

Preparation of POE/PS Blends with Fine Particle Sizes by Diffusion and Subsequent Polymerization of Styrene in POE Pellets^{*}

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Abstract Ethylene- α -octene copolymer (POE)/polystyrene (PS) blend pellets with fine particle sizes were prepared by diffusion and subsequent polymerization of styrene in POE pellets through a one-pot procedure. The effects of the amounts of styrene and BPO on PS content, monomer efficiency and monomer conversion were investigated. The blend pellets were characterized by Micro-FTIR and FESEM, showing homogeneous diametrical distributions of PS and particle size. After melt-processing into rods, the average particle sizes are almost doubled, but still in submicron scale. Compared to neat POE rods, the blend rods with PS content higher than 15% exhibit improved tensile modulus and tensile strength without significantly losing ductility, being attributed to the small sizes, complex nature of particles and the existence of POE-*g*-PS copolymer that result in good interfacial adhesion. POE/PS pellets were compared with the previously reported PP/PS pellets, and the differences between the two systems are attributed to the different morphology of the two matrices: POE is completely amorphous at the diffusion and polymerization temperature, while *i*PP is semicrystalline. Without efficient impediment of the crystal lamellae in POE pellets, styrene diffuses easily in POE pellets.

Keywords Blends; Mechanical properties; Nanostructured polymers; Polystyrene

INTRODUCTION

The size of the dispersed phase in polymer blends is of prime importance in view of mechanical properties. In conventional melt compounding, the common way of reducing particle size is adding a compatibilizer such as a block copolymer. Even so, the particle size can hardly approach 100 nm^[1–3]. In the literature, there are a certain number of methods for preparing polymer nanoblends or quasi-nanoblends in which the size of the dispersed phase is smaller than or approaches 100 nm, including *in situ* polymerization and *in situ* compatibilization reactive extrusion, supercritical carbon dioxide-assisted infusion and subsequent polymerization, conventional melt mixing with small amount of minor component, high-shear processing, solid-state shear pulverization, *etc*^[1, 4–14]. The polymer nanoblends have better mechanical properties than their micrometer counterparts. For example, both polypropylene (PP)/polystyrene (PS) and polypropylene (PP)/poly(methyl methacrylate) (PMMA) nanoblend films have better mechanical strength than neat PP films without losing ductility, in contrast to the macrophase-separated conventional blends^[15, 16].

Previously, our research group has reported a method for preparing polymer blend pellets with fine particle sizes by diffusion and subsequent polymerization of a monomer (or monomer mixture) in commercial polymer pellets^[14, 17–24]. The main advantages of the blend pellets are their direct use in plastic production without the

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need for pre-compounding and the limited degree of particle coalescence during low shear processing that results in improved mechanical properties^[22, 23]. So far, only semicrystalline polymer pellets such as *i*PP, high density polyethylene (HDPE) and polyamide 6 (PA6) have been used as the matrices. The monomer styrene and initiator benzoyl peroxide (BPO) diffuse into the amorphous regions of the pellets. Spherical PS particles are formed by polymerization-induced phase separation shortly after polymerization is initiated. The confinement coming from crystal lamellae is thought of importance in obtaining fine particle size. An intriguing question then arises as whether this method can be extended to amorphous polymer pellets.

Ethylene- α -octene copolymer (POE) is a well-known polyolefin-type thermoplastic elastomer, which is widely used in plastic industry. It has a low degree of crystallinity with a melting temperature of 55 °C. At the diffusion and polymerization temperature used in our method (90 °C), it is completely amorphous. POE/PS blends prepared by conventional melt compounding have been reported^[25]. The PS particle size is in micrometer range, and the tensile strengths and elongations at break of the blends significantly decrease^[25]. Extensive research^[25–31] has been devoted to reducing PS particle size, including the use of poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SEBS) triblock copolymer as a compatibilizer, *in situ* generation of PS-graft-POE copolymer through Friedel-Crafts alkylation reaction in the presence of a Lewis acid catalyst (AlCl₃), and the assistance of ultrasound. In the resulting blends, the particle size significantly decreases and the particle size distribution is more even. The tensile strengths of the blends compatibilized by SEBS are significantly greater than those of the uncompatibilized blends and neat POE, but the elongation at break is significantly lower than that of neat POE^[25]. Neither stress at break nor elongation at break of the POE/PS (mass ratio = 80/20) blend prepared with the assistance of ultrasound is better than those of neat POE, although the stress at break is greater than that without ultrasound^[31].

