Study on the Properties of Polyethylene–Octene Elastomer/ Wood Flour Blends

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ABSTRACT: In the present study, the properties of metallocene polyethylene–octene elastomer (POE) and wood flour (WF) blends were examined by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), an Instron mechanical tester, and scanning electron microscopy (SEM). The results showed that the mechanical properties of POE were obviously lowered, due to the poor compatibility between the two phases, when it was blended with WFs. A fine dispersion and homogeneity of WF in the polymer matrix could be obtained when acrylic acid-grafted POE (POE-*g*-AA) was used to replace POE for manufacture of the blends. This better dispersion is due to the formation of branched and crosslinked macromolecules since the POE-*g*-AA copolymer had carboxyl groups to react with the hydroxyls. This is reflected in the mechanical and thermal properties of the blends. In comparison with a pure POE/WF blend, the increase in tensile strength at break was remarkable for the POE-*g*-AA/WF blend. The POE-*g*-AA/WF blends are more easily processed than are the POE/WF blends, since the former had a lower melt viscosity than that of the latter. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1919–1924, 2003

Key words: blends; polyethylene (PE); graft copolymers

INTRODUCTION

In past decades, blending of plastic materials with organic fillers, such as wood flour (WF), has received considerable industrial and academic interest for developing new materials with desired combinations of properties.[1–10] This is due to the advantage that WF is an abundant, inexpensive, renewable, and fully biodegradable natural raw material. However, WF and hydrophobic polymers blends have poor mechanical properties because the hydrophilic character of WF leads to poor adhesion to the synthetic polymer. A compatibilizer and/or a toughener, which can be produced by introducing a reactive functional group into the synthetic polymer, is required to enhance the compatibility between two immiscible polymers and to improve the mechanical properties of blends.[11–13] Previous work on polyethylene and WF (PE/WF) composites showed that the styrene–butadiene–styrene block copolymer, which is located at the interfacial region between WF surfaces and the PE matrix, can be used as a compatibilizer to give a positive effect on the composite's properties.[14] In a polypropylene and cellulose fiber (PP/CF) composite system, a maleated PP was chosen as a compatibilizer to increase the compatibility between the CF and the PP matrix.[15]

Recently, a metallocene-based polyethylene octene elastomer (POE), which was developed using a metallocene catalyst by Dow and Exxon, has received much attention due to its unique uniform distribution of comonomer content and narrow molecular weight distribution.[16] Maleic anhydride (MAH)-grafted POE has been used as a modifier to improve the compatibility and mechanical properties of incompatible blends.[17–19] For example, the POE-*g*-MAH copolymer was used as the toughener in a Nylon 6/POE system and the result showed that the impact strength of Nylon 6 was obviously enhanced.[18,19] Although POE typically exhibits faster mixing and better dispersion than does a conventional polyolefin elastomer, such as ethylene propylene diene rubber (EPDM), when blending with PE, it is expensive.[20] To lower the cost and to heighten the biodegradable property, the POE/WF blend can be used to replace the pure POE. As described above, POE/WF blends will give poor mechanical properties due to low adhesion and dispersivity between the two immiscible phases. So, the POE must be modified to obtain a compatible blend. In this research, we introduced a reactive functional group into the synthetic polymer by the graft reaction of POE and acrylic acid (AA). The purpose of this article was to systematically investigate the structure and properties of POE/WF and POE-*g*-AA/WF blends. The main reason for using WF in the present work is that some articles showed that higher amounts of WF can be incorporated with LDPE.[7,13,14] The blending products were characterized using FTIR

spectroscopy and differential scanning calorimetry (DSC) to understand the structural change of POE/WF blends when POE-*g*-AA was used to replace POE as the plastic material. Moreover, a scanning electron microscope (SEM) and an Instron mechanical tester were used to examine the morphology and mechanical properties of blends.

