Improved Processing Behaviors and Mechanical Properties of Polyolefin Elastomer Blends Prepared by Ultrasound-Assisted Extrusion

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ABSTRACT: To improve the processability of ethylene-α-olefin copolymers (POE), POE and POE/polystyrene (PS) blends were extruded in the presence of ultrasound. On the one hand, the effect of ultrasound on the die pressure drop, extrudate productivity, melt viscosity of POE, and the processing behaviors of POE and POE/PS (80/20) blend were studied. The results showed that with increasing ultrasound power, the die pressure and melt-apparent viscosity of POE decreased whereas the productivity of POE extrudates increased, then the processability of POE was greatly improved. On the other hand, the effects of ultrasound on the morphology, rheological, and mechanical properties of POE/PS (80/20) blend were studied. Capillary rheological results showed that the merger of ultrasound and the addition of PS showed a synergistic improvement of processability of POE. From morphological observation and rheological analysis, the compatibility of the blend was also improved in the presence of 200W ultrasound. As a result, the stress at break of compatibilized POE/PS (80/20) blend increased from 9.2 to 11.0 MPa, and the dynamic storage modulus increased at experimental temperature range, indicating that the mechanical properties of POE/PS blends can be improved by ultrasound-assisted extrusion. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2136–2142, 2009

Key words: ethylene-α-olefin copolymers (POE); processing behaviors; mechanical properties; compatibility; ultrasound-assisted extrusion

INTRODUCTION

The ethylene-α-olefin copolymer (EOC or POE), a new type of thermoplastic elastomer (TPE) materials which is prepared through Dow's INSITE™ constrained-geometry catalyst and process technology, has received much attention because of its unique molecular characteristics.[1] It can be used not only as thermoplastics and thermoset rubber, but also as a good impact modifier, especially for polypropylene. However, compared with thermoplastics materials, the processability of POE is relatively bad due to narrow molecular weight distribution and long-time molecular chain relaxation during processing. The poor processing behaviors of POE which include higher die pressure, higher apparent viscosity, and lower critical shear rate when melt fracture (sharkskin and gross fracture) appears, are main limits to its wide application. Some kinds of processing oils or fluoropolymer[2–4] and orgnaosilicon chemical processing aids[5] have been used to reduce the viscosity and eliminate surface irregularities during the processing of POE. These methods can only improve the processability of POE to a limited extent, and cannot solve the processing problem of POE totally. With the addition of some kinds of processing oils, the melt-apparent viscosity of POE can be reduced dramatically, but the mechanical properties of the materials also decrease. Furthermore, due to relatively low molecular weight of processing oil, it may transfer easily to the surface of the resulting products when the oil is used during the processing of POE. Thus, to extend the application range of POE materials, it is significative to seek efficient and balanced approach to improve the processability of POE materials.

In recent years, ultrasound technology has been attempted to introduce into polymer processing, mainly in the field of thermoplastic welding,[6] devulcanization of vulcanized elastomers,[7,8] melting

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preparation nanocomposites,[9,10] and *in situ* compatibilization of immiscible polymer blends[11–15] and so on. In our laboratory, a special ultrasound extrusion system was developed to improve the rheological and processing properties of polystyrene (PS),[16] linear low-density polyethylene (LLDPE),[17] metallocene-catalyzed-LLDPE,[18] and so forth. The previous experimental results[17–20] showed that the die pressure and melt-apparent viscosity of the polymer in extrusion are greatly reduced, the sharkskin melt fracture phenomenon can been restricted to a certain extent, and the appearance of the extrudate is improved in the presence of ultrasound, indicating that the processability of the mentioned polymers are improved through ultrasound-assisted extrusion technology.

