Influence of a Compatibilizer on the Properties of Polyethylene–Octene Elastomer/Starch Blends

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ABSTRACT: The effect of a compatibilizer on the properties of corn starch-reinforced metallocene polyethylene–octene elastomer (POE) blends was studied. The compatibility between POE and starch was improved markedly with an acrylic acid-grafted POE (POE-*g*-AA) copolymer as a compatibilizer. Fourier transform infrared spectroscopy, X-ray diffraction spectroscopy, differential scanning calorimetry, and scanning electron microscopy were used to examine the blends produced. The size of the starch phase increased with an increasing content of starch for noncompatibilized and compatibilized blends. The POE/starch blends compatibilized with the POE-*g*-AA copolymer lowered the size of the starch phase and had a fine dispersion and homogeneity of starch in the POE matrix. This better dispersion was due to the formation of branched and crosslinked macromolecules because the POE-*g*-AA copolymer had anhydride groups to react with the hydroxyls. This was reflected in the mechanical properties of the blends, especially the tensile strength at break. In a comparison with pure POE, the decrease in the tensile strength was slight for compatibilized blends containing up to 40 wt % starch. The POE-*g*-AA copolymer was an effective compatibilizer because only a small amount was required to improve the mechanical properties of POE/starch blends. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1792–1798, 2002

Key words: blends; compatibilization; starch

INTRODUCTION

In the past decade, the blending of plastic materials with organic fillers such as starch has attracted considerable interest in industry and academia for developing new materials with desired combinations of properties.[1–8] This is due to the advantages that starch has, being an abundant, inexpensive, renewable, and fully biodegradable natural raw material. However, starch and hydrophobic polymer blends have poor mechanical properties because the hydrophilic character of starch leads to poor adhesion with the synthetic polymer. A compatibilizer and/or a toughener is required that can be produced by the introduction of a reactive functional group into the synthetic polymer to enhance the compatibility between two immiscible polymers and to improve the mechanical properties of blends.[1,2,9] Bikiaris and Panayiotu[1] showed that maleic anhydride (MAH)-grafted polyethylene could increase the compatibility between low-density polyethylene (LDPE) and plasticized starch. This was reflected in the mechanical properties of the blends and especially in the tensile strength. Recently, a metallocene-based polyethylene–octene elastomer (POE), developed with a metallocene catalyst by Dow and

Exxon, has received much attention because of its unique uniform distribution of the comonomer content and narrow molecular weight distribution.[10,11] MAH-grafted POE has been used as a modifier to improve the compatibility and mechanical properties of incompatible blends.[12] For example, an MAH-grafted POE copolymer was used as the toughener in a nylon-6/POE system, and the results showed that the impact strength of nylon-6 was enhanced.[12–14] Although POE typically exhibits faster mixing and better dispersion than conventional polyolefin elastomers such as ethylene propylene diene rubber when blended with polyethylene,[15] it is expensive. To lower the cost, we can use a POE/starch blend to replace pure POE. As previously described, the POE/starch blend will give poor mechanical properties because of the low adhesion and dispersivity between the two immiscible phases. This study was devoted to systematically investigating the effect of a compatibilizer [acrylic acid-grafted POE (POE-*g*-AA) produced in our laboratory] on the structure and properties of POE/starch blends. The main reason we used starch is that some researchers have reported that higher amounts of starch can be incorporated with LDPE.[1,2,9] The blending products were characterized with Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) spectroscopy, and differential scanning calorimetry (DSC) so that we could understand the structural changes in POE/starch blends when POE-

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g-AA was introduced into the system. Moreover, scanning electron microscopy (SEM) (Hitachi, Noka, Japan) and an Instron mechanical tester (Segensworth Fareham, UK) were also used to examine the morphology and mechanical properties of the blends.

EXPERIMENTAL

Materials

POE with 18% octene (Engage 8003) was supplied by Dow Chemical Corp. (Wilmington, DE) Acrylic acid (AA), a commercial product of Aldrich (Milwaukee, WI), was purified by recrystallization from chloroform before use. The initiator was benzoyl peroxide (BPO), which was purified by dissolution in chloroform and reprecipitation with methanol. The starch, which was received from Sigma Chemical Corp. (Steinheim, Germany), was 27% amylose and 73% amylopectine. The POE-*g*-AA copolymer was made in our laboratory, and its grafting percentage was about 5.65%.