EXPERIMENTAL

Materials

POE with 18% octene (Engage 8003) was supplied by the 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 used in this study was benzoyl peroxide (BPO, Aldrich), which was purified by dissolving it in chloroform and reprecipitating with methanol. The WFs, supplied by Zell Wildshausen GMBH (Steinheim, Germany), were Celluflex. The grain size distributions of the WFs are 100% finer than 250 μm, 87% finer than 100 μm, and 37% finer than 50 μm. The moisture content and apparent density of the WFs were 8 ± 2% and 0.10–0.12 g/cm^3, respectively. The POE-*g*-AA copolymer was made in our laboratory and its graft percentage was about 5.65%.

Samples preparation

POE-*g*-AA copolymer

The grafting of AA onto molten POE was performed using xylene as an interface agent and BPO as an initiator under a nitrogen atmosphere at 85 ± 2°C. The reaction lasted for 6 h with a rotor speed of 60 rpm. The grafting product (4 g) was dissolved in 200 mL refluxing xylene at 85°C and then the solution was extracted five times using 600 mL cold acetone for each extraction operation. The acetone-insoluble polymer, which was dried at 80°C overnight, was used to measure the grafting percentage by a titration method.[21] The result 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.

Blends preparation

Blends were prepared by a Brabender "Platograph" 200-Nm mixer W50EHT instrument with blade-type rotor for 15 min and the rotor speed and blending temperature were kept at 50 rpm and 160–170°C, respectively. The WF was cleaned with acetone and then dried in an oven at 105°C for 24 h prior to blending. The mass ratios of WF to POE or to POE-*g*-AA were chosen as 10/90, 20/80, 30/70, 40/60, and 50/50. To eliminate the effect of unreacted AA on POE-*g*-

AA/WF blends, it was removed from the grafting product by acetone extraction before preparation of the POE-*g*-AA/WF blends. After blending, the blends were pressed into thin plates by a hot presser and then put into a dryer for cooling. Next, the thin plates were made into standard specimens for characterizations.

Characterizations of blends

FTIR/DSC analysis

Infrared spectra were obtained from a Bio-Rad FTS-7PC-type FTIR spectrophotometer using thin films. The melting temperature (T_m) and the fusion of heat (ΔH_f) were determined from a TA Instrument 2010 DSC system. For DSC tests, sample sizes ranged from 4 to 6 mg and the melting curves were taken at a temperature range of −30 to 120°C and scanned at a rate of 10°C/min.

Mechanical testing

According to the ASTM D638 method, an Instron mechanical tester (Model LLOYD, LR5K type) was used to measure the tensile strength and the elongation at break. The testing films, which were conditioned at 50 ± 5% relative humidity for 24 h prior to the measurements, were prepared in a hydrolytic press at 140°C and then the measurements were done using 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

A scanning electron microscope (Hitachi microscope Model S-1400) was used to study the morphology of the blends. Before the tests, the blend was prepared in a thin film by a hydrolytic press and then the film was treated with hot water in 80°C for 24 h. Afterward, the films were coated with gold and observed by SEM.

RESULTS AND DISCUSSION

Infrared spectroscopy

Figure 1(A–D) shows FTIR spectra of POE, POE-*g*-AA, POE/WF (30 wt %), and POE-*g*-AA/WF (30 wt %), respectively. From the results of Figure 1, it can be seen that all the characteristic peaks of POE at 2840–2928, 1465, and 720 cm^{-1} appear in four polymers.[22] From a comparison of Figure 1(A) and (B), it is seen that there are two extra peaks (at 1710 and 1247 cm^{-1}), which are the characteristic peaks of —C=O and —C—O, and an extra broad O—H stretching absorbance at 3000–3600 cm^{-1} for the modified POE. A similar result can be found in the proposed article.[23] So, one can confirm that AA was really grafted onto