In our previous study,[21] we investigated the effects of the addition of PS and SEBS on the morphology, processability, rheological, and mechanical properties of POE. PS is a typical rigid polymer, which is sensitive to heat. Its melt viscosity is lower than that of POE during processing. When PS with low melt viscosity was incorporated into POE, the total melt viscosity of the POE/PS blends was lower than the bulk of POE, indicating that the processabilty of POE could be improved with the addition of a certain amount of PS. But the mechanical properties of POE/PS blends became bad due to the immiscibility between POE and PS. SEBS could act as a good compatibilizer for POE/PS blend, then improved the mechanical properties of the blend. But when SEBS was incorporated, the melt-apparent viscosity of the blends increased due to poor flowability of SEBS itself during extrusion. According to the present studies,[22,23] it has been proved that immiscible polymer blends in melt can be very quickly induced to undergo an *in situ* copolymer formation at the polymer interfaces during ultrasound-assisted extrusion. As a result, the interfacial adhesion between the polymer phases is enhanced, which causes the significant improvement in the mechanical properties of the resulting polymer blends.

In this article, for the sake of improving both the processability and mechanical properties of POE, the merger of ultrasound and the addition of PS are used during extrusion. The processing behavior and mechanical properties of POE in the presence of ultrasound are studied. The effects of ultrasound on processability, morphology, rheological behaviors, and mechanical properties of POE/PS blends are also investigated.

EXPERIMENTAL

Materials and equipment

The elastomer studied was a metallocene-catalyzed copolymer of ethylene and 1-octene (ENGAGE™ 8150, denoted as POE) supplied by the DOW Chemical Company (Midland, MI), with MI = 0.5 g/10 min (190°C/2.16 Kg) and density = 0.868 g/cm^3. PS resin (PG-33) was purchased from Zhenjiang Chimei Co. (China) with MI = 8.5 g/10 min (200°C/5 kg) and density = 1.05 g/cm^3.

Our main experimental equipment was a specially designed ultrasound extrusion system, whose schematic diagram and working principle were described in our previous article.[16]

Sample preparation

Firstly, POE/PS blends were prepared in a co-rotating twin-screw extruder (diameter of screw = 20, length/diameter ratio = 40/1) with a barrel temperature profile of 140/205/210/205°C from hopper to die. To compare the experimental results reasonably, POE also extruded at the same processing condition before ultrasound-assisted extrusion. Then the resulting POE/PS blends were extruded in our specially designed ultrasound extrusion system, at 10 rpm in the absence or presence of ultrasound. The processing temperature for POE/PS blends at different zones from hopper to die was set at 170, 190, 200, and 200°C.

The resulting products were compressed in mold at 200 ± 3°C for 10 min into plates with the thickness of 1 or 4 mm. The compression molding pressure was 15 MPa.

Measurements and characterization

On-line measurements for die pressure and flow rate in the absence and presence of ultrasound during extrusion were performed at superimposed ultrasound power between 0W and 200W in steps of 50W. The shear rate on the capillary wall γ, shear stress τ, and apparent viscosity η_a were calculated as the same as that in Ref. 19.

Capillary rheological properties were measured by an advanced capillary rheometer RH7 (BohLin Instrument, United Kingdom) at the die temperature of 200°C. Diameter and L/D ratio of the capillary are 1 and 20 mm, respectively.

The surfaces of POE extrudates in the absence and presence of ultrasound and the morphology of POE/PS blends were observed by using a Hitachi X-650 scanning electron microscope (SEM, made in Japan) at an accelerating voltage of 20 kV. POE/PS blends were fractured in liquid nitrogen and coated with gold before observation. To provide a better insight into blend morphology, the PS phase was etched in ethyl acetate at room temperature, under continuous stirring for 4 h. Thereafter, the samples were dried under vacuum at a temperature of 50°C for a period of 24 h before being coated with gold.