Sample preparation

POE-*g*-AA copolymer

The grafting of AA onto molten POE was performed with xylene as an interface agent and with BPO as an initiator under a nitrogen atmosphere at 85 ± 2°C. The reaction lasted for 6 h with the rotor speed kept at 60 rpm. The grafting percentage was determined by a titration method, and the results showed that the grafting percentage of the graft reaction product was about 5.65 wt % when BPO and AA loadings were kept at 0.3 and 10 wt %, respectively.[16]

Blend preparation

Blends were prepared with a Brabender Platograph 200Nm Mixer W50EHT instrument (Duisburg, Germany) with a blade-type rotor for 5 min with the rotor speed and blending temperature kept at 50 rpm and 140°C, respectively. The starch was dried in an oven at 100°C for 24 h before blending. For all blends, five different levels of starch were used: 10, 20, 30, 40, and 50 wt %. The amount of compatibilizer (POE-*g*-AA) used in all compatibilized blends was kept at 5 wt %. After blending, the blends were pressed into thin plates by a hot presser and then were put into a dryer for cooling. Next, the thin plates were made into standard specimens for characterization.

Characterization of the blends

FTIR/XRD/DSC analysis

Infrared spectra were obtained with a Bio-Rad FTS-7PC-type FTIR spectrophotometer (Madison, WI) with

thin films. The XRD intensity curves were recorded with a Rigaku D/max 3V X-ray diffractometer (Tokyo, Japan), with Co Kα radiation at a scanning rate of 2°/min, to study the changes in the crystal structure. The melting temperature (T_m) and fusion heat (ΔH_f) were determined with a TA Instrument 2010 DSC system (New Castle, DE). For DSC tests, sample sizes ranged from 4 to 6 mg, and the melting curves were taken within a temperature range of −30 to 120°C scanned at a rate of 10°C/min. The crystallinity percentage of various samples was determined as follows:[2,17]

$$\text{Crystallinity} = \frac{\Delta H_f^*}{\Delta H_f^o} \times 100\% \qquad (1)$$

where $\Delta H_f^o = 289$ J/g is the fusion heat of 100% crystalline LDPE[2] and ΔH_f^* is the fusion heat of blends.

Mechanical testing

According to the ASTM D 638 method, an Instron Lloyd LR5K mechanical tester was used to measure the tensile strength and elongation at break. The films of testing samples, which were conditioned at 50 ± 5% relative humidity for 24 h before the measurements, were prepared in a hydrolytic press at 140°C, and then the measurements were done at a 20 mm/min crosshead speed. Five measurements were conducted for each sample, and the results were averaged to obtain a mean value.

Blend morphology

An S-4100 scanning electron microscope (Hitachi) was used to study the morphology of the blends. Before testing, blends were prepared as thin films with a hydrolytic press, and then the films were treated with hot water at 80°C for 24 h. Afterward, the films were coated with gold and observed with SEM.

