on the surface. This fact indicates that the interfacial adhesion of blend samples containing reactive compatibilizer is appreciably improved by the interfacial chemical reaction. The effect of the reactive compatibilizer might be also reconfirmed from the results in the enlarged micrograph in Figure 7(d). Similar observations were also made from other blend systems with different blend compositions.

The increased interfacial adhesion for the blend system containing reactive compatibilizer, m-PE, is believed to be due to the chemical reaction of MAH group with hydroxyl group on starch at the interface. It is not clear at this moment how the reactive compatibilizer is exactly distributed in the blends system. Even though some of the compatibilizer appears to be situated at the interface between the PE matrix and starch dispersed phases, thus enhancing the interfacial adhesion, some might be included in the PE matrix. If some fractions of m-PE form micellar domains in the PE matrix, those will not contribute to the improvement of the interfacial adhesion strength. Furthermore, such a micellar structure might deteriorate the mechanical properties of the blend system. More experimental observations have to be made to clarify the exact distribution of m-PE and to optimize the composition of each component in the blend system.

Mechanical properties were measured for the three blend series denoted in Figure 1. Series one, two, and three contain 0, 5, and 10 wt % reactive compatibilizer, m-PE03, respectively. Tensile strength and elongation at break values
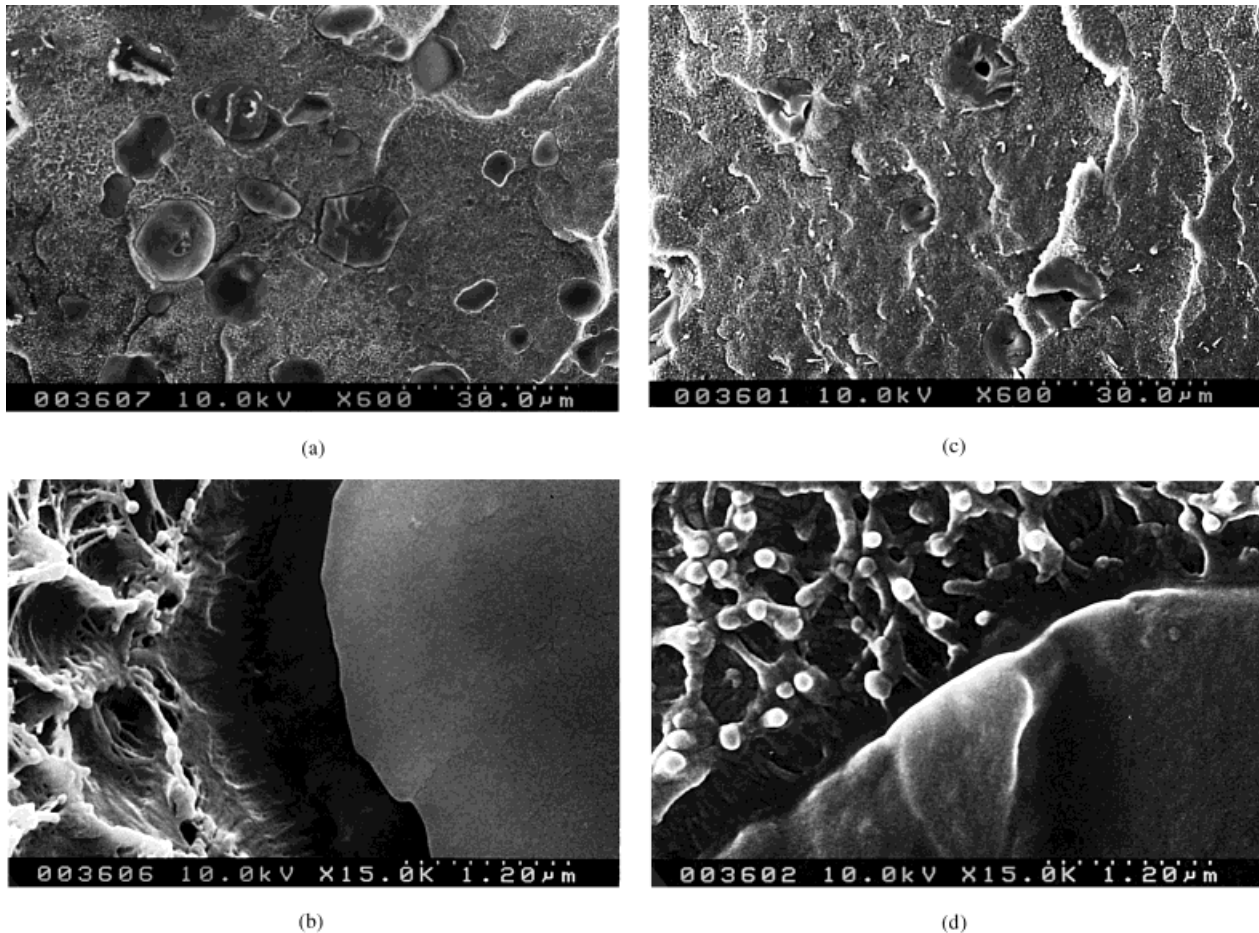
Figure 7 SEM micrographs of LLDPE/starch and LLDPE/m-PE03/starch blends: (a) LLDPE (80 %)/starch (20%); ×600; (b) LLDPE (90 %)/starch (10%); ×15,000; (c) LLDPE (60%)/m-PE (30%)/starch (10%); ×600; (d) LLDPE (60%)/m-PE(30%)/starch(10%); ×15,000.