In this work, commercial POE pellets are used as the matrices to carry out the diffusion and subsequent polymerization of styrene. The goal is to find out whether the method is suitable for amorphous polymer pellets. The important process parameters (the amounts of styrene and BPO) are investigated in view of PS content, monomer efficiency and monomer conversion. POE/PS blend pellets are characterized by Micro-FTIR and FESEM, and melt-processed into rods for evaluation of mechanical properties. Distinguishing features are found compared to the previously reported PP/PS blend pellets obtained with semicrystalline *i*PP pellets by similar type of procedure. The differences are attributed to the difference between the morphology of POE and that of *i*PP pellets. The blend rods with PS content higher than 15% exhibit improved tensile modulus and tensile strength without significantly losing ductility.

EXPERIMENTAL

Materials

POE pellets (Engage 8150) were from Dupont Dow Elastomer. They are short cylinders with ellipsoidal-shaped cross-section. The average height of the cylinders is 1.5 mm, and the long and short axes of the ellipse are 5 and 4 mm in average. Polyvinyl alcohol (PVA) with a degree of polymerization of (1750 $\pm$ 50) and degree of alcoholysis of 88% were purchased from Beijing Organic Chemical Plant (Beijing, China). Styrene and benzoyl peroxide (BPO) were purchased from Fuchen Chemical Reagent Plant (Tianjin, China) and purified by vacuum distillation and recrystallization twice from chloroform/methanol, respectively. PS used for making calibration curve was purchased from BASF-YPC Company Limited (Bycolene 158 K). Chloroform, methanol, xylene and ethyl acetate were analytical grade and used as received. Tetrahydrofuran (THF) was of chromatographic grade.

General Procedure for Synthesizing POE/PS Blends

To a 250 mL three-necked flask equipped with a condenser and mechanical stirrer were added 60 mL of deionized water and 1 mL of aqueous PVA (0.8 wt% in water) at room temperature. 8 g of POE pellets (m_{POE}), styrene (12.5 wt% to POE, m_{St}) and BPO (0.75 wt% to styrene) were added. With efficient stirring the mixture was heated to 90 °C over 30 min and kept at 90 °C for 2 h. Then, 60 mL of deionized water was added, and the

POE/PS blend pellets were separated by vacuum filtration. After washing with deionized water, the pellet surfaces were dried with filter paper. The pellets that contained unreacted styrene were weighed and denoted as m_1 , then thoroughly dried in a ventilated oven at 60 °C for 12 h and at 100 °C for 1.5 h, weighed again and denoted as m_2 . The PS content, monomer efficiency and monomer conversion are calculated as follows:

$$\text{PS content} = \frac{m_2 - m_{\text{POE}}}{m_{\text{POE}}} \times 100\% \quad (1)$$

$$\text{Monomer efficiency} = \frac{m_2 - m_{\text{POE}}}{m_{\text{St}}} \times 100\% \quad (2)$$

$$\text{Monomer conversion} = \frac{m_2 - m_{\text{POE}}}{m_1 - m_{\text{POE}}} \times 100\% \quad (3)$$

Melt-processing of POE/PS Blend Pellets

POE/PS blend pellets were cut into small pieces, and put into a melt flow indexer (GT-7100-MI, GOTECH). After heating for 4 min at 230 °C, rods were extruded through a die of a diameter of 2 mm under a load of 5635 g.

Microscopic Fourier Transform Infrared Spectroscopy (Micro-FTIR)

A thin section was cut through the center of the blend pellet, then placed between two pieces of clean glass slides and pressed into a thin film at 80 °C to get it thinner for a better resolution in Micro-FTIR, because very thin slice is not easy to obtain by cutting elastomers. The diameter of the hot-pressed slice is slightly bigger than the real diameter of the pellet, but the measurements do give useful information about the diametrical distribution of PS. Micro infrared tests were carried out along the long axis of the samples with Thermo-Nicolet 6700 FTIR and Nicolet Continuum FTIR Microscope, and the step length was 100 μm . A_1/A_2 was defined as the ratio of the peak areas of the absorptions at 1600 cm^{-1} (PS) and 2674 cm^{-1} (POE) to represent PS/POE.

Field Emission Scanning Electron Microscopy (FESEM)

JSM-7401 field emission scanning electron microscope (FESEM) was used to observe the morphology of the pellets and rods. The samples were cryo-fractured in liquid nitrogen, and the cross-sections were observed by scanning electron microscope with an accelerating voltage of 1 and 3 kV. Particle sizes were counted by using the Smile View software.

Measurement of PS Grafting

The percentage of PS grafting is defined as the mass ratio of grafted PS (*i.e.* POE-g-PS) to POE and obtained by analyzing the mixture of POE/POE-g-PS with FTIR spectrometer. The isolation of POE/POE-g-PS mixture was as follows: POE/PS blend pellets (PS content = 51.6%, 1 g) were heated with stirring in xylene (50 mL) at 130 °C for 30 min. After cooling, the solution was added dropwise to ethyl acetate (200 mL) stirred in a beaker to produce fine precipitate, which was then filtered, washed thoroughly with ethyl acetate and dried.