RESULTS AND DISCUSSION

Infrared spectroscopy

Figure 1(A–C) shows the FTIR spectra of pure POE, a POE/starch (20 wt %) blend, and a POE/starch (20 wt %)/POE-*g*-AA (5 wt %) blend, respectively. In Figure 1, all the characteristic peaks of POE at 2840–2928, 1465, and 721 cm^{-1} appear in the three polymers.[2,18,19] A comparison of Figure 1(A,B) shows that there are two extra peaks, the characteristic peaks of the —C—O bond stretching vibration, at 1186 and 959 cm^{-1} in the FTIR spectrum of the POE/starch (20 wt %) blend.[19–21] Moreover, broad O—H bond stretching at 3000–3600 cm^{-1} and O—H bond bending at 1640 cm^{-1} appear in the FTIR spectrum of the POE/starch
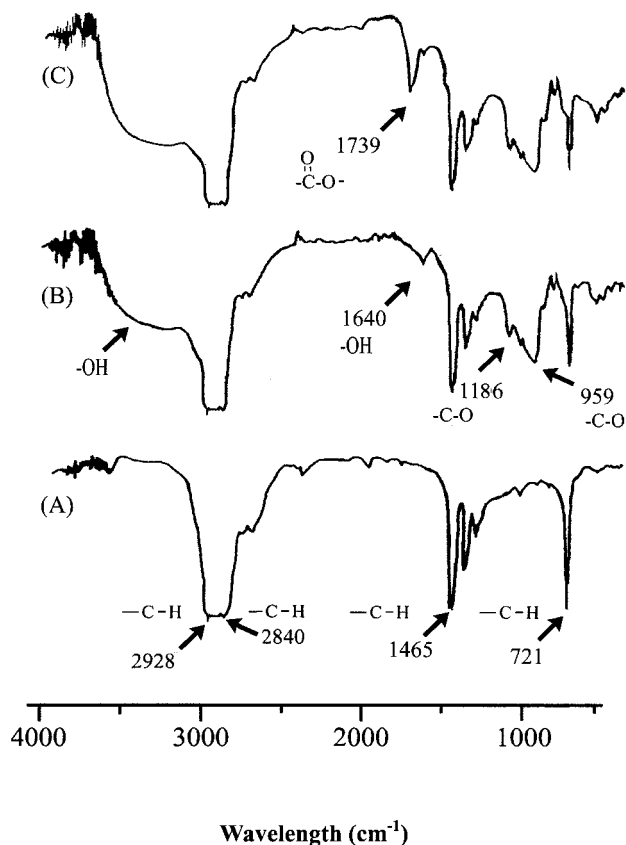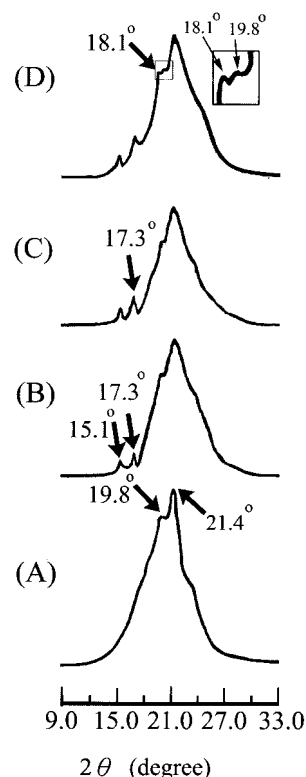
Figure 1 FTIR spectra of pure POE and its blends: (A) pure POE, (B) POE/starch (20 wt %), and (C) POE/starch (20 wt %)/POE-*g*-AA (5 wt %).

(20 wt %) blend. Similar results can be found in some articles.[2,19,20] For the POE/starch (20 wt %)/POE-*g*-AA (5 wt %) blend [Fig. 1(C)], besides the common peaks appearing in the spectrum of the POE/starch (20 wt %) blend, there is a new absorption peak, which is assigned to the ester carbonyl stretching vibration in the copolymer, at about 1739 cm^{-1}. According to Bikiaris et al.,[21] who studied LDPE/plasticized starch blends, the FTIR spectrum of ester carbonyl showed its function group at 1735 cm^{-1}. The appearance of this new absorption peak is likely due to the formation of an ester carbonyl function group from the reaction between the —OH group of starch and the —COOH group of the compatibilizer when POE-*g*-AA was blended with POE and starch.
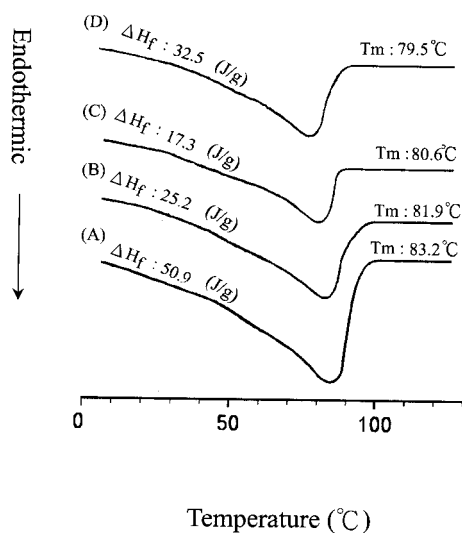
XRD