POE since the discernible peak near 1710 cm^{-1} based on free acid appears in the spectrum of POE-g-AA. From the result of Figure 1(C), compared to pure POE, it can be found that there are extra peaks assigned to the —C—O bond stretching vibration at 1247–1100 cm^{-1} in the FTIR spectrum of the POE/WF (30 wt %) blend.[11,22,24] The FTIR spectrum of the POE/WF (30 wt %) blend also showed an extra broad O—H bond stretching at 30003–600 cm^{-1} and an extra O—H bond bending at 1641 cm^{-1}. A similar result can be found in some proposed articles.[14,22,25] Compared to pure POE, the new absorption peak about 1735 cm^{-1} that appeared in the FTIR spectrum of the POE/WF blend is assigned to the characteristic peak of WF.[14,15] In a comparison between the FTIR spectra of POE/WF (30 wt %) and POE-g-AA/WF (30 wt %) blends [Fig. 1(C,D)], it is seen that the peak at 1735 cm^{-1} shifted to 1746 cm^{-1} and the peak at 1641 cm^{-1} nearly disappeared when POE-g-AA was used to replace POE. This phenomenon may be due probably to the formation of an ester carbonyl functional group from the
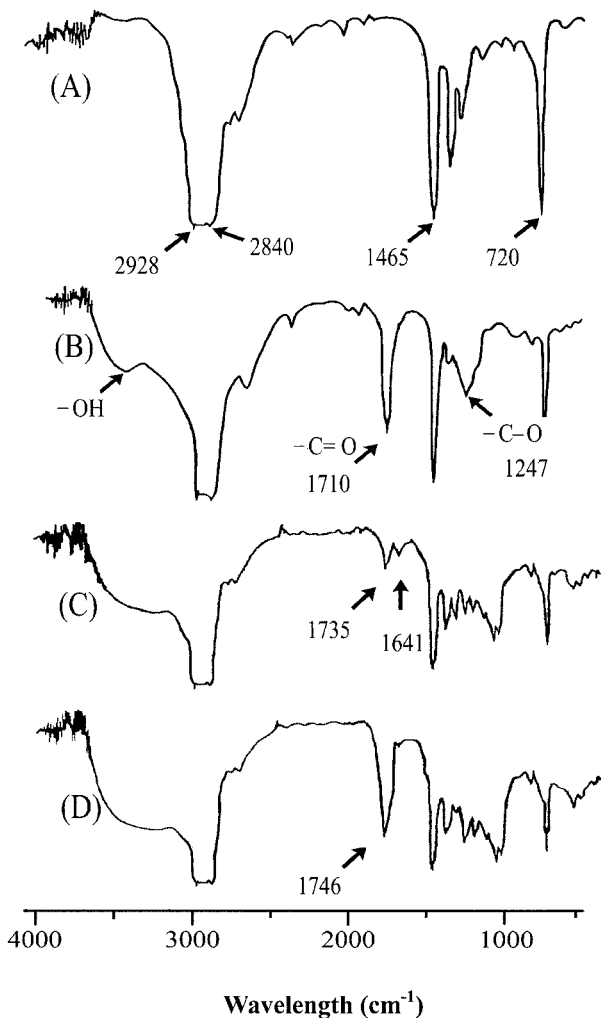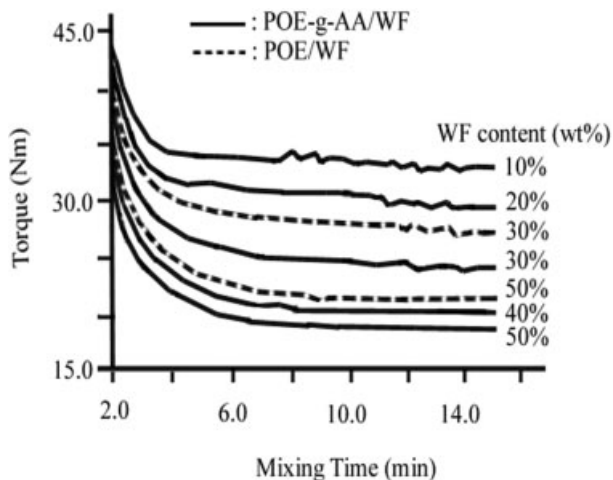

