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Influence of Compatibilizer on Morphology and Dynamic Rheological Behavior of Polyethylene-Octene Elastomer/Starch Blends

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The morphology and rheology of polyethylene-octene elastomer (POE)/crosslinked starch (CS) immiscible blends with various amounts of compatibilizer were experimentally examined. A graft copolymer, POE-g-MAH, acting as the compatibilizer, was used to modify the interface of the blend. The particle radius in the POE/CS 80/20 system decreased with increasing compatibilizer up to 5 wt%, beyond which the particle size slightly increased. This indicates that the interface reaches saturation when the compatibilizer content is 5 wt%, leading to reduced effectiveness of the compatibilizer. From the SEM micrographs, the compatibilized blends were found to have better interfacial adhesion between the POE and starch phase than the uncompatibilized blends. Rheological examination shows a sharp reduction of the viscoelastic modulus and complex viscosity in blends containing 10 wt% compatibilizer. When the content of compatibilizer is less than 5 wt%, the viscoelastic modulus and complex viscosity of the blends increase with increasing the content of compatibilizer.

Keywords: blends, morphology, polyethylene-octene elastomer, rheology, starch

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INTRODUCTION

More and more plastics and rubbers are becoming necessary in industry, agriculture, food, medicine, and so on. Unfortunately, these materials produce secondary waste, which remains in the environment for a long time, causing serious environmental problems. So far, the high cost and nonbiodegradability of these materials have limited their general application. In order to overcome these problems, an intriguing method is to blend these synthetic polymers with natural polymers, which can lead to the development of new kinds of biodegradable polymeric materials.

Starch is a natural polymer, which is cheap, plentiful, renewable, fully biodegradable, and has been widely used to make biodegradable materials, such as composites of starch/PE [1], starch/LDPE [2–4], starch/PCL [5,6], starch/PLA [7], and so on. Recently, the metallocene-based polyethylene-octene elastomer (POE) has received much attention, because it has not only thermoplastic properties, but also crosslinking of rubber [8]. POE is a commercially important elastomer widely used in applications such as automotive parts, foamed sheets, durable goods, impact modifiers in engineering plastics, and wire and cable owing to its good balance of mechanical properties along with favorable processability [9]. Moreover, POE may be used in biodegradable materials for more commercial requirements by blending with starch. However, POE is hydrophobic, and starch is hydrophilic, so they are immiscible when blended together. This leads to poor adhesion between the two components, with poor and irreproducible performance. One way to improve the compatibility of starch and polymer blends is to use a compatibilizer. Pedroso and Rosa [10] used PE-g-GMA as a compatibilizer to enhance LDPE/starch blends, and Bikiaris et al. [11,12] studied the effect of PE-g-GMA as a compatibilizer on PE/starch blends. The compatibilized blends have better interfacial adhesion between the polymer and starch phase and mechanical properties than the uncompatibilized blends, which is due to the reaction between the functional chemical groups of compatibilizer and the hydroxyl groups of starch. Therefore, the compatibilizer can significantly affect the structure and properties of the composite, especially the morphology and mechanical properties.

In addition, the rheology of the composite is also strongly affected by interfacial characteristics [13,14]. In the case of immiscible blends, the rheological properties depend on the blend composition, properties of the components as well as the morphology and interactions between phases, characterized by the interfacial tension between the polymers forming the blend. So rheology is connected to the morphology of the

composite. Therefore, in order to discern the interfacial compatibility between the POE and starch after adding the compatibilizer, studies on the morphology and dynamic rheology of the composite are needed.

In the present work, maleic anhydride (MAH) was grafted onto POE to form a graft copolymer, POE-g-MAH, used as the compatibilizer. In order to discern the compatibility of POE/CS 80/20 blend after adding a compatibilizer, the morphology and dynamic rheology of the blend were studied. The microstructures of POE/CS 80/20 blend containing 0, 1, 2, 5, 8 and 10 wt% content of POE-g-MAH were measured using scanning electron microscopy (SEM), and the storage modulus, loss modulus, loss tangent and complex viscosity vs. frequency were measured using an ARES rheometer.