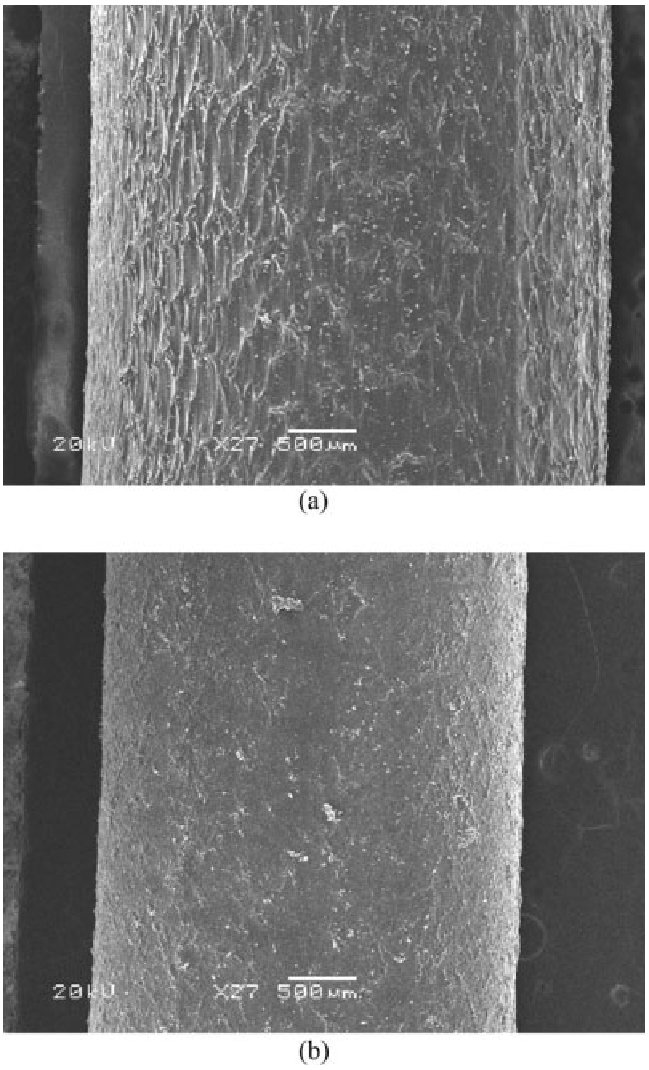


Figure 1 SEM photos of POE extrudates in the absence and presence of ultrasound.

Dynamic rheological properties of the samples were measured in a Bohlin Gemini 200 Advanced Rheometer (Malvern, United Kingdom) with a 25 mm parallel plate fixture under dry nitrogen atmosphere. The gap between the plates was 1 mm. Dynamic frequency sweep tests were executed in the frequency range of 0.1–100 rad/s at 200°C with strain amplitude of 2% for which the rheological behavior was in the linear viscoelastic range.

Dynamic mechanical thermal analysis was performed through a TA DMTA Q-800 instrument with the specimen dimension of 30 × 10 × 4 mm^3 in the single cantilever mode. The samples were examined from −100 to 80°C at a constant frequency of 1 Hz and a heating rate of 3°C /min.

Mechanical properties of the blends were tested at room temperature by using an Instron 4302 Tensile Tester (Canton, MA) with the specimen dimension of 25 × 4 × 1 mm^3 and a crosshead speed of 500 mm/min.

RESULTS AND DISCUSSION

Effects of ultrasound on the extrudate surface of POE

In general, main processing problems for polyolefin elastomers include melt fracture and extrudate expansion. As shown in Figure 1, the extrudates of POE 8150 in the ordinary extrusion are very rough and show a shark-skin appearance. However, the shark-skin phenomenon becomes unconspicuous when it is extruded in the presence of ultrasound at the same temperature and screw speed. It also can bee seen from Figure 1 that the diameter of extrudate with superimposed 200W ultrasound decreased, indicating that ultrasound can greatly inhibit the expansion of POE extrudate. Therefore, it can be concluded that the ultrasound can improve the processability of POE to a certain extent.