Samples for FTIR analyses were prepared as follows: POE/POE-g-PS was dissolved in xylene at 130 °C, and then the solution was cooled, dropped onto KBr discs and dried. The percentage of PS grafting was calculated according to a calibration curve obtained from samples prepared by dropping solutions of POE/PS with different compositions in xylene to KBr discs and thorough drying. A_3/A_4 ratio, defined as the ratio of the peak areas of the absorptions at 700 cm^{-1} (PS) and 720 cm^{-1} (POE), was used in the calibration curve to represent the ratio of PS/POE, since the resolution of these two peaks was better in this type of samples than that of 1600 cm^{-1} (PS) and 2674 cm^{-1} (POE) used for the blend films cut from the blend pellets.

Gel Permeation Chromatography (GPC)

Pellets were hot pressed into a film of about 100 μm thickness and stirred in ethyl acetate for 24 h to extract PS. The film was taken out, and then the solution was evaporated to remove ethyl acetate. The obtained PS was

dissolved in THF. The weight-average molecular weights (M_w) and molar-mass dispersity (M_w/M_n) of PS were determined using a gel permeation chromatography (GPC) apparatus using THF as the eluent (1 mL/min) at room temperature and calibrated by means of polystyrene narrow standards. The instrument was equipped with a refractive index detector (Wyatt Optilab rEX) as well as a PLgel 5 μ m mixed-D column.

Annealing Experiments

The POE/PS pellets were annealed on a heating stage at three different temperatures (120, 150 and 180 °C) for 30 min.

Tensile Testing

The mechanical properties of melt-extruded rods were measured with a GT-TCS 2000 machine (GOTECH). The tests were performed at a crosshead speed of 100 mm/min until the rods broke. The initial distance between fixtures was 3 cm. Data from at least five measurements were averaged.

RESULTS AND DISCUSSION

Preparation of POE/PS Blend Pellets

As illustrated in Fig. 1, POE/PS blend pellets were prepared by a one-pot procedure where all the materials and reagents were added to the flask at room temperature and then the mixture was heated to 90 °C over 30 min and kept at 90 °C for 2 h. Previously, a two-pot procedure involving the separation and transfer of the pellets after diffusion of styrene from the original flask into a new flask for carrying out the polymerization was recommended for the preparation of PP/PS blends in order to avoid polymerization-induced diffusion of styrene (St) which can significantly increase the particle size of some areas^[14, 22]. Since the melting temperature of the crystalline region of POE is 55 °C, the crystalline region of POE is completely melted at the temperature of diffusion. The initial purpose of considering a one-pot procedure was to avoid the troublesome manipulation caused by the sticky POE pellets. Later on, we found that the particle size distribution was quite narrow and the enrichment of further coming styrene during polymerization in some areas did not happen because hardly any structural hierarchy exists in the amorphous POE pellets.

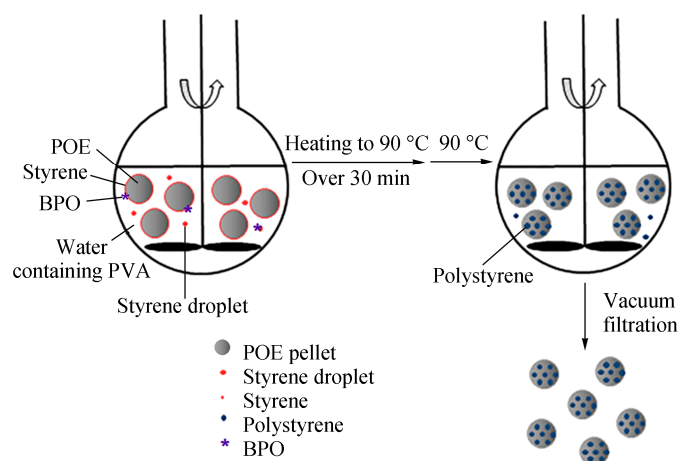


Fig. 1 Illustration of the one-pot procedure for synthesizing POE/PS blend pellets

In the previous procedures for PP/PS blends, BPO was added to the reaction mixture after the diffusion of styrene into pellets to avoid the initiation and polymerization of styrene during the diffusion process and ensure the arrival of styrene at the center of iPP pellets^[14, 17–22]. In the current case, although BPO was added along with styrene at room temperature, styrene could successfully diffuse into the center of POE pellets at the heating stage

because styrene and BPO diffuse more easily in amorphous POE pellets than in semicrystalline *i*PP pellets, without any impediment of crystal lamellae^[19]. The one-pot procedure used in this work is much simpler than both the two- or one-pot procedures previously used for preparing PP/PS blend pellets by diffusion and subsequent polymerization of styrene in *i*PP pellets, and this is advantageous for scaling up of the procedure.