EXPERIMENTAL

Materials

Polyethylene-octene elastomer (POE, type 8150) was supplied by Dow Chemical Corp. Crosslinked cassava starch (CS) was received from TianJin TingFung Starch Development Co. Ltd. Maleic acid anhydride (MAH) was supplied by Shandong Zibo Qifeng Organic Chemical Limited Company. Dicumyl peroxide (DCP) under study was supplied by Shanghai Gaoqiao Chemical Company. The POE-g-MAH copolymer was made in our laboratory, with a grafting percentage of about 0.8%.

Sample Preparation

Grafting of POE with maleic acid anhydride (MAH), POE-g-MAH, was conducted by using a co-rotating intermeshing twin-screw extruder with a screw configuration adapted for grafting. 0.08 ~ 0.1 wt% DCP was used as an initiator, with 2 wt% MAH content. POE, MAH, initiator and other additives were blended uniformly with the help of a little dispersant, and then, the mixtures were extruded with a twin screw extruder (TE-35). The temperature profile during the extrusion was 100/140/170/190/190/180°C, and the temperature of the hand piece was 180°C. The screw speed was 60 rpm, and the feeding speed was 300 rpm.

Blend Preparation

Before blending, POE and POE-g-MAH were dried for at least 3 h in a vacuum at 40°C, and the starch was dried in an oven at 105°C for 24 h. For the POE and crosslinked starch blends, the starch content was

20 wt%, with 5 wt% POE-g-MAH added as a compatibilizer. During the extrusion, the temperature profile was 120/140/140/120°C (from feed zone to die). The screw speed was 50 rpm, and the blend time was 8 min. The blends were compression molded into 1.5 mm-thick sheets in a plate vulcanizing press (XLB-D) at 140 ~ 150°C and 6 ~ 8 MPa for 3 min.

Scanning Electron Microscopy

The fractured microstructure surfaces of POE/CS 80/20 blend with various amounts of compatibilizer were observed by using a JSM-6330F Field Emission Scanning Electron Microscope. The specimens were frozen in liquid nitrogen and snapped immediately. The cross sections of the specimens were coated with gold film in an automatic sputter coater (Polaron) to avoid charging under the electron beam.

Rheological Measurements

The rheological measurements were performed using an Advance Rheometric Expansion System (ARES, TA) at 160°C with a parallel plate geometry (plate diameter of 25 mm, gap of 2 mm). Frequency sweeps were carried out from 100 to 0.01 rad/s. The strain amplitude was 1%. All applied strains were within the linear viscoelastic range.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows SEM micrographs of the fractured surface of POE/CS 80/20 blends with various amounts of compatibilizer. This demonstrates the dispersion of starch particles and the activating effect caused by these particles. Figure 1a shows that without compatibilizer, the starch particles are big and smooth, with large numbers of them absent from the POE matrix when the samples are broken, which is due to the incompatibility between the POE and starch phase. The POE and starch phases have poor adhesion, because there is little interaction and large interfacial tension between them, leading to the phase separation of the two polymers in the molten state [15]. Figure 1(b~f) illustrate that the particle size gradually shrinks with increasing the content of compatibilizer, with the fractured surfaces exhibiting slight deformation. It is obvious that the starch particles do not just stay on the fractured surface, but embed tightly in the POE matrix with a mucilage-like coat. This is because there is a reaction

