Research Article

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Fabrication of LDPE/PS interpolymer resin particles through a swelling suspension polymerization approach

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Abstract: A facile method to prepare low-density polyethylene (LDPE)/polystyrene (PS) interpolymer resin particles by swelling suspension polymerization without addition of extra swelling agent was developed. The polymerization temperature, polymerization time, and initiator concentration were investigated. Fourier transform infrared spectroscopy analysis confirmed that the LDPE/PS interpolymer resin particles were successfully prepared and a small amount of PS-g-LDPE existed in the resin. Scanning electron microscopy revealed that PS was uniformly distributed in the LDPE matrix, indicating excellent compatibility between PS and LDPE. The mechanical properties of LDPE/PS interpolymer resin were intermediate between PS and LDPE polymers.

Keywords: interpolymer resin, swelling suspension polymerization, compatibility

1 Introduction

Polystyrene (PS) and polyethylene (PE) are the most widely used polymeric materials, which can be applied

in various fields including packaging, electronics, construction, automotive, home appliance, instrument, and daily necessity (1–3). PS has many significant properties such as excellent shaping and processing ability, good chemical resistance, and low hygroscopic property (4–6). However, neat PS has several defects such as brittleness, poor impact resistance, low solvent resistance, and low heat distortion temperature due to the rigid benzene ring structure in the molecular chain (7), which limit its utilization. PE is a good toughening material, especially low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) (1,8). But, the modulus of PE is low due to the olefin structure in the molecule chain. An effective way to overcome the shortcomings of the two materials is to combine PS with PE. However, as most of other immiscible polymer blends, PE/PS blends form large dispersed phase domain structure with weak interfacial adhesion, thus affecting the mechanical property and other end performances (9). Improvement in the phase dispersion in PE/PS blends plays an important role in enhancing their final properties and expanding the industrial applications (10). The conventional process for the preparation of PE/PS composite was melt blending (11); however, this process often led to severe phase separation. To improve compatibility, Gemini surfactant-modified montmorillonite was prepared and incorporated into the immiscible PE/PS to fabricate composites (12). Grafting copolymerization was an alternative approach to preventing phase separation between polymers.

Supercritical CO₂ could control the phase morphologies of PE/PS composite and influence the mechanical property, creep resistance, and foamability (13,14). Supercritical CO₂ was used as a solvent and a swelling agent to facilitate the distribution of PS in the PE matrix and improve the compatibility of the phase interface. Other swelling agents such as cyclohexane also promote the miscibility of the PE phase and PS phase, but they could influence the final properties of materials as the plasticizer. Many studies prepared high-grafting PE/PS

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blends to improve the compatibility by using catalyst, but specific equipment for reaction and granulation was required. In addition, the viscosity of this system was severely high, leading to instability of the polymerization system (3,15). Previous studies reported that ethylene-styrene interpolymers (ESI) could toughen PS and improve the compatibility of PS and PE or polypropylene (PP) (16–18). However, the catalyst used for the preparation of ESI was expensive. Grafting copolymerization of styrene in a suspension polymerization system was a simple and inexpensive technology (3,7,9). The combination of PS and PE via in situ grafting polymerization to improve the properties of PS/PE blends has attracted much attention. However, only a few studies proposed this process for preparing LDPE/PS interpolymers resin particles in suspension polymerization (2,16).

In this article, a facile method was employed to prepare LDPE/PS interpolymers resin particles via swelling PE with styrene under certain temperature and stirring in suspension polymerization. Instead of using extra ingredients, such as cyclohexane, styrene was utilized as the swelling agent directly. During the polymerization process, methylene blue (MB) was used as a water-phase polymerization inhibitor to restrain the formation of styrene homopolymer. The LDPE/PS interpolymers resin particles were confirmed by Fourier transform infrared spectroscopy (FTIR). Additionally, the morphology and thermal behavior of particles were characterized by scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA), respectively. Moreover, the mechanical properties of LDPE/PS interpolymers resin were evaluated.