In the current procedure the ratio of pellet/water is much lower than in the previous procedures^[14, 17] to avoid the coalescence of the sticky pellets. As shown in Fig. 2, most of the blend pellets remain single and retain the original shape of POE pellets although somewhat bigger; some pellets coalesce, forming bigger pellets, but the maximum number of the primary pellets in one coalesced pellet is limited to 2, which does not affect the direct use of blend pellets in plastic production. The blend pellets are no longer transparent due to the incorporation of PS particles that have a different refractive index.

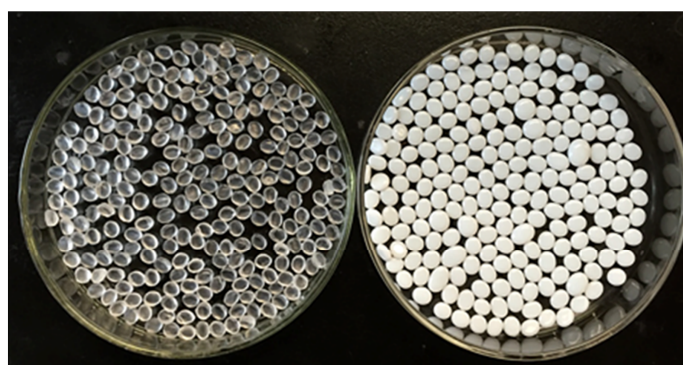


Fig. 2 Images of POE pellets (left) and POE/PS blend pellets (PS content = 51.6%, right)

The effects of the amounts of styrene and BPO on PS content, monomer efficiency and monomer conversion were investigated by keeping the amounts of all other components constant. As shown in Figs. 3(a) and 3(b), for a fixed amount of styrene (expressed in weight percentage relative to POE) both PS content and monomer efficiency increase when the amount of BPO (expressed in weight percentage relative to styrene) increases because the monomer conversion increases (Fig. 3c). Similar trend found for the two variables is reasonable, because the monomer efficiency is proportional to PS content at constant amount of styrene. When the amount of styrene increases, both PS content and monomer efficiency increase no matter what amount of BPO is used, indicating that the degree of PS incorporation can be controlled through the amount of styrene and high process efficiency can only be reached at high styrene loading.

It is noted that even with 75% styrene and 0.75% BPO, where the PS content is as high as 51.6%, the PS content is still non-saturated. This is completely different from the case of *i*PP matrix where a saturation of 25% was reported for PS content when the amount of styrene was higher than 30%. Higher maximum PS content in POE than in PP matrix can be reasonably explained by their morphological difference. Because the diffusion and subsequent polymerization of styrene only occur in the amorphous regions of *i*PP pellets^[14, 17], the crystalline regions of *i*PP not only slow down the diffusion rate of styrene but also limit the diffusion amount of styrene, being in contrast to the amorphous POE pellets. In fact, in PP/POE (mass ratio = 8/2) blend pellets the crystalline regions of *i*PP also play similar roles but with a smaller effect; the maximum PS content is 38%, higher than that in neat PP pellets^[19].

The highest monomer efficiency is 69%, somewhat lower than the case of *i*PP matrix presumably due to the use of different preparation procedure, most probably the earlier addition of BPO.

As shown in Fig. 3(c), the monomer conversion increases with the amounts of styrene and BPO. When the amount of styrene is low, the ratio of BPO/water is very low and a considerable percentage of BPO is wasted in water. Consequently, BPO/styrene is significantly lowered, resulting in low monomer conversion.