Figure 2 Torque diagrams versus mixing for POE/WF and POE-g-AA/WF blends.

reaction between the —OH group of WF and the—COOH group of POE-g-AA. This result is similar to that of Oksman et al.,[14] in which LDPE/WF blends were studied and the FTIR spectrum of ester carbonyl showed its functional group that appeared at 1746 cm^{-1}. As the result of Figure 1(D), one can infer that branched and crosslinked macromolecules may be produced because the POE-g-AA copolymer has carboxyl groups to react with the hydroxyls.

Torque measurements

The curves of torque versus mixing time for POE/WF and POE-g-AA/WF blends with different amounts of WF are presented in Figure 2. It was observed that the torque value of each blend decreased with an increasing WF content and mixing time, and it approached a stable value when the mixing time was greater than 12 min. One can suggest that good mixing has occurred with a mixing time of 15 min. The reason that the final torque decreased with an increasing WF content is due to the lower viscosity of the WF melt as compared to POE and to POE-g-AA. This caused a decrease in the melt viscosity of the blend as the WF concentration was increased. By comparing the torque responses of POE-g-AA/WF and POE/WF blends having the same WF content (30 and 50 wt %), we can observe that the melt torque values of the former are significantly lower than are those of the latter. This improved rheological behavior is due to the formation of an ester carbonyl functional group (as discussed under FTIR and DSC Analysis), as this functional group leads to conformation changes in the WF molecule.[26] In a previous study,[27] it was shown that the melt viscosity of esterified starches decreased with an increasing molecular weight of the ester group.
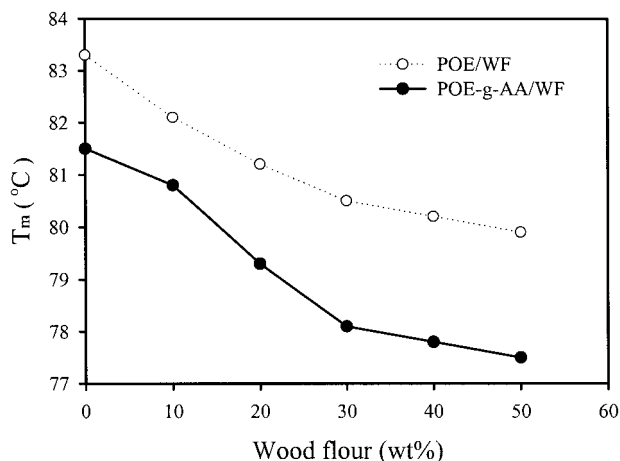

Figure 1 FTIR spectra of (A) POE, (B) POE-g-AA, (C) POE/WF (30 wt %), and (D) POE-g-AA/WF (30 wt %).

Figure 3 Melt temperature versus WF content for POE/WF and POE-*g*-AA/WF blends.

DSC test

DSC was used to study the thermal properties of the blends. The variations of the fusion of heat (ΔH_f) and melt temperature (T_m) with the WF contents for the POE/WF and POE-*g*-AA/WF blends were determined from the DSC heating thermograms (not shown here) and the results are given in Figures 3 and 4. In Figure 3, it can be seen that a decrease in the melt temperature was observed with an increasing WF content for both the POE/WF and the POE-*g*-AA/WF blends. This result is due to the reason, as discussed in the torque study, that WF could lower the melt viscosity of POE and the POE-*g*-AA copolymers. This decrease is almost linear for WF contents up to 30 wt %. With the same WF content, it can be seen from Figure 3 that the POE/WF blends show a higher melt temperature compared to that of the POE-*g*-AA/WF blends. This observation is in accordance with the corresponding torque measurements, which showed that the POE-*g*-AA/WF blends have a lower melt torque than that of the POE/WF blends for the same WF content (Fig. 2). These two observations (lower values of melt temperature and torque) for POE-*g*-AA/WF blends agree with the fact that they also present a lower melt viscosity compared to POE/WF blends. The low melt viscosity of POE-*g*-AA/WF blends makes them more easily processable than are the POE/WF blends.