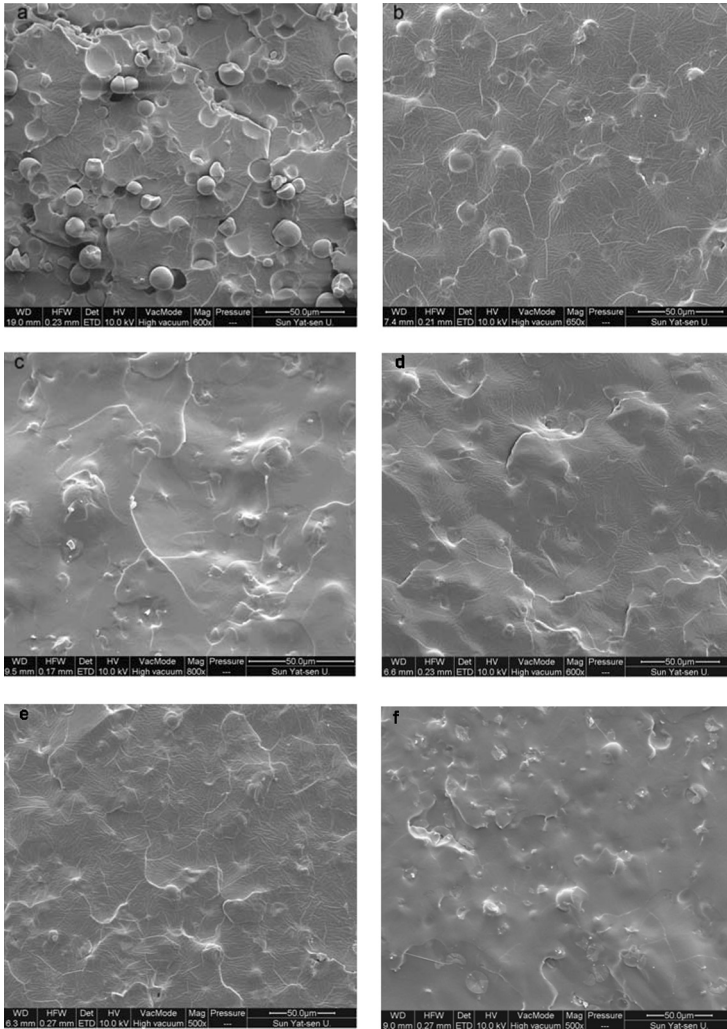


FIGURE 1 SEM micrographs of POE/CS 80/20 blends with various amounts of POE-g-MAH (wt% based on neat POE and CS): (a) 0; (b) 1; (c) 2; (d) 5; (e) 8; (f) 10.

between the anhydride groups of POE-g-MAH and the hydroxyl groups of starch, forming branched and crosslinked macromolecules [16]. It indicates that the compatibilizer is of benefit to the better dispersion of the starch particles in the POE matrix, and improves the interfacial adhesion between the starch and POE phase by reducing

the interfacial tension. From Figure 1, it can be found that with increasing the POE-g-MAH content, the starch particle size decreases and has better dispersion and homogeneity in the POE matrix. But comparing the blends containing 8 and 10 wt% POE-g-MAH content with the 5 wt% (see Figure 2), the starch particle size slightly increased. When the POE-g-MAH copolymer is added to the POE/CS 80/20 blend up to 5 wt%, the size of the starch is decreased from 6.08 to 3.82 μm . When the POE-g-MAH concentration is higher than 5 wt%, it was observed that the starch size slightly increases, from 3.82 to 4.56 μm . These results are consistent with results obtained from the dynamic rheology of the POE/CS 80/20 blend, which shows the viscoelastic modulus and complex viscosity of the POE/CS/POE-g-MAH blends have maximum at 5 wt% POE-g-MAH due to the effect of the compatibilizer on the POE-g-MAH copolymer.

Figure 2 illustrates the number average radius of the dispersed phase as function of the concentration of POE-g-MAH added to the blend. The number average radius is defined as:

$$R_n = \frac{\sum_i n_i R_i}{\sum_i n_i}$$

where R_i is the radius of each starch-dispersed particle, n_i is the number of dispersed particles with a radius of R_i . R_n of uncompatibilized POE/CS 80/20 blend is the largest, and with the compatibilizer adding,

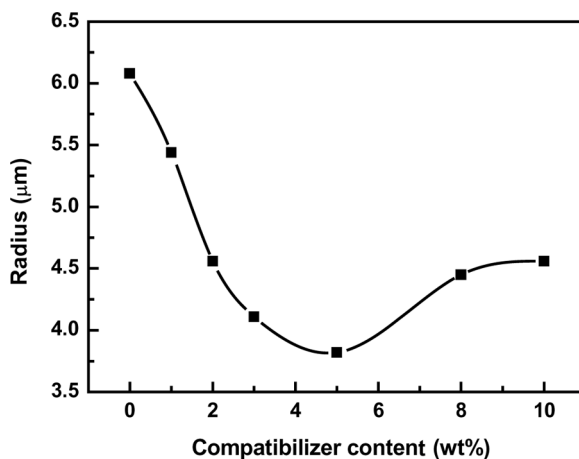


FIGURE 2 Number-average particle radius, R_n , of starch in POE/CS 80/20 blends with different contents of the compatibilizers.