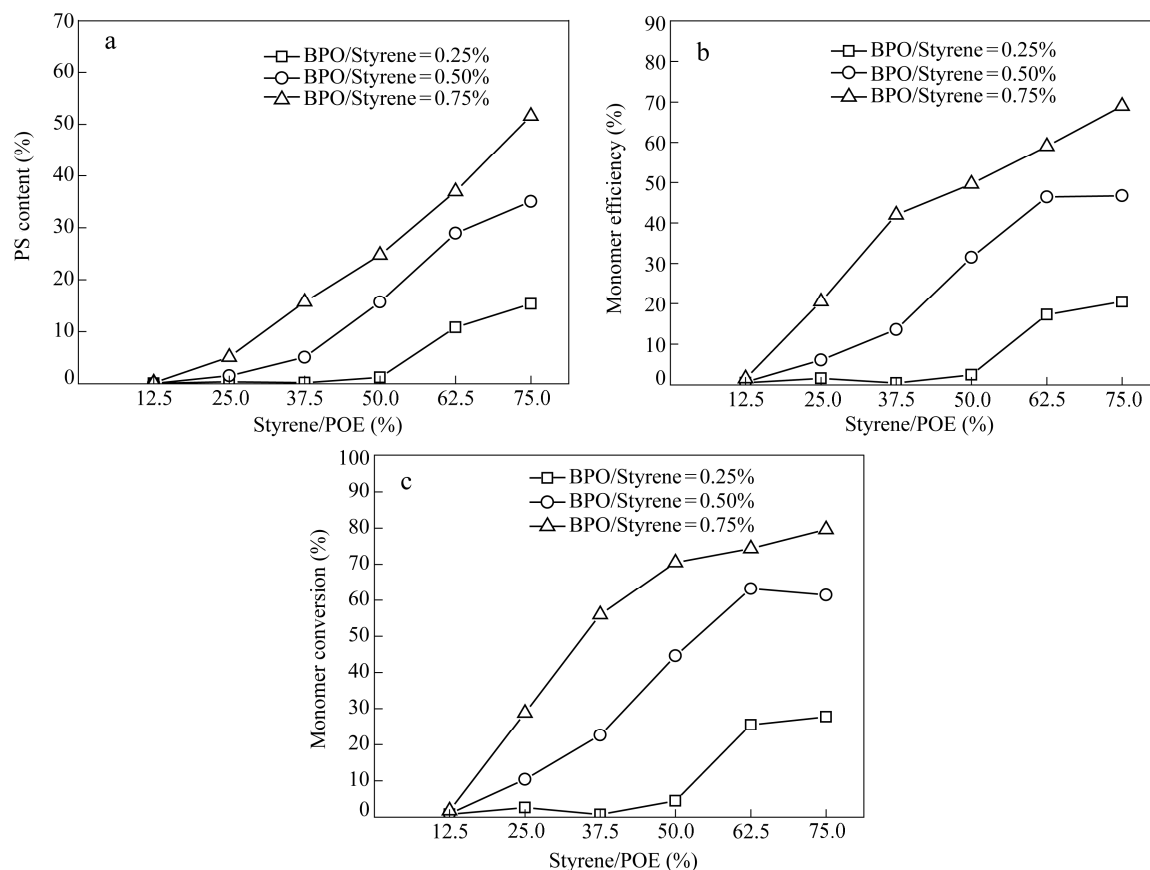


Fig. 3 (a) PS content, (b) monomer efficiency and (c) monomer conversion as a function of styrene/POE at various amounts of BPO/styrene

Distribution of PS, Phase Morphology of POE/PS Blend Pellets and M_w of PS

The blend pellets having different PS contents synthesized with 0.75% BPO were investigated by Micro-FTIR, and the diametrical distributions are shown in Fig. 4. Distance 0 is the center of the pellets. A_1 and A_2 are the peak intensities of PS at 1600 cm^{-1} and POE at 2674 cm^{-1} , respectively. The curves have similar shape for all the samples except for the one with a PS content of only 0.2%. The PS distributions are almost homogeneous over

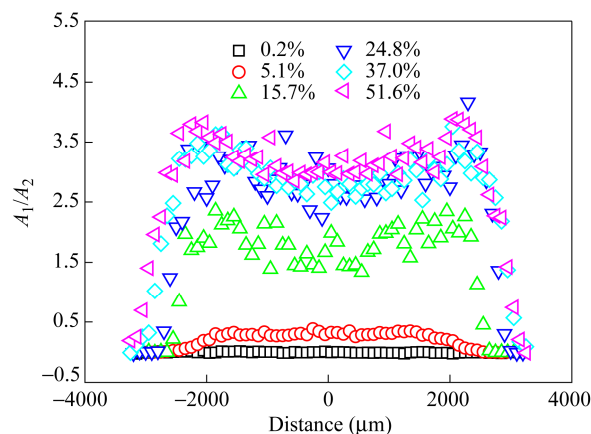


Fig. 4 Diametrical distributions of PS in POE/PS blend pellets containing different PS contents synthesized with 0.75% BPO

large regions around the pellet centers, and the regions near the pellet edges do not contain PS for samples having low PS contents such as 5.1% and 15.7%, revealing that styrene and BPO tend to diffuse into the central regions of POE pellets in all the cases. This is in big contrast to the case of *i*PP pellets where the lowest PS incorporation was found in the central regions^[17]. The difference in the diametrical distribution of PS can also be attributed to the difference in morphology of POE and PP pellets, similar to the difference in maximum PS content. Because there is no impediment of the crystal lamellae in POE pellets, hydrophobic styrene can diffuse easily to the centers of POE pellets that are the most hydrophobic regions. When PS content increases from 0.2% to 24.8%, A_1/A_2 in the PS-inclusive region increases and the width of PS-exclusive region decreases. The samples containing 24.8% to 51.6% have almost the same A_1/A_2 value; their main difference is the width of the PS-exclusive region. With increasing PS content, the PS-exclusive region decreases, down to 0 with the PS content of 51.6%.