Effects of ultrasound on the die pressure drop of POE

The relative die pressure drop (ΔP), which means decreasing degree of the die pressure due to the presence of ultrasound during extrusion, can be written as:

$$\Delta P = \frac{P_0 - P_u}{P_0} \times 100\%$$

In which P_0 and P_u are the die pressure in the absence and presence of ultrasound, respectively. Die pressure changes with ultrasound power measured at a die temperature of 150°C. As shown in Figure 2, ΔP increases with increasing ultrasound power. ΔP amounts to 47% at a screw rotation speed of 5 rpm, a die temperature of 150°C and ultrasound

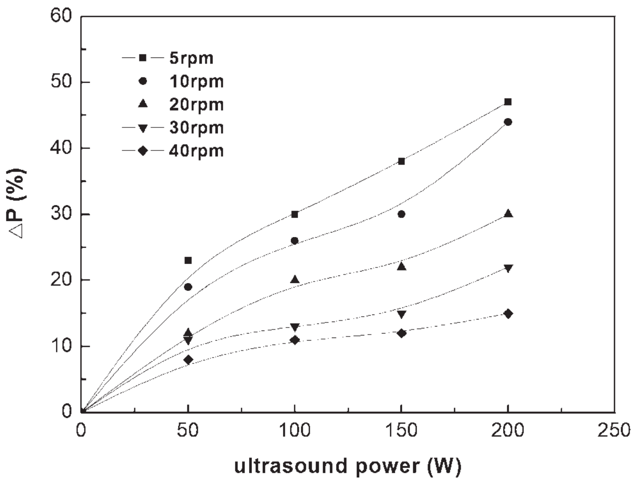


Figure 2 Dependence of ΔP on ultrasound power at various screw rotation speeds and a die temperature of 150°C.

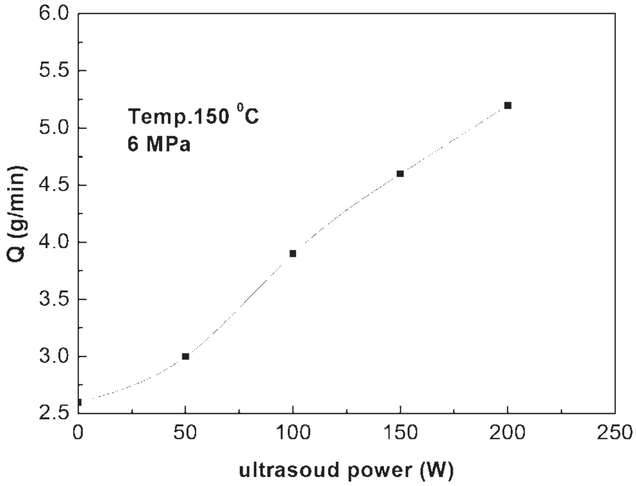


Figure 3 Q versus ultrasound power at a die temperature of 150°C and a die pressure of 6 MPa.

power of 200W, which means that the die pressure of POE could be greatly decreased during ultrasound-assisted extrusion.

Figure 3 shows mass flow rate (Q) of POE versus ultrasound power at the die temperature of 150°C and the die pressure of 6 MPa. It is obvious that the mass flow rate of POE increases with increasing ultrasound power at the same die temperature and pressure. The productivity of POE extrudate can be increased through ultrasound-assisted extrusion.

Effect of ultrasound on the on-line rheological behavior of POE

The on-line melt-apparent viscosity curves during extrusion in the absence and presence of ultrasound is shown in Figure 4. The presence of ultrasound decreases the melt-apparent viscosity during extrusion. At the same shear rate, the higher ultrasound power, the lower melt viscosity. In our opinion, it is ascribed that POE molecular chains can be disentangled or broken during ultrasound-assisted extrusion, resulting in the reduced intermolecular effects and easier movement of POE molecular chains at the same shear rate.