Figure 4 shows that the values of the fusion of heat (ΔH_f) of pure POE and POE-*g*-AA are 50.9 and 36.0 J/g, respectively. The lower fusion of heat for POE-*g*-AA, compared to pure POE, was probably due to the grafted branches that disrupted the regularity of the chain structures in POE and increased the spacing between the chains.[28] It can be seen from the dotted line of Figure 4 that the corresponding ΔH_f values of the POE/WF blends having WF contents of 10, 20, 30, 40, and 50 wt % are 31.2, 26.8, 19.8, 17.9, and 15.6 J/g,

respectively. For the POE-*g*-AA/WF blends with 10, 20, 30, 40, and 50 wt % WFs, the corresponding values of ΔH_f are 35.2, 32.0, 27.6, 24.8, and 23.8 J/g (the solid line of Fig. 4). It is clear that the ΔH_f values of POE/WF and POE-*g*-AA/WF, which indicate percent crystallinity of the blends, both decreased as the extent of WF was increased. These phenomena are similar to the result of Aburto et al.,[26] who studied the properties of octanoated starch and its blends with PE. The marked decrease in crystallinity for POE/WF blends was probably caused by increase in the difficulty of polymer chain arrangements, as the WF prohibited the movements of the polymer segments, and was also due to the steric effect because the hydrophilic character of WF leads to poor adhesion with hydrophobic POE.[26,29] In comparison between the results of POE/WF and POE-*g*-AA/WF, it was found that the latter gave higher ΔH_f values than those of the former and the increment was about 5–9 J/g. The increase of ΔH_f is due to the generation of the ester carbonyl functional group from the reaction between the —OH group of WF and the—COOH group of POE-*g*-AA.

Blend morphology

It is necessary to study the morphology of polymer blends since the mechanical properties depend on it. In general, good dispersion of WF in the matrix, effective wetting of WF by the matrix, and strong interfacial adhesion between two phases are required to obtain a composite material with satisfactory mechanical properties. Scanning electron microscopy (SEM) was used to study the tensile fracture surfaces of composite samples based on POE/WF (30 wt %) and POE-*g*-AA/WF (30 wt %) blends and the SEM microphotographs of the fracture surfaces are shown in Figure 5. In the blends studied in this article, the major component (POE or POE-*g*-AA) forms the matrix,
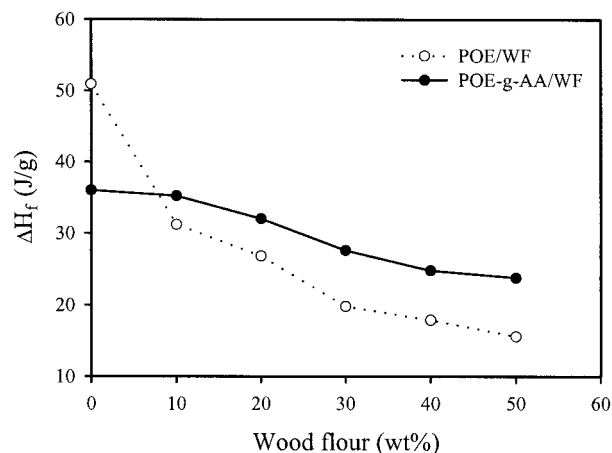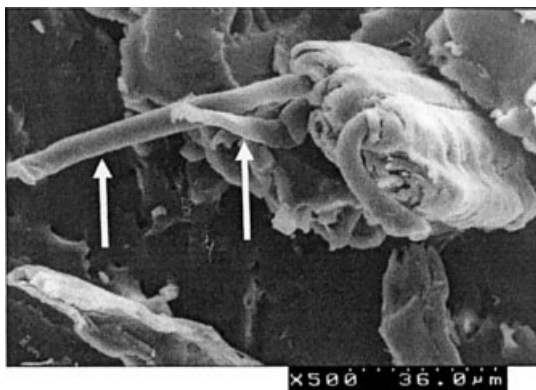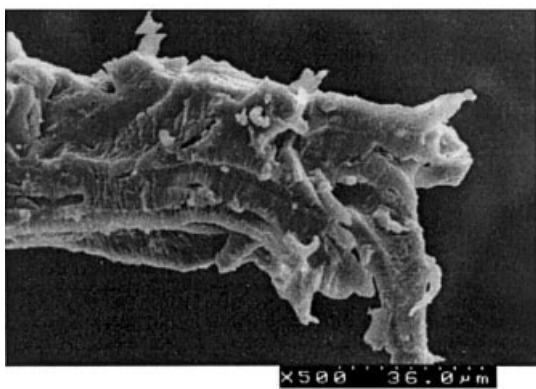