2 Experimental

2.1 Materials

Styrene (Sigma-Aldrich, St. Louis, MO, USA) was washed with aqueous sodium hydroxide, dried over anhydrous sodium sulfate, and distilled twice under reduced pressure before polymerization. Benzoyl peroxide (BPO; Sigma-Aldrich Co., Ltd) as an initiator was purified by recrystallization before use. LDPE was provided by Yangzi Petrochemical Co., Ltd, China. Poly(vinyl alcohol) (PVA; degree of polymerization was 1,700; degree of hydrolysis was 88%) and calcium-trihydroxy phosphate (TCP) (diluted to 8 wt% aqueous solution before use) were purchased from Sinopharm Chemical Reagent Co.,

Ltd, China. Xylene, tetrahydrofuran (THF), and MB were supplied by Sinopharm Chemical Reagent Co., Ltd, China. PS (code 383) with M_n of 1.2×10^5 was purchased from Zhenjiang Chimei Chemical Co., Ltd, China.

2.2 Preparation of LDPE/PS interpolymers resin particles

First, defined amounts of LDPE, BPO, St, and TCP were introduced into a 250-mL three-necked round-bottom flask equipped with a mechanical stirrer for swelling. Then, a suitable value of expand ratio (ER) as the best condition of the swelling process was selected. Next, 120 g deionized water and 6 g 8 wt% PVA aqueous solution were added. When a stable suspending medium was formed, the system was heated to 90°C gradually. When the temperature reached 60°C, 0.0001 g MB was added. After the polymerization was completed, diluted HCl was added to remove the tricalcium phosphate on the surface of the particles, and the beads were rinsed off with ethanol and deionized water. The above process was repeated several times to remove the residual styrene. Finally, the beads were separated from the system and dried at 60°C for 24 h. The detailed formulas for the synthesis of LDPE/PS interpolymers resin particles are listed in Table 1.

2.3 Measurements of the ER and monomer conversion ratio

The ER was defined as the weight percent of styrene swelling into LDPE. The ER was calculated according to the following equation:

$$ER = \frac{W_t - W_0}{W_0} \times 100\% \quad (1)$$

where W_t is the weight (g) of LDPE after swelling and W_0 is the weight (g) of LDPE before swelling.

Monomer conversion ratio was defined as the weight ratio of PS contained by LDPE particles after polymerization to St diffused into pellets, which was measured by the gravimetric method. The weight gain was regarded as the St diffused into pellets, which was polymerized. The weight of PS contained by LDPE particles after polymerization was obtained through drying the particles to remove unreacted St compared with original addition of St.

Table 1: Preparation ingredients of LDPE/PS interpolymer resin particles

Sample	LDPE (g)	St (g)	BPO (g)	H ₂ O (g)	PVA (g)	TCP (g)	MB (g)	PT (°C)	T (h)
1	12	16	0.1162	120	6	0.05	0.0001	75	9
2	12	16	0.1169	120	6	0.05	0.0001	80	9
3	12	16	0.1162	120	6	0.05	0.0001	85	9
4	12	16	0.1057	120	6	0.05	0.0001	90	9
5	12	16	0.1045	120	6	0.05	0.0001	95	9
6	12	16	0.1620	120	6	0.05	0.0001	90	6
7	12	16	0.1622	120	6	0.05	0.0001	90	7
8	12	16	0.1619	120	6	0.05	0.0001	90	8
9	12	16	0.1621	120	6	0.05	0.0001	90	9
10	12	16	0.1620	120	6	0.05	0.0001	90	10
11	12	16	0.0483	120	6	0.05	0.0001	90	9
12	12	16	0.0817	120	6	0.05	0.0001	90	9
13	12	16	0.1629	120	6	0.05	0.0001	90	9
14	12	16	0.2395	120	6	0.05	0.0001	90	9
15	12	16	0.3245	120	6	0.05	0.0001	90	9

PVA – poly(vinyl alcohol); TCP – calcium-trihydroxy phosphate; MB – methylene blue; PT – polymerization temperature; T – polymerization time.