FESEM was used to investigate the phase morphology of the same blend pellets mentioned above. Three positions were observed in detail for each sample after cryo-fracture: the center, mid-depth from the center to the surface and the edge. For simplicity, only the micrographs of the centers of selected samples are shown in Fig. 5. Typical sea-island structure was observed for all the samples. The average particle sizes of all the samples are listed in Table 1. No particles were observed at the pellet edges. Those at the centers were practically same as those at the mid-depth from the surface to the center without exception, revealing homogeneous size distribution of particles throughout the PS-inclusive regions. When the amount of styrene increases, the average particle size increases, revealing that the particle size is PS content-dependent. It is noted that a significant number of particles are broken in FESEM micrograph of POE/PS blend pellet with PS content of 51.6%, and small spherical particles at size scale of about 30 nm are observed in the broken particles (Fig. 5d). This suggests that the interface between the matrix and particles is sufficiently strong and the particles observed in POE matrix are

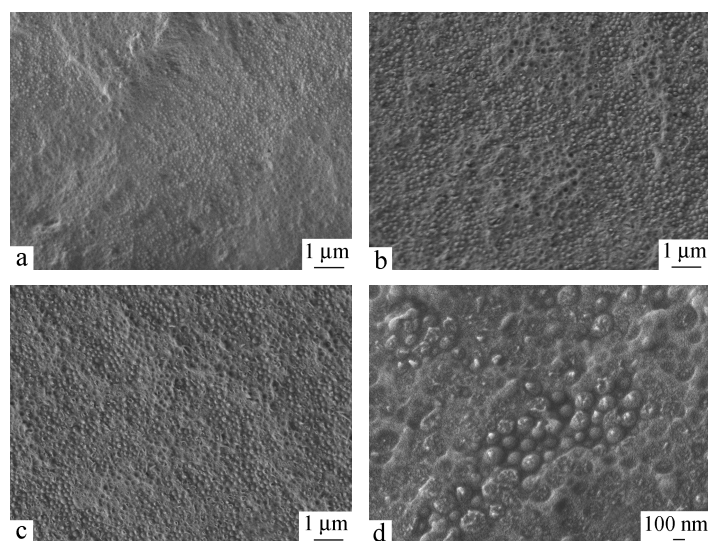


Fig. 5 FESEM images of the cryo-fractured surfaces of POE/PS blend pellets with different PS contents at the central positions: (a) 5.1%, (b) 24.8% and (c, d) 51.6%

Table 1 M_w and M_w/M_n of PS, particle sizes in POE/PS blend pellets and in melt-processed rods

St/POE (%)	PS content (%)	$M_w \times 10^{-5}$ (g/mol)	M_w/M_n	Particle sizes at center (nm)	Particle sizes at mid-depth (nm)	Particle sizes in rods (nm)
25.0	5.1	1.4	1.84	107 ± 17	101 ± 20	164 ± 45
37.5	15.7	1.0	2.09	131 ± 25	124 ± 31	237 ± 91
50.0	24.8	1.0	2.17	149 ± 33	150 ± 36	261 ± 111
62.5	37.0	1.0	2.23	167 ± 30	162 ± 29	341 ± 183
75.0	51.6	0.9	2.30	191 ± 32	195 ± 36	395 ± 188

not pure PS, but complex aggregates composed of both PS and POE. The formation of such complex particles may be due to the occurrence of PS grafting onto POE chains. The percentage of grafting is 4.8%, as measured by FTIR after isolation of POE/POE-*g*-PS mixture by dissolving the blend pellets in hot xylene and precipitating into ethyl acetate.

Comparing the POE/PS blend pellets with the PP/PS blend pellets having a similar PS content (~25%) prepared by diffusion and subsequent polymerization of styrene in polymer pellets through one-pot procedure, the particle sizes are similar while the difference is whether there is a diametrical particle size distribution. In our previous work on PP/PS blend pellets, the polymerization-induced styrene diffusion that made styrene enriched at about 200 μm distance to the pellet edge due to the structural hierarchy of *i*PP pellets was identified to be the main reason for the uneven diametrical particle size distribution. The POE pellets are 100% amorphous at 90 $^{\circ}\text{C}$ and there is not any structural hierarchy inside POE pellets, so styrene can diffuse homogeneously to the regions where styrene is polymerizing inside the pellets. This comparison allows us to conclude that the existence of the crystalline regions is not prerequisite for forming fine dispersed phase.