Figure 4 Fusion heat versus WF content for POE/WF and POE-*g*-AA/WF blends.

(A) POE/WF (30wt%)

(B) POE-g-AA /WF (30wt%)

Figure 5 SEM micrographs of POE/WF (30 wt %) and POE-g-AA/WF (30 wt %) blends.

whereas the minor component (WF) is the dispersed phase. An SEM microphotograph of the POE/WF (30 wt %) blend [Fig. 5(A)] shows that it tends to agglomerate into bundles and becomes unevenly distributed throughout the matrix. The bad dispersion of WF in the POE matrix is due to the formation of hydrogen bonds and the wide difference in character between POE and the WFs. The markers in Figure 5(A) also show the poor wetting of WF when POE/WF was used. The reason for this is the large difference in the surface energy between WF and the POE matrix.[15] For the POE-g-AA/WF (30 wt %) blend, as shown in Figure 5(B), there is a better dispersion and homogeneity of the WF in the POE-g-AA matrix. It can also be seen from Figure 5(B) that better wetting is obtained since layers of the matrix material have been pulled out together with the WF, covering the entire WF. The reason for this result is that the properties of the WF surfaces and the POE-g-AA matrix become more similar because the POE-g-AA/WF blend can produce branched and crosslinked macromolecules and prevent hydrogen bonds from being formed.
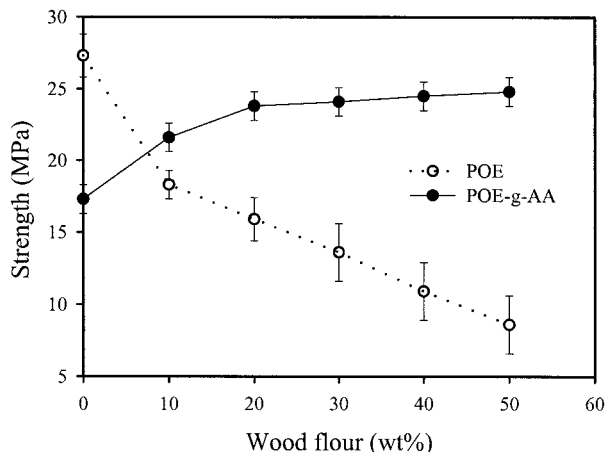

Figure 6 Tensile strength at break versus WF content for POE/WF and POE-g-AA/WF blends.