The XRD spectra of pure POE, a POE/starch (20 wt %) blend, a POE/starch (40 wt %) blend, and a POE/starch (20 wt %)/POE-*g*-AA (5 wt %) blend are illustrated in Figure 2(A–D), respectively. Similarly to the results of Perez et al.,[22] Figure 2(A) gives two peaks at about $2\theta = 19.8°$ and $2\theta = 21.4°$ for pure POE. The peak (at $2\theta = 21.4°$) reflects characteristics of the or-

thorhombic cell of polyethylene, and the peak (at $2\theta = 19.8°$) may be considered indicative of the side branches of 1-octadecene in the crystalline structure. For POE/starch blends [Fig. 2(B,C)], there are two peaks at about $2\theta = 15.1°$ and $2\theta = 17.3°$, except for the characteristic peaks of pure POE. The appearance of peaks at about $2\theta = 15.1°$ and $2\theta = 17.3°$ may be due to the change in the coordinate property of POE molecules when starch is blended with POE.[5,23] A comparison of Figure 2(B,C) shows that the higher starch content will give larger peak at $2\theta = 17.3°$. This phenomenon is in agreement with the results of Arvanitoyannis et al.[5] The peaks at about $2\theta = 15.1°$ and $2\theta = 17.3°$ are assigned to amylose and amylopectine of starch, respectively. Therefore, Figure 2(B,C) proves that starch is dispersed physically in the POE matrix. Figure 2(D) shows that there is a new peak at $2\theta = 18.1°$ for the POE/starch (20 wt %)/POE-*g*-AA (5 wt %) blend. The appearance of this new peak at $2\theta = 18.1°$, which may be due to the generation of an ester carbonyl functional group as described in the discussion of FTIR analysis, is similar to the results of Shogren et al.[23] As a result, the crystalline structure of the POE/starch blend was actually changed when POE-*g*-AA was used as a compatibilizer in the POE/starch system.

Figure 2 XRD spectra of pure POE and its blends: (A) pure POE, (B) POE/starch (20 wt %), (C) POE/starch (40 wt %), and (D) POE/starch (20 wt %)/POE-*g*-AA (5 wt %).

Figure 3 DSC heating thermograms of pure POE and its blends: (A) pure POE, (B) POE/starch (20 wt %), (C) POE/starch (40 wt %), and (D) POE/starch (20 wt %)/POE-g-AA (5 wt %).

DSC testing

DSC was used to study the thermal properties of the blends. DSC heating thermograms of pure POE, a POE/starch (20 wt %) blend, a POE/starch (40 wt %) blend, and a POE/starch (20 wt %)/POE-g-AA (5 wt %) blend are given in Figure 3(A–D), respectively. A shoulder is observed in each crystallization peak because of the amorphous phase of POE. For pure POE, curve A gives the values of T_m and ΔH_f, 83.2°C and 50.9 J/g, respectively. It can be determined from curves B and C that the corresponding T_m and ΔH_f values of POE/starch (20 wt %) and POE/starch (40 wt %) blends are 81.9°C and 25.2 J/g and 80.6°C and 17.3 J/g, respectively. It is clear that the values of T_m and ΔH_f, which indicate the crystallinity percentage of POE/starch blends, both decreased as the amount of starch was increased. The decrease in crystallinity was probably caused by the increase in the difficulty of polymer chain arrangements as the starch prohibited the movement of the polymer segments and was also due to a steric effect because the hydrophilic character of starch led to poor adhesion with the hydrophobic POE.[2,24,25] These phenomena are similar to the results