are plotted as a function of starch content for all three series in Figure 8. LLDPE used in this study showed ~21.8 MPa tensile strength and 826% breaking elongation. On adding starch to LLDPE, tensile strength and breaking elongation were reduced for all blend series, regardless of the existence of reactive compatibilizer. This general phenomenon is because of the presence of starch that does not contribute to the mechanical properties of the blends and has been observed in many studies. However, the main purpose of this work is to test the effect of reactive compatibilizer on the mechanical properties of LLDPE/starch blends.

It is to be noted that for samples with 0 % starch content, the tensile strength and breaking elongation are somewhat decreased as the compatibilizer is added. This fact indicates that m-PE itself might deteriorate the mechanical properties of matrix PE. Upon adding compatibilizer to LLDPE/starch blends, breaking strength is noticeably increased for the blends samples containing starch up to 40 wt %. The enhanced breaking strength of the samples studied is believed to be due to the interfacial adhesion reaction between anhydride group on m-PE and hydroxyl group on starch. Breaking elongations of the blend samples containing 5 wt % m-PE are also noticeably enhanced compared with the corresponding blend series without compatibilizer. However, the breaking elongations of samples with 40% starch are very low, regardless of the existence of reactive compatibilizer. At this composition, LLDPE, as a matrix, seems to lose its continuity. Even though series three samples show somewhat scattered breaking elongation results, the general tendency appears to be maintained.
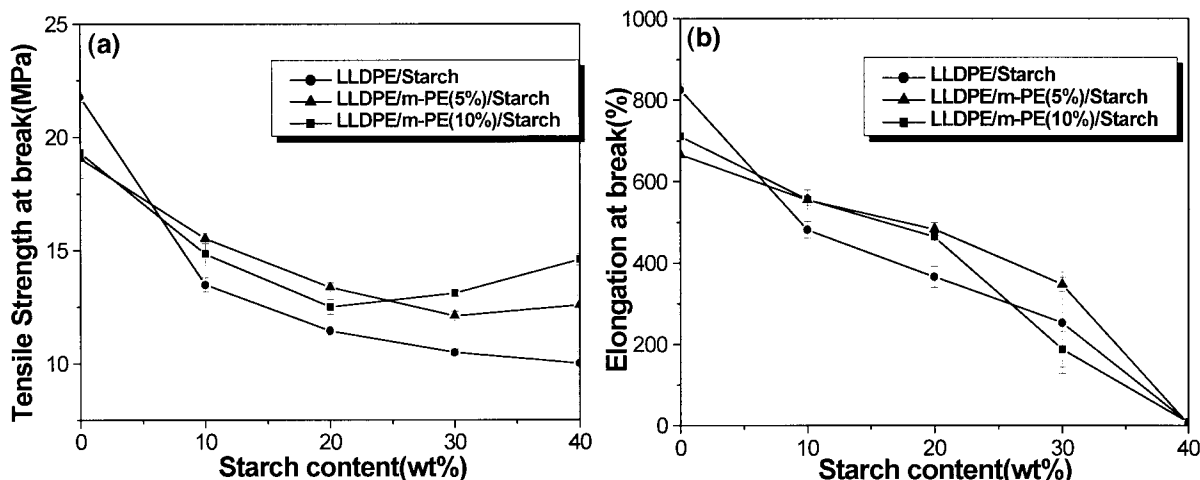
Figure 8 Mechanical properties of LLDPE/starch and LLDPE/m-PE03/starch blends: (a) tensile strength at break (MPa) as a function of starch content; (b) elongation at break(%) as a function of starch content. (Error bars corresponds to the standard deviation of ~10 measurements).

CONCLUSIONS

Interfacial adhesion reaction of LLDPE and starch using m-PE was directly characterized by FTIR spectroscopy. Significant amounts of anhydride groups on m-PE exist as hydrolyzed states forming carboxyl groups. Using a vacuum-heat-cell designed in our laboratory, all carboxyl groups on m-PE were successfully transformed into the dehydrolyzed states, providing a route for the direct FTIR spectroscopy observation of the interfacial adhesion reaction.

The reactivity of anhydride groups with hydroxyl groups was initially tested with m-PE and hydroxyl-terminated PTMO, which has high mobility due to its low molecular weight. On heating the m-PE and PTMO samples up to 170 °C and maintaining at that temperature for 2 h, the interfacial adhesion reaction was directly verified from the formation of ester functional group.