2.4 Characterization techniques

2.4.1 FTIR

The FTIR analysis was carried out with an attenuated total reflection FTIR machine (Nicole 6700; Thermo-fisher Technology Co. Ltd, USA). The analysis was performed by measuring transmittance versus wave numbers in the range of 4,000–500 cm⁻¹ at room temperature with 16 consecutive scans.

2.4.2 Gel permeation chromatography (GPC)

Pellets were heat-pressed into a thin film and then stirred in THF for 24 h to extract PS. The molecular weights (MWs) and distribution of PS were determined using a GPC apparatus operated using THF as the eluent (1 mL/min) at 25°C and calibrated by means of PS narrow standards.

2.4.3 TGA

All samples were dried overnight before measurement. The TGA curves were recorded on a TGA1100SF machine (Mettler, Switzerland) under nitrogen flow at 50 mL/min and heating at 10°C/min from 50 to 700°C.

2.4.4 Tensile test

The PE, PS, and LDPE/PS interpolymer resin particles were heated slowly to 180°C on an H-X608 tablet

reometer detection instrument (China). For tensile testing, dumbbell-shaped strips (115 × 6 × 1 mm³, $n = 5$) were cut from the composite films and mechanical properties were studied on an Instron 5967 Dual Column Tabletop Testing System at room temperature with a tensile rate of 50 mm/min (Chinese Standard of GB/T1040-1992). Before testing, the samples were kept at room temperature for 24 h to release the stress. Tensile strength and elongation at break were recorded. The values were the average of five tests.

2.4.5 SEM

SEM (S-4800; Hitachi, Japan) was used to investigate the LDPE/PS interpolymer resin particles. Liquid-nitrogen-frozen fractured surfaces of the polymers were dried and sputter-coated with gold prior to examination.

3 Results and discussion

3.1 Swelling temperature and time

Instead of using extra ingredients, styrene was utilized as a swelling agent at the temperature of 30–50°C, while LDPE/PS interpolymer resin particles could be easily formed. The interpolymer included LDPE, PS, and PS-g-PE polymer resins, and PS-g-PE increased the compatibility of LDPE and PS. The solubility parameter (δ) of

styrene and PE was 8.66 and $8.1 \text{ cal}^{1/2} \text{ cm}^{-3/2}$, respectively, according to similar compatible principle and experimental results. It could be concluded that styrene swelled PE, but did not dissolve PE. Figure 1 exhibits the swelling curves of LDPE under different conditions. The weight of LDPE increased with increasing swelling time. When the swelling temperature was below 30°C , the dissolved styrene monomer was less in PE and needed more time to reach the equilibrium. If the temperature reached 50°C , the styrene monomer began to polymerize. Thus, 40°C and 150 min were selected as the best swelling conditions in this study.

Figure 1: Swelling curves of LDPE under different temperatures and times.

3.2 Polymerization temperature and time

Figure 2 depicts the influence of polymerization temperature on the monomer conversion ratio. The conversion ratio increased before 90°C , but dropped thereafter. This was because more styrene monomer and initiator swelled into PE with increasing temperature. And when the temperature exceeded 90°C , the volatilization of styrene was too fast (17,18), resulting in very small amounts of styrene in particles, but the initiator decomposed too fast at high temperature; it could terminate easily between radicals, which consumed part of the free radicals, and thus the conversion ratio reduced. When the polymerization temperature was 90°C , the conversion ratio of styrene reached 70%. Thus, 90°C was selected as the suitable polymerization temperature.

Figure 3 shows the effect of polymerization time on the monomer conversion ratio. The conversion ratio increased before 9 h and then remained constant. It could be explained that the initiator gradually decomposed with

Figure 2: Effect of polymerization temperature on styrene conversion.