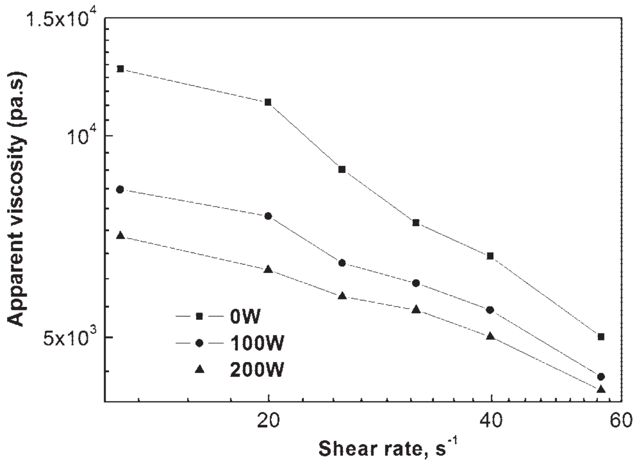
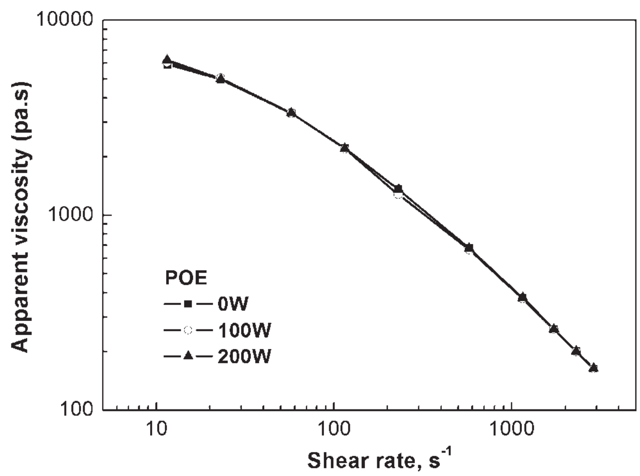


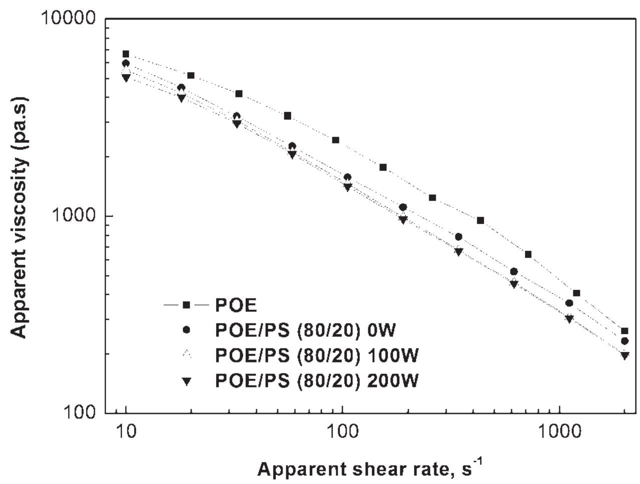
Figure 4 Apparent flow curves of POE in the presence of ultrasound at a die temperature of 150°C.

Capillary rheological behavior of POE and POE/PS blends

The measured apparent viscosity data of POE and POE/PS blends in the absence and presence of ultrasound are presented in Figure 5 as a function of shear rate. It is clearly that both POE and POE/PS blends tend to present a typical pseudoplastic behavior. From Figure 5(a), the apparent viscosity curves of POE melts prepared through ordinary and ultrasound-assisted extrusion are almost the same, indicating that ultrasound can not influence the processability of POE, which is contrary to the on-line rheological results. Actually the contradiction between these two results is attributed to the



(a)



(b)

Figure 5 Apparent viscosity of POE (a) and POE/PS blends (b) versus shear rate at 200°C.

difference between these two kinds of rheological measurement methods. The decrease of melt-apparent viscosity measured by on-line rheological method is owing to the polymer chain disentanglement induced by ultrasound during extrusion. However, there is no ultrasound effect when the rheological behavior is off-line measured by the capillary rheometer. The off-line capillary rheological properties are related to the structure of bulk polymer, such as molecular weight, molecular weight distribution and so on. From these two rheological results, it is implied that the improved processability of POE during ultrasound-assisted extrusion is not due to the degradation of POE, but depends on the polymer chain disentanglement induced by ultrasound.