Table 1 lists the weight-average molecular weights (M_w) and molar-mass dispersity (M_w/M_n) data of PS extracted from the POE/PS blend pellets. The M_w is all around a hundred thousand with the M_w/M_n around 2, revealing that BPO/styrene ratio inside the pellets does not vary much. The M_w is in the same order of magnitude as that of PS in PP/PS quasi-nanoblend pellets synthesized previously^[14]. The almost constant molecular weights of PS indicate that the particle size in the blend pellet is only related to St/POE ratio.

Stability of Phase Morphology of POE/PS Blend Pellets

To study the stability of phase morphology of POE/PS blend pellets, the pellets (PS content = 51.6%) were annealed at three different temperatures (120, 150 and 180 $^{\circ}\text{C}$) for 30 min. As shown in Fig. 6, the particle size has almost unchanged, but the particles tend to get closer at higher temperature. As reported in the literature^[30], physical POE/PS blends have a quick growth of droplet size during annealing, while the variation of droplet size in reactive POE/PS blend is rather limited; the presence of POE-*g*-PS copolymer, which exists as micelles to slow down the approaching velocity and at interface to extend the drainage time, suppresses coarsening. In this work, the morphology stabilization can also be attributed to the existence of POE-*g*-PS graft copolymer (4.8%).

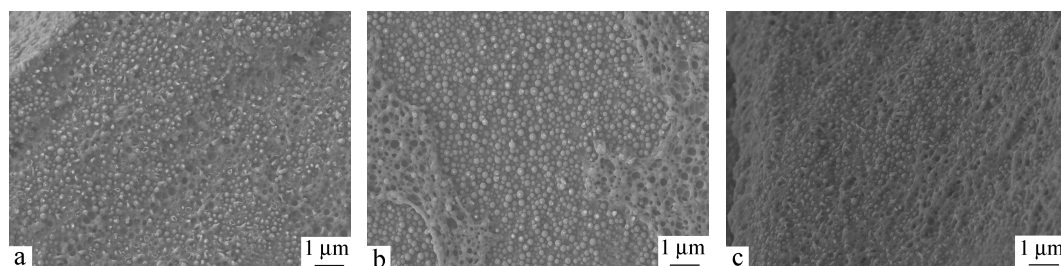


Fig. 6 FESEM images of the cryo-fractured surfaces of POE/PS blend pellets (PS contents = 51.6%) annealed at different temperatures for 30 min: (a) 120 $^{\circ}\text{C}$, (b) 150 $^{\circ}\text{C}$ and (c) 180 $^{\circ}\text{C}$

Morphology of the Melt-extruded Rods

Injection molding of the POE/PS blend pellets was not attempted because big scale production of POE/PS blend pellets is not straightforward with ordinary laboratory glassware due to the low POE/water ratio used to avoid the coalescence of the pellets at 90 $^{\circ}\text{C}$, although the procedure can scale up. The POE/PS blend pellets were processed by melt flow indexer instead to mimic ram-injection molding. The morphology of the melt-extruded rods was investigated by FESEM, and the micrographs of the cryo-fractured surfaces are shown in Fig. 7. Typical sea-island structure is observed, and the particle size distribution is of larger extent than that in the corresponding pellets. For samples having high PS contents, the particle size distribution is more obvious: the smaller particles are supposed to be those retained from the pellets, while the bigger particles can be up to 1 μm and are resulted from particle coalescence during melt processing (Fig. 7c). For rods with PS contents of 24.8% and 51.6%, only few particles are observed as spheres, for most of them are broken, suggesting strong interfacial

adhesion. Small spherical particles of a size of about 30 nm are clearly shown in the particles (Fig. 7d), being in agreement with those observed in POE/PS pellets with a PS content of 51.6% shown in Fig. 5(d).

The average particle sizes for all the samples are almost doubled compared to those in the corresponding pellets due to the occurrence of particle coalescence. Even so, they are still much smaller than those in the conventional POE/PS blends with similar compositions, and even smaller than those in the melt-mixed POE/PS/SEBS blends where SEBS plays the role of compatibilizer^[25]. This shows the advantage of the current method.