R_n tends to decrease. When the POE-g-MAH concentration is 5 wt%, R_n is at a minimum, and beyond 5 wt%, R_n tends to increase a little.

Dynamic Rheology

Figure 3 shows the storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) with frequency for the pure POE, POE/CS 80/20 blend, and pure POE-g-MAH at 160°C. For the POE-g-MAH, the storage modulus, loss modulus and complex viscosity are higher than those of POE and POE/CS 80/20 blend. POE and POE/CS 80/20 blend almost follow the same trend in their viscoelastic modulus and complex viscosity. However, it can be seen that for low frequencies (0.01 ~ 1 rad/s) the storage moduli of the POE/CS 80/20 blend are greater than those of pure POE. This type of behavior has already been reported by many researchers [17,18] for different polymer blends. The increase in elasticity for low frequencies can be attributed to a relaxation process of the dispersed droplets of the minor phase when it is slightly deformed [19].

Figure 4 shows the storage modulus (G') of compatibilized POE/CS 80/20 blend at 160°C. The storage modulus of the blends shows slight difference with differing concentration of compatibilizer. It can be seen that in comparison with the uncompatibilized blend, the

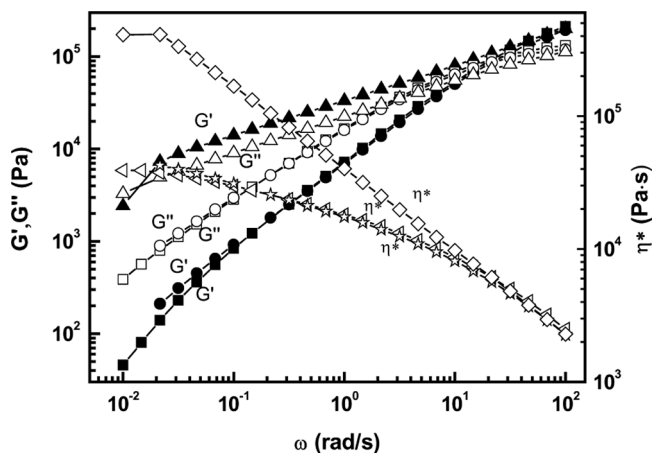


FIGURE 3 Storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) vs. frequency plot for pure POE, POE/CS 80/20 blends and pure POE-g-MAH at 160°C. POE: (■) G' , (□) G'' , (◁) η^* ; POE/CS 80/20 blends: (●) G' , (○) G'' , (▷) η^* ; POE-g-MAH: (▲) G' , (△) G'' , (◇) η^* .

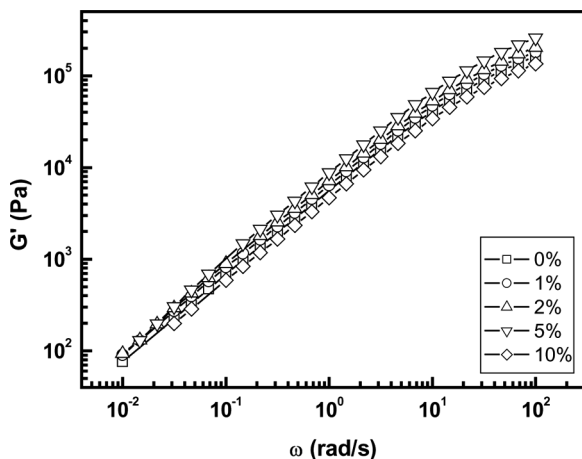


FIGURE 4 Storage modulus (G') vs. frequency plot for POE/CS 80/20 blends with various amounts of POE-g-MAH at 160°C.

compatibilized blends (for concentration below 8 wt%) have higher storage moduli. This may be attributed to three reasons [20]: (1) the role of compatibilizer in reducing the dispersed phase size; (2) narrowing of the particle size distribution; (3) contribution to blend storage modulus because of the interactions of compatibilizer, at the interface, with other components. The blend containing 5 wt% content of compatibilizer showed the highest storage modulus, but the blend containing 8 wt% content of compatibilizer had the lowest storage modulus. As would be expected, the reasons can be obtained from G'' and η^* .