The apparent viscosity of POE/PS (80/20) blend [shown in Fig. 5(b)] is obviously lower than POE at all range of shear rate measured, indicating that the processability of POE is improved by the addition of PS. It is also found that the apparent viscosity of POE/PS (80/20) blends prepared by ultrasound-assisted extrusion further decreases. In our previous article,[16] it was found that ultrasound caused the degradation of PS melt and its molecular weight distribution became wide to a certain extent. The low molecular weight PS formed by mechanochemical degradation under ultrasound can act as a plasticizer to improve flow-ability of polymer blend melt. Therefore, the merger of ultrasound and the addition of PS show synergistic improvement of processability of POE.

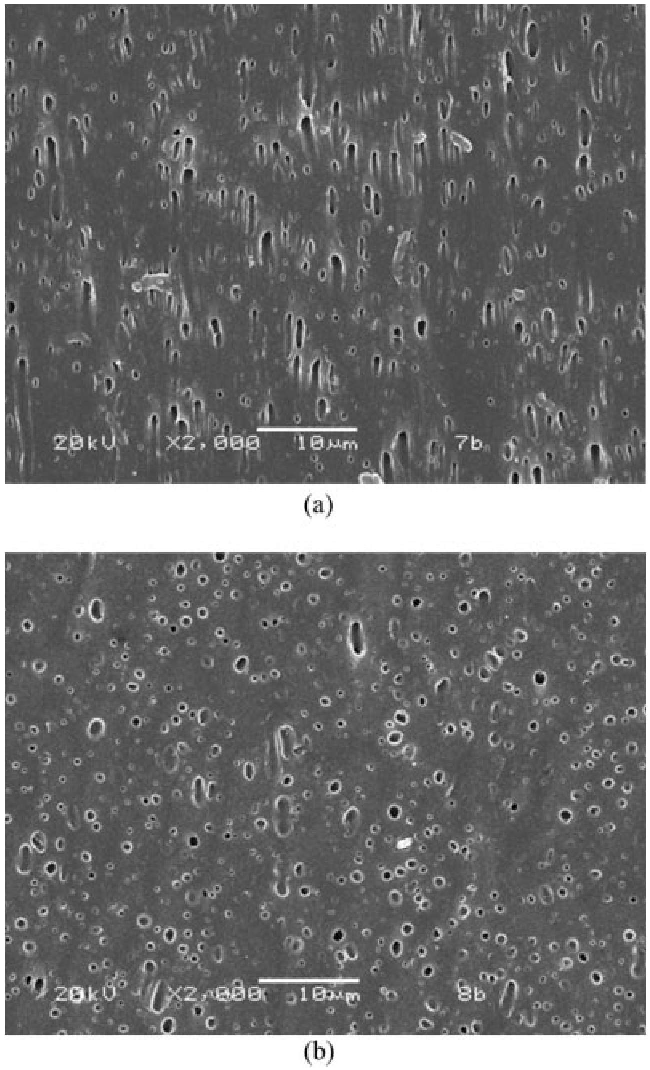


Figure 6 SEM micrographs of POE/PS blend in the absence and presence of 200W ultrasound (a) POE/PS 80/20 (0W) and (b) POE/PS 80/20 (200W).

Morphology analysis of POE/PS blends

The SEM photos of cryo-fractured surfaces of POE/PS (80/20) blends in the absence and presence of 200W ultrasound are shown in Figure 6. It was observed in Figure 6(a), the morphology of ordinary extruded POE/PS (80/20) blend, that large and irregular PS domains are dispersed in POE matrix. When the blend was extruded in the presence of 200W ultrasound, the PS domains become smaller and more even in the matrix, just shown in Figure 6(b). Generally, POE and PS are immiscible. When a compatibilizer is added, the size and its distribution of the dispersed phase tend to decrease, indicating that the blend is compatibilized. From the above morphological observation, it is likely that the compatibility of POE/PS blend was improved during ultrasound-assisted extrusion.