of Aburto et al.,[25] who studied the properties of octanoated starch and its blends with polyethylene. Curve D gives the values of T_m and ΔH_f for a POE/starch (20 wt %)/POE-g-AA (5 wt %) blend, about 79.5°C and 32.5 J/g, respectively. A comparison with the results of the POE/starch (20 wt %) blend shows that the T_m value decreased but ΔH_f increased when the POE-g-AA copolymer was introduced into the POE/starch system. The decrease in T_m and the increase in ΔH_f were due to the generation of an ester carbonyl functional group from the reaction between the —OH group of starch and the —COOH group of POE-g-AA. The effect of the starch content on the thermal properties of noncompatibilized and compatibilized POE/starch blends was also examined, and the results are given in Table I. Table I shows that the T_m and crystallinity percentage values obtained from eq. (1) were both reduced as the amount of starch was increased for noncompatibilized and compatibilized POE/starch blends. The decrease in T_m was due to the lower melt viscosity of starch in comparison with that of POE.[25] A comparison between compatibilized and noncompatibilized blends shows that T_m and ΔH_f of POE/starch blends decreased and increased about 1–3°C and 5–9 J/g, respectively, for up to 40 wt % starch when POE-g-AA was kept at 5 wt %.

Blend morphology

It was necessary to study the morphology of the polymer blends because the mechanical properties depended on it. In the POE/starch blends, the major component (POE) formed the matrix, whereas the minor component (starch) was the dispersed phase. SEM microphotographs of pure POE, a POE/starch (20 wt %) blend, a POE/starch (40 wt %) blend, and a POE/starch (20 wt %)/POE-g-AA (5 wt %) blend are presented in Figure 4. With different starch contents, the average pore diameter, that is, the phase size of starch, of fractured surfaces of noncompatibilized and compatibilized blends is given in Table II. From the morphology of POE/starch blends containing 20 and 40 wt % starch [Fig. 4(B,C)], we found that the average pore diameter (ca. 8 μm) of the former was smaller than that (ca. 16 μm) of the latter. Therefore, by exam-

TABLE I
Crystallinity (%) of Compatibilized and Uncompatibilized Blends at Different Starch Contents

Starch (wt %)	Uncompatibilized			Compatibilized		
	T_m (°C)	ΔH (J/g)	Crystallinity (%)	T_m (°C)	ΔH (J/g)	Crystallinity (%)
0	83.2	50.9	17.6	—	—	—
10	82.4	30.2	10.4	80.9	38.6	13.4
20	81.9	25.2	8.7	79.5	32.5	11.2
30	81.2	21.5	7.4	78.9	27.8	9.6
40	80.6	17.3	6.0	78.4	22.1	7.6
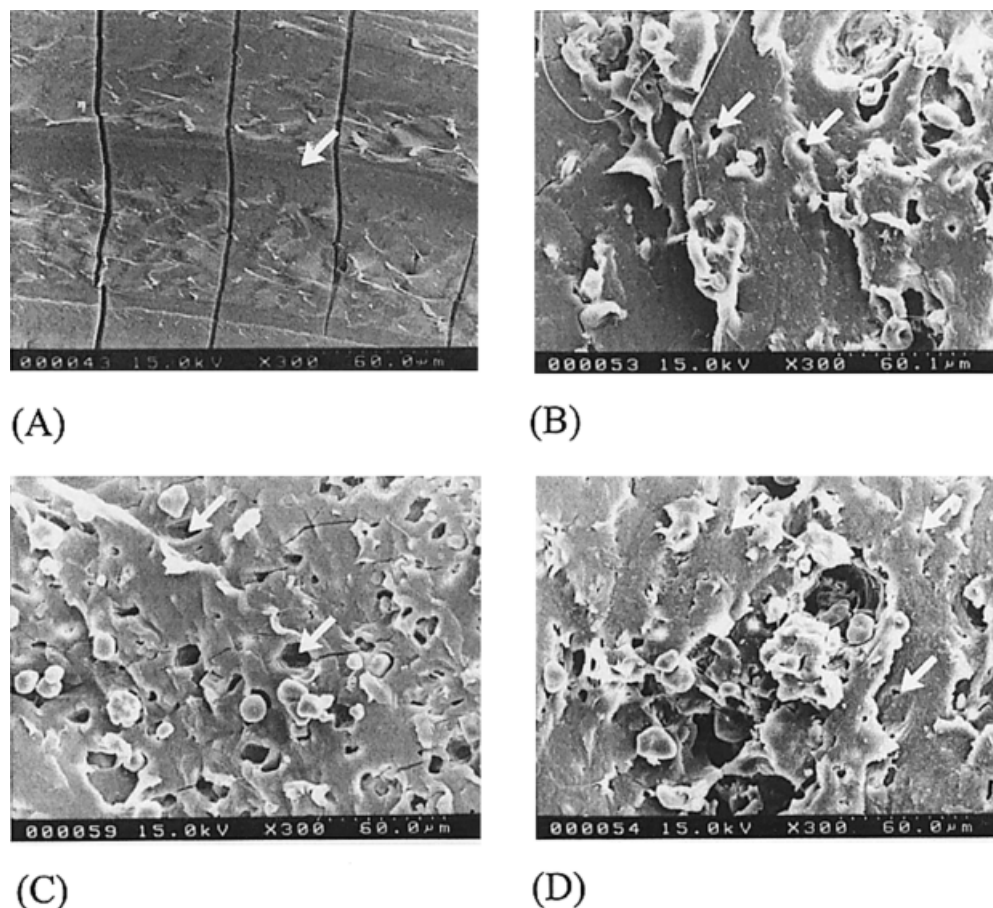
Figure 4 SEM micrographs of pure POE and its blends: (A) pure POE, (B) POE/starch (20 wt %), (C) POE/starch (40 wt %), and (D) POE/starch (20 wt %)/POE-*g*-AA (5 wt %).