The loss modulus (G'') of POE/CS 80/20 blends with various levels of compatibilizer is shown in Figure 5, which shows the same trend. The loss modulus of the blends with compatibilizer increases more rapidly than those without compatibilizer, leading to a relatively larger elasticity at higher frequencies. This may be the reason that unstable flow occurs more easily for blends with compatibilizer under the processing conditions [21]. With increasing compatibilizer concentration, the loss modulus first increases (up to concentration of 5 wt%), and then decreases. This phenomenon agrees with the storage modulus and complex viscosity of the blends. The same phenomenon has already been observed by other researches for other polymer blends [19,22]. The increase of modulus is probably due to the compatibilizing effect of POE-g-MAH. When POE-g-MAH is added to the blend (up to content of 5 wt%), it gives better adhesion between the POE and starch phase. When the content of POE-g-MAH is beyond 5 wt%, the

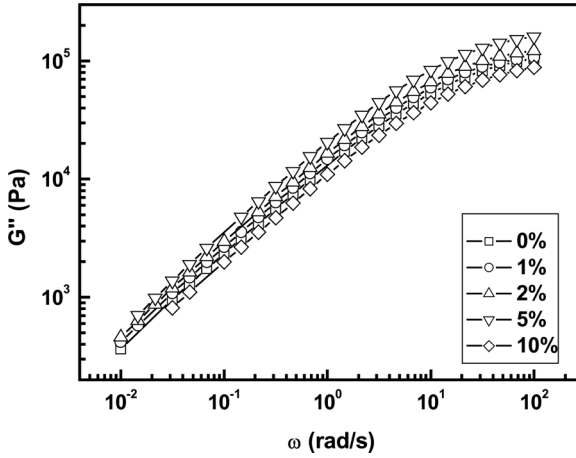


FIGURE 5 Loss modulus (G'') vs. frequency plot for POE/CS 80/20 blends with various amounts of POE-g-MAH at 160°C.

interface is already saturated with POE-g-MAH and no further increase of viscoelastic modulus is observed. This behavior also affects the complex viscosity of the blend.

The loss tangent ($\tan \delta$) of POE/CS 80/20 blends with various levels of compatibilizer is illustrated in Figure 6. The loss tangent is defined as $\tan \delta = G''/G'$. Figure 6 shows that the influence of compatibilizer

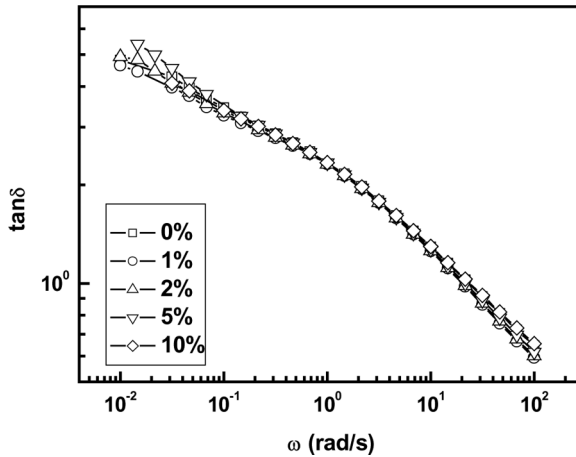


FIGURE 6 Loss tangent ($\tan \delta$) vs. frequency plot for POE/CS 80/20 blends with various amounts of POE-g-MAH at 160°C.

on the loss tangent is more significant in lower frequencies. This may be due to the interfacial interactions between the compatibilizer and starch at higher shear rates leading to a reduced contribution of interfacial interactions to the blends rheological properties.