Mechanical properties

Figures 6 and 7 show the variations of tensile strength and elongation at break with the WF content for the POE/WF and POE-g-AA/WF blends. It can be seen that the tensile strength and elongation of pure POE were both decreased when it was grafted with AA. For POE/WF blends, as shown by the dotted line of Figure 6, the tensile strength at break decreased markedly and continuously as the WF content was increased. This behavior can be explained from the result of the SEM micrograph of the POE/WF blend [Fig. 5(A)], because the dispersion of WF in the POE matrix is poor. As the result, it is certain that the effect of the incompatibility between the two polymers on the mechanical properties is great. For POE-g-AA/WF blends (the solid line of Fig. 6), a quite different behavior of tensile strength at break was obtained, namely, the tensile strength of the POE-g-AA/WF blends increased obviously with increasing of the WF content, although POE-g-AA had a lower value of the
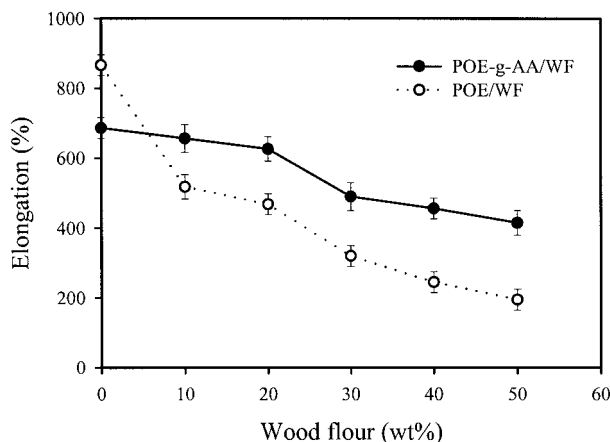

Figure 7 Elongation at break versus WF content for POE/WF and POE-g-AA/WF blends.

tensile strength than that of the pure POE. It can be seen that the tensile strength of the POE-*g*-AA/WF blends increased obviously with increasing of the WF content, although POE-*g*-AA has a lower value of tensile strength than that of the pure POE. It was also found that the POE-*g*-AA/WF blends not only gave larger values of tensile strength than those of the POE/WF blends but also provided stable values of the tensile strength while the WF content is beyond 30 wt %. A contribution to this behavior may be better dispersion, coming from the formation of branched or crosslinked macromolecules, of WF in the POE-*g*-AA matrix.

Figure 7 gives the variation of the elongation at break with the WF content for the POE/WF and POE-*g*-AA/WF blends and showed that the former exhibited lower values in the elongation at break compared to the latter. The decrease in elongation for the POE/WF blend was marked, since the addition of WF made the blend tend to agglomerate into bundles and gave poor compatibility between the two phases. In the POE-*g*-AA/WF blends, as shown by the solid line of Figure 7, the elongation at break also decreased with an increasing content of WF, but they had larger values of elongation than those of the POE/WF blends. However, the elongation at break still remains lower compared to that of pure POE. The result of the mechanical properties in our work is similar to that of Bikiaris.[30] As the result of Figures 6 and 7, one can conclude that the POE-*g*-AA/WF blends can improve the tensile strength and elongation of the POE/WF blends, but the increment of elongation is smaller than that of the tensile strength.

CONCLUSIONS

To improve the compatibility and mechanical properties of POE/starch blends, a POE-*g*-AA copolymer produced in our laboratory was taken to replace the pure POE for preparation of the blends. We investigated systematically the properties of POE/WF and POE-*g*-AA/WF blends. According to the FTIR results, due to the generation of an ester carbonyl functional group from the reaction between the —OH group of WF and the—COOH group of the POE-*g*-AA copolymer, the crystalline structure of the POE/WF blend was changed when POE-*g*-AA was used in the blending system. The DSC tests showed that melt temperatures of POE/WF and POW-*g*-AA/WF both decreased as the content of WF was increased. It was also found that the POE-*g*-AA/WF blends have an easy processing property due to the low values of the melt temperature and torque compared to the POE/WF blends. The morphology of the POE-*g*-AA/WF blends confirmed a good adhesion between the WF and the POE-*g*-AA matrix. As the result of the mechanical test, compared the to POE/WF blends, the POE-*g*-AA/WF blends can enhance the mechanical properties of the blends, especially the tensile strength. Finally, we can conclude that the POE-*g*-AA copolymer produced in our laboratory can be used to lower the cost and to improve the properties of POE/WF blends.

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