Ultrasound *in situ* compatibilization of POE/PS blends

Some research had confirmed that by means of ultrasound-assisted extrusion, immiscible polymer blends in melt under high pressure can be very quickly induced to form an *in situ* copolymer, which can act as a kind of compatibilizer to improve the compatibility of immiscible blends, at the interface between two polymer phases. Chen et al.[24] reported the formation of POE-PS copolymer in POE/PS (50/50) melting blend through extraction and FTIR analysis, but their experiments were conducted by using a "static" ultrasound system. We also tried to confirm the formation of POE-PS copolymer, which causes the ultrasound compatibilization of POE/PS (80/20) blend. However, extraction experiment result showed that the amount of *in situ* formed POE-PS copolymer is not enough to be detected by FTIR analysis.

On the other hand, rheological measurements have been widely used to characterize compatibilizing effects of the compatibilizer on the immiscible blends. It was found that with increasing compatibilizer concentration the complex viscosity of PP/PS blends[25–27] compatibilized by SBS or SEBS increases and levels

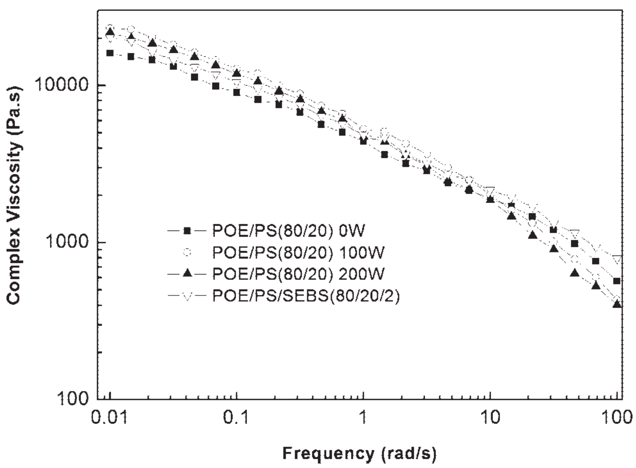


Figure 7 Complex viscosity (η*) of POE/PS (80/20) blends and POE/PS/SEBS (80/20/2) blend.

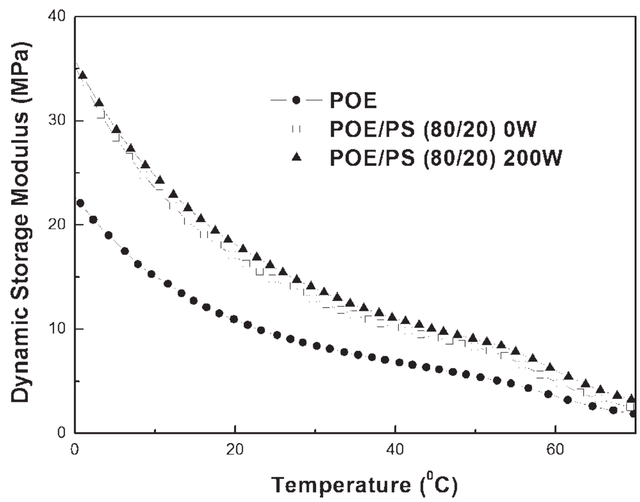


Figure 8 Temperature dependence of dynamic storage modulus of POE and POE/PS (80/20) blends.

off for a certain concentration. The increases of complex viscosity can be attributed to the enhanced interfacial adhesion, which is a result of compatibilizing effect of the copolymer. This phenomenon is more pronounced at lower frequencies (0.01–1 rad/s). To prove ultrasound *in situ* compatibilization of POE/PS blend, the complex viscosity of POE/PS (80/20) blends in the absence and presence of ultrasound was measured. The results are shown in Figure 7.