The interfacial adhesion reaction between m-PE and starch was also successfully verified. Even though the reaction occurs only at the interface, the ester and carboxyl groups were unambiguously observed by FTIR spectroscopy. This fact that the adhesion reaction occurs at the interface suggests that the blend system containing reactive compatibilizer will show improved blend morphology and mechanical properties compared with the corresponding blend system without compatibilizer.

The effect of reactive compatibilizer on the blend morphology was examined from the fracture surface by SEM. On fracturing the blend samples without reactive compatibilizer, many dispersed starch phased were detached, leaving smooth-surfaced cavities. However, all starch phases remained on the fracture surface for the blend samples containing reactive compatibilizer. This result supports the enhanced adhesion through the interfacial chemical reaction between anhydride group on m-PE and hydroxyl group on starch.

Mechanical properties were measured to correlate the interfacial adhesion reaction with the ultimate tensile properties. It was found that for LLDPE/starch blend samples studied, breaking strength was noticeably enhanced on adding reactive compatibilizer. A similar observation has been made for the breaking elongation.

REFERENCES

1. Zuchowska, D.; Steller, R.; Meissner, W. Polymr Degrad Stability 1998, 60, 471.
2. Aburto, J.; Thiebaud, S.; Alric, L.; Borredon, E.; Bikiaris, D.; Prinos, J.; Panayiotou, C. Carbohydr Polym 1997, 34, 101.
3. Doane, W.M.; Swanson, C.L.; Fanta, G.F. In Engineering Technologies for Materials and Chemicals from Biomass, ACS Symposium Ser. No. 476; Row-

ell, R.M.; Schultz, T.P.; Narayan, R., Eds.; American Chemical Society: Washington, DC, 1992; p197.

4. Zobel, H.F. Starch 1988, 40, 44.

5. Griffin, G.J.L. U.S. Pat. 4,016,177 (1977).

6. Griffin, G.J.L., U.S. Pat. 4,021,388 (1977).

7. Griffin, G.J.L. U.S. Pat. 4,125,495 (1978).

8. Otey, F.H.; Westhoff, R.P.; Doane, W.M. Ind Eng Chem Prod Res Dev 1980, 19, 592.

9. Otey, F.H.; Westhoff, R.P. Ind Eng Chem Prod Res Dev 1984, 23, 284.

10. Otey, F.H.; Westhoff. R.P.; Doane, W.M. Ind Eng Chem Res 1987, 26, 1659.

11. Fanta, G.F.; Swanson, C.L., Doane, W.M. J Appl Polym Sci 1990, 40, 811.

12. Shogren, R.L.; Greene, R.V.; Wu, Y.V. J Appl Polym Sci 1991, 42, 1701.

13. Fanta, G.F.; Swanson, C.L.; Shogren, R.L. J Appl Polym Sci 1992, 44, 2037.

14. Imam, S.h.; Gould, J.M.; Kinney, M.P.; Ramsay, M.; Tosteson, T.R. Curr Microbiol 1992, 25, 1.

15. Bikiaris, D.; Prinos, J.; Koutsopoulos, K.; Vouroutzis, N.; Pavlidou, E.; Frangis, N.; Panayiotou, C. Polym Degrad Stabil 1998, 59, 287.

16. Lee, Y.S.; Char, K.H. Macromolecules 1994, 27, 2603.

17. Vaidya, U.R.; Bhattacharya, M.; Zhang, D. Polymer 1995, 36, No. 6, 1179.

18. Li, H.; Chiba, T.; Higashida, N.; Yang, Y.; Inoue, T. Polymer 1997, 38, No. 15, 3921.

19. Cho, K.W.; Seo, K.H.; Ahn, T.O.; Kim, J.A.; Kim, K.U. Polymer 1997, 38, No. 19, 4825.

20. Zhang, X.; Tasaka, S.; Inagaki, N. Macromol Rapid Commun 1999, 20, 459.

21. Bayer, T.; Eichhorn, K.J.; Grundke, K.; Jacobasch, H.J. Macromol Chem Phys 1999, 200, 852.

22. Koning, C.; Ikker, A.; Borggreve, R.; Leemans, L.; Moller, M. Polymer 1993, 34, No. 21, 4410.

23. Chandra, R.; Rustgi, R. Polym Degrad Stability 1997, 56, 185.

24. Smith, B.C. Infrared Spectral Interpretation: A Systematic Approach; CRC Press: New York, 1999; Chapter 4, p.106.

25. Yang, C.Q. J Polym Sci: Part A: Polym Chem 1993, 31, 1187.

26. Yang, C.Q. Textile Res J 1993, 63, 706.

27. Rim, P.B.; O'Connor, K.M. J Appl Polym Sci 1986, 32, 4679.

28. Bikiaris, D.; Panayiotou, C. J Appl Polym Sci 1998, 70, 1503.

29. Kim, S.H.; Kim, J.K.; Park, C.E. Polymer 1997, 38, No. 9, 2113.