ining the morphology of the POE/starch blends, we can see that the size of the starch phase increased with an increasing content of starch (Table II). It is remarkable that there is a fine dispersion and homogeneity of starch in the POE matrix for POE/starch blends containing less than 10 wt % starch. The large sizes of the starch phases produced, especially in the blend containing 40 wt % starch, suggest that the adhesion between starch and POE is very poor and that the two polymers are strongly incompatible.[1]

When the POE-*g*-AA copolymer was added as the compatibilizer [Fig. 4(D) and Table II], the size of the starch phase decreased with respect to that of the

noncompatibilized blends. Table II also shows that there is a fine dispersion and homogeneity of starch in the POE matrix for all compatibilized blends containing up to 40 wt % starch. The phase size in all compatibilized blends was lower than 4 μm and was detectable only at a higher magnification; this better dispersion arose from the formation of branched and crosslinked macromolecules because this POE-*g*-AA copolymer had anhydride groups to react with the hydroxyls. Branched and crosslinked macromolecules, which were produced by the reaction between POE-*g*-AA and starch, contained different parts, each compatible with one of the two polymers. This structure gave them the ability to place themselves in the interface of the POE/starch blends during melt blending. The result was a reduction in the interfacial tension between the two polymers and a finer distribution of starch in all the compatibilized blends. Our results are similar to what was proposed by Bikiaris and Panayiotu,[1] who studied the compatibility of starch particles in LDPE/starch blends and found that the compatibilized blends (with LDPE-*g*-MAH as a compatibilizer) could give smaller pore sizes under tensile disruption.

TABLE II
The Starch Phase Size of Compatibilized and Uncompatibilized Blends at Different Starch Contents

Starch (wt %)	Phase size (μm)	
	Uncompatibilized	Compatibilized
10	4.5	1.5
20	8.0	2.0
30	12.5	3.0
40	16.0	3.5
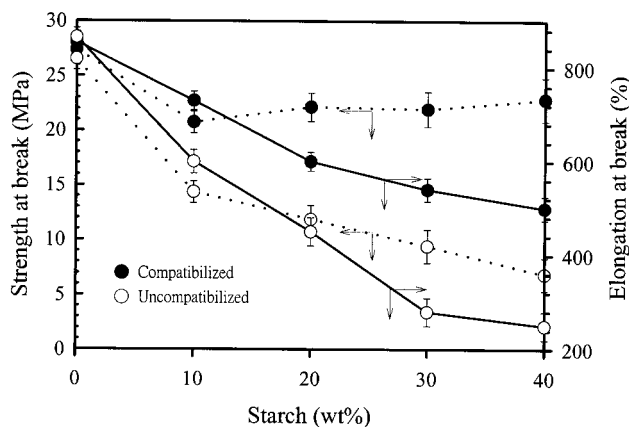
Figure 5 Tensile strength and elongation at break versus the starch content for compatibilized blends (solid lines) and noncompatibilized blends (dotted lines).