The complex viscosity of POE/PS (80/20) blend compatibilized by the addition of SEBS (10 wt % relative to the minor phase PS) is also given in Figure 7. It is expected that the complex viscosity of POE/PS/SEBS (80/20/2) blend at lower frequencies is greater than that of POE/PS blend due to the compatibilizing effect of SEBS. As for the blends prepared by ultrasound-assisted extrusion, their complex viscosities at lower frequencies are greater than that of the blend prepared by ordinary extrusion, even higher than that of POE/PS/SEBS (80/20/2) blend. So it could be proved that POE/PS blend is compatibilized during ultrasound-assisted extrusion.

Mechanical properties of POE and POE/PS blends

A uniaxial tensile test was used to evaluate the effect of ultrasound on mechanical properties of POE and POE/PS (80/20) blend. The results are listed in Table I. It is generally expected the mechanical properties of the compatibilized polymer blends will be improved compared with those of the corresponding incompatibilized ones. It can be found that ultrasound have little effect on the mechanical properties of POE, but the stress at break of POE/PS (80/20) blend increases from 9.2 to 11.0 MPa in the presence of 200W ultrasound. It should be ascribed to the *in situ* compatibilization of POE/PS blend during ultrasound-assisted extrusion. As a result, the enhanced interfacial adhesion of POE and PS phase makes stress transfer more efficiently between the phases during uniaxial tensile test, and then the stress at break of the POE/PS (80/20) blend prepared by 200W ultrasound-assisted extrusion is enhanced.

Dynamic mechanical properties of POE and POE/PS blends

Dynamic mechanical analysis (DMA), one of the important methods for investigating the mechanical properties of polymer blends within a wide range of temperature, can be applied to study thermodynamic miscibility of polymer blends and interfacial adhesion in polymer blends.[28,29] Figure 8 is dynamic storage modulus of POE, POE/PS (80/20) blends in the absence and presence of 200W ultrasound as a

TABLE I
Effect of Ultrasound on Mechanical Properties of POE and POE/PS (80/20) Blends

POE/PS	Ultrasound power (W)	Elongation at break (%)	Stress at break (MPa)
100/0	0	750 ± 25	12.2 ± 0.5
	200	710 ± 20	12.1 ± 0.5
80/20	0	758 ± 25	9.2 ± 0.5
	200	757 ± 25	11.0 ± 0.5

TABLE II
Selected Data for Dynamic Storage Modulus (E') of POE and POE/PS (80/20) Blends

Sample	E' (MPa) 0°C	20°C	40°C	60°C	70°C
POE	22.8	10.5	6.9	3.5	1.6
POE/PS (80/20) 0W	35.6	17.5	10.2	4.9	2.5
POE/PS (80/20) 200W	36.7	18.1	11.0	6.0	3.2

function of temperature. Table II lists a survey of the measurement results of the storage modulus (E') at the chosen temperature of 0, 20, 40, 60, and 70°C.

From the above results, it is clearly found that the dynamic storage moduli of POE/PS (80/20) blends are higher than that of POE at the temperature range from 0 to 70°C. Moreover, the storage modulus of the blend prepared by 200W ultrasound-assisted extrusion improved further, indicating that the interfacial adhesion between POE and PS phases was improved due to compatibilizing effect during ultrasound-assisted extrusion. It can be concluded that the mechanical properties of POE materials are improved by the merger of addition of PS and ultrasound-assisted extrusion.

CONCLUSIONS

The die pressure and melt viscosity of POE in extrusion are greatly decreased with increasing the ultrasound power, and the productivity of POE extrudate at the same die pressure level is increased, then the processability of POE is greatly improved due to the polymer chain disentanglement induced by ultrasound during extrusion. The processability of POE can be further improved by the merger of addition of PS and ultrasound-assisted extrusion. Compared with POE/PS (80/20) blend prepared by ordinary extrusion, the size of the dispersed PS phase and its distribution in the blend prepared by ultrasound-assisted extrusion are reduced, and the complex viscosity of that at lower frequencies is increased, which all mean that the compatibility of POE/PS blends can be improved by mean of ultrasound. As a result, the mechanical properties of POE/PS blend are increased by ultrasound-assisted extrusion, which are characterized by a uniaxial tensile test and DMA.

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