The complex viscosity, which is defined as $\eta^* = [(G'/\omega)^2 + (G''/\omega)^2]^{1/2}$, of POE/CS 80/20 blends with various levels of compatibilizer at 160° is depicted in Figure 7. The complex viscosity curves are more evident than the viscoelastic modulus with different blends. The complex viscosity of POE/CS blends is the lowest without compatibilizer, while the blends containing 5 wt% POE-g-MAH is the highest. A significant enhancement of viscosity is obtained until 5 wt% POE-g-MAH, while a slight difference is achieved by adding more compatibilizer up to 10 wt%. The increase of complex viscosity may be due to the compatibilizing effect of the copolymer [23], which causes the dispersed domain size to become smaller with increasing amounts of POE-g-MAH. Further addition of compatibilizer unexpectedly leads to a sharp decrease in blend complex viscosity as well as the viscoelastic modulus. This may be associated with the generation of micelles inside the continuous phase which have a plasticizing effect on the viscosity and modulus of the blends [24]. The compatibilizer itself is high molecular weight and has copolymer chains with high molecular weight. What's more, there is a reaction between the anhydride groups of POE-g-MAH and the starches' hydroxyl groups, forming branched and crosslinked macromolecules [25]. These generally prefer to form

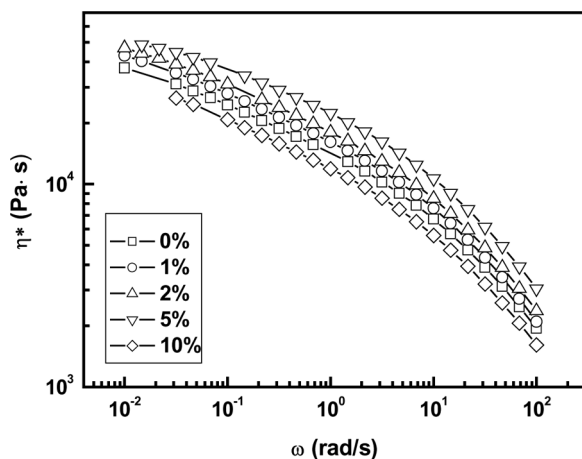


FIGURE 7 Complex viscosity (η^*) vs. frequency plot for POE/CS 80/20 blends with various amounts of POE-g-MAH at 160°C.

micelles instead of localizing at the interface, so the compatibilizer tends to form micelles. Therefore, POE/CS blends with compatibilizer are also believed to form micelles which accounts for the sharp drop of blend complex viscosity and the viscoelastic modulus.

CONCLUSIONS

The influence of compatibilizer on the morphology and dynamic rheological behavior of POE/CS 80/20 blend has been studied. In our research, the uncompatibilized POE/CS 80/20 blend has poor compatibility, because there is little interaction and large interfacial tension between the starch and POE phase. After adding the compatibilizer, the adhesion between the POE and starch phase improves, and the starch particles become small and disperse in the POE matrix. This is due to a reaction between the anhydride groups of POE-g-MAH and the hydroxyl groups of starch. Increasing POE-g-MAH content up to 5 wt% decreases the dispersed size of starch in the POE matrix. However, the size of dispersed starch tends to slightly increase beyond 5 wt% POE-g-MAH. This agrees with the dynamic rheology results of POE/CS 80/20 blends with various amounts of compatibilizer.

The rheological results show an increase of rheological parameters up to 5 wt% compatibilizer and a marked drop at 10 wt% compatibilizer. For the POE/CS 80/20 blend with 5 wt% content of POE-g-MAH, the storage modulus, loss modulus and complex viscosity are the highest. When the compatibilizer content (not more than 5 wt%) increases, the storage modulus, loss modulus and complex viscosity of the blend also increases, which is due to the effect of the compatibilizer. However, when the content of POE-g-MAH is beyond 5 wt%, the rheological properties of the blends decrease. This is because there is too much POE-g-MAH to react with the starch. What's more, the generation of micelles inside the continuous phase has a plasticizing effect on the viscosity and modulus of the blends.

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