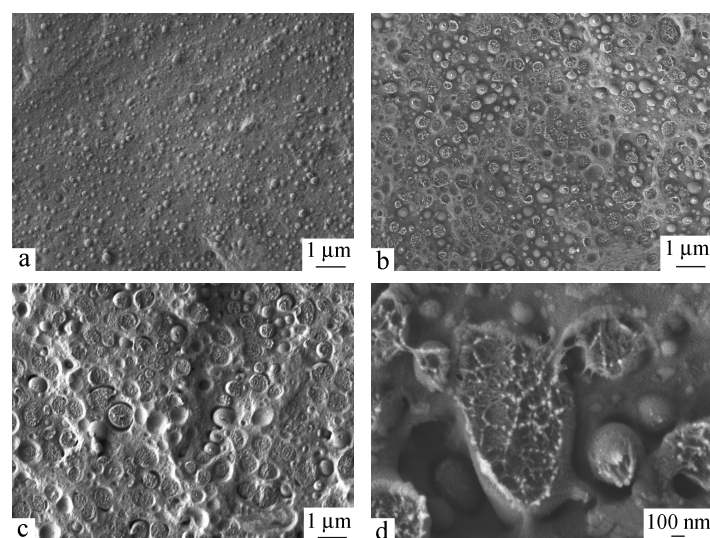


Fig. 7 FESEM images of the cryo-fractured surfaces of the melt-extruded rods with different PS contents: (a) 5.1%, (b) 24.8% and (c, d) 51.6%

Mechanical Properties of the Melt-extruded Rods

The mechanical properties of the melt-extruded rods were evaluated by uniaxial tensile testing, and the results are listed in Table 2. The tensile modulus, tensile strength and elongation at break of POE/PS blends with low PS contents (0.2% and 5.1%) have almost unchanged, revealing that a small incorporation of PS does not significantly affect the mechanical properties of POE due to the formation of nano-sized particles. When PS content increases to 15.7% and 24.8%, tensile modulus increases significantly, tensile strength increases slightly and elongation at break has no change, showing significant reinforcement effect without losing ductility. When PS content increases further to 37.0% and 51.6%, tensile modulus further increases at the expense of slight loss of ductility. The mechanical properties of POE/PS blends reported in this work are much better than those of the blends prepared by conventional melt-mixing where the lowering of both tensile strength and elongation at break occurred^[25]. This can be attributed to the small size and complex nature of the dispersed phase and the occurrence of PS grafting, which ensure good interfacial adhesion. Although PS is brittle, good ductility is maintained for POE/PS blends, similar to the case of PP/PS blends because the small particles do not act as stress concentrators^[22].

Table 2 Mechanical property data of POE/PS blend rods

St/POE (%)	PS content (%)	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Neat POE	0	4.1 ± 0.5	8.9 ± 0.8	1030 ± 100
12.5	0.2	4.7 ± 0.2	9.8 ± 0.8	1146 ± 106
25.0	5.1	4.5 ± 0.1	9.8 ± 1.2	1078 ± 26
37.5	15.7	6.2 ± 0.5	10.5 ± 1.1	1054 ± 141
50.0	24.8	7.4 ± 0.7	10.8 ± 1.6	1018 ± 165
62.5	37.0	10.5 ± 0.5	10.6 ± 0.9	850 ± 98
75.0	51.6	13.7 ± 0.8	11.6 ± 1.2	755 ± 154

CONCLUSIONS

POE/PS blend pellets with fine particle sizes and suitable for direct use in low-shear processing can be prepared by diffusion and subsequent polymerization of styrene in amorphous POE pellets through a one-pot procedure. The POE/PS pellets possess a number of distinguishing features compared to the previously reported PP/PS blend pellets obtained by similar type of procedure. Firstly, the maximum PS content is much greater. The PS content can be as high as 51.6% with a styrene/POE ratio of 75%, but is still non-saturated; however, it is limited to 25% when *i*PP pellets were used as the matrices with styrene/PP ratios more than 30%. Secondly, styrene tends to diffuse into the central regions of POE pellets, while only under suitable conditions it can reach the center of *i*PP pellets. In the styrene-inclusive regions, the diametrical PS distribution is homogeneous in POE pellets and inhomogeneous in *i*PP pellets where enrichment at about 200 μm distance to the pellet edge was observed. Thirdly, the diametrical distribution of particle size is homogeneous in POE pellets and inhomogeneous in *i*PP pellets where big-size particles appeared at about 200 μm distance to the pellet edge.

All the above-mentioned differences between the two types of blend pellets can be attributed to the difference in pellet morphology: POE has a low degree of crystallinity at room temperature and is completely amorphous at 90 °C, while *i*PP is semicrystalline with a much higher degree of crystallinity. Without efficient impediment of the crystal lamellae in POE pellets, styrene diffuses easily in POE pellets.

The common features of POE/PS and PP/PS blend pellets prepared by the method of diffusion and subsequent polymerization of styrene in polymer pellets include fine particle size, low degree of coalescence during melt-processing and improved mechanical properties due to the fine particle size.

This work shows that the method of diffusion and subsequent polymerization of a monomer in polymer pellets is a versatile approach for preparing polymer blends having fine particle sizes and improved mechanical properties, not only viable for semicrystalline polymer matrices but also suitable for amorphous polymer matrices.

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