Mechanical properties

Figure 5 shows the variation of the tensile strength and elongation at break with the starch content for POE/starch and POE/starch/POE-g-AA (5 wt %) blends. For the noncompatibilized blends, the tensile strength at break decreased continuously as the starch content increased. This behavior can be explained with the results of SEM micrographs of the respective blends. A blend containing 40 wt % starch gave the lowest tensile strength at break because the higher content of starch increased the phase size. Therefore, it was certain that the effect of incompatibility between the two polymers on the mechanical properties was great. For compatibilized blends, Figure 5 shows quite different behavior with respect to the tensile strength at break. Although a decrease in the tensile strength at break, compared to that of pure POE, was observed as the content of starch increased, this decrease was smaller than the corresponding decrease in the noncompatibilized blends. The absolute value of the tensile strength at break for all compatibilized blends was, of course, higher than that of their noncompatibilized counterparts. Moreover, the compatibilized blends not only had greater tensile strength than the noncompatibilized blends but also provided stable values of the tensile strength when the starch content was greater than 10 wt %.

Figure 5 also shows that the compatibilized blends exhibited an increase in the elongation at break in comparison with the noncompatibilized blends. In the noncompatibilized blends, the reduction in the elongation at break increased with an increasing content of starch. For the compatibilized blends, the elongation at break was higher than that of the noncompatibilized blends, and the reduction in the elongation at break decreased with an increasing content of starch. However, the elongation at break still remained lower than that of pure POE. The results concerning the mechanical properties in our work are similar to those of Bikiaris et al.[9] It is evident that the mechanical properties strongly depended on the dispersion and phase size of starch in the POE matrix. As the size of the dispersed phase became smaller, an increase in the mechanical properties, especially the tensile strength, was observed. A contribution to this behavior might have come from the presence of branched or crosslinked macromolecules produced by the reaction of the compatibilizer and the starch macromolecules. These macromolecules had higher tensile strength than the linear ones but lower elongation at break. Therefore, the elongation at break for POE/starch blends could be improved by the addition of POE-g-AA, but to a smaller extent in comparison with the tensile strength.

CONCLUSIONS

For improved compatibility and mechanical properties of POE/starch blends, a POE-g-AA copolymer was chosen as a compatibilizer. We produced this compatibilizer in our laboratory, and we systematically investigated the properties of POE/starch blends and the effect of POE-g-AA on them. According to the characterizations of FTIR and XRD, because of the generation of an ester carbonyl functional group from the reaction between the —OH group of starch and the —COOH group of the compatibilizer, the crystalline structure of the POE/starch blends changed when POE-g-AA was used as a compatibilizer in the POE/ starch system. In comparison with pure POE, DSC tests showed that the decrements of T_m and ΔH_f both increased as the content of starch was increased for POE/starch blends. Moreover, the decrease in T_m and the increase in ΔH_f were both slight when POE-g-AA was used as a compatibilizer in the POE/starch blends. The morphology of the POE/starch blends showed that the starch phase size increased with an increasing content of starch, suggesting that the compatibility between the POE and starch was very poor. For POE/starch/POE-g-AA blends, the size of the starch phase, which was less than 4 μm and was detectable at a higher magnification for all compatibilized blends, decreased markedly in comparison with that of the respective noncompatibilized blends. Mechanical testing of the POE/starch blends showed that the tensile strength and elongation at break decreased obviously and continuously as the starch content was increased. It was also proven that the compatibilized blends could enhance the mechanical properties of the noncompatibilized blends, especially the tensile strength at break. Finally, we can conclude that the POE-g-AA copolymer produced in our laboratory is an effective compatibilizer for POE/starch blends because only a small amount of it was required to improve the properties of the noncompatibilized blends.

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