Figure 3: Effect of polymerization time on styrene conversion.

increasing temperature, and more free radicals induced monomers to form polymers, but the concentration of free radical decreased with increasing time. So, the polymerization time of 9 h was selected as the optimum time.

3.3 Initiator concentration

Table 2 exhibits the effects of BPO concentration on the MW and MW distribution of PS in LDPE/PS interpolymer resin particles. The MW of the particles decreased with increasing BPO content. The concentration of free radical increased with increasing initiator content, thus triggering more monomers to polymerize (19,20). With

Table 2: Effect of different BPO contents on the MW and MW distribution of PS in LDPE/PS interpolymer resin particles

BPO (%)	PT (°C)	$M_n (\times 10^4)$	$M_w (\times 10^4)$	PDI	Conversion (%)
0.3	90	7.4	16.6	2.25	34.75
0.5	90	5.3	13.7	2.56	52.63
1.0	90	3.4	9.6	2.85	94.50
1.5	90	2.3	5.7	2.46	88.44
2.0	90	1.8	4.2	2.35	85.94

PDI – polydispersity index; PT – polymerization temperature.

increasing free radical concentration, the polymerization rate also increased. However, when the initiator concentration was more than 1%, increasing collision between free radicals appeared, resulting in the termination of free radicals (21,22). Thus, the MW decreased. On the other hand, high concentration of initiator could cause PE cross-linking. Therefore, 1 wt% St was chosen as the optimum amount of initiator.

3.4 Characterization of LDPE/PS interpolymer resin particles

The suspension polymerization of styrene was a free radical polymerization process. BPO decomposed and produced free radicals that induced polymerization. The mechanism of polymerization is shown in Scheme 1. The

FTIR spectra of LDPE, PS, and LDPE/PS interpolymer particle residue after Soxhlet extraction by xylene were determined. As shown in Figure 4, the peaks at 694, 760, and 3,030 cm⁻¹ were assigned to the C–H stretching vibration of benzene ring. Compared with the FTIR spectrum of neat PE, two additional weak absorption peaks at 1,600 and 1,500 cm⁻¹ were observed in PE/PS interpolymer particle residue, which corresponded to the aromatic C–C stretching (23). This revealed the existence of PS-g-PE. All the above data confirmed that LDPE/PS interpolymer resin particles were successfully prepared.

3.5 Morphology

Figure 5 represents the cross-sectional SEM images of the LDPE/PS interpolymer resin particles before and

Scheme 1: Mechanism of preparation of LDPE/PS interpolymer resin particles.

Figure 4: FTIR spectra of LDPE, PS, and LDPE/PS interpolymer resin particles.

after etching PS component by THF. The fracture surface of LDPE/PS interpolymer resin particles is rough in the red frame of Figure 5a and a-1, which indicates the better compatibility of LDPE and PS due to the presence of LDPE-g-PS. As shown in Figure 5b and b-1, PS was dispersed in the PE matrix and formed co-continuous or interlocking structure (24), which greatly improved the compatibility between LDPE and PS.

3.6 Thermal properties

The thermal behaviors of PS, LDPE, and LDPE/PS interpolymer resin in nitrogen atmosphere were investigated by TGA, and the results are represented in Figure 6a. The corresponding differential thermal gravity (DTG) curves are presented in Figure 6b. The initial degradation temperatures of neat PS, LDPE, and LDPE/PS interpolymer resins were 305.5, 402.1, and 378.5°C, respectively. As shown in Figure 6b, the $T_{\max}$ value of LDPE/PS interpolymer resin

Figure 5: Cross-sectional SEM images of LDPE/PS interpolymer resin particles before and after etching PS component by THF: (a) before etching and (b) after etching.

Figure 6: Thermal behavior of PS, LDPE, and LDPE/PS interpolymer resin particles in nitrogen atmosphere: (a) TGA curves and (b) DTG curves.

Table 3: Mechanical properties of PS, LDPE, and LDPE/PS interpolymer resin particles

Sample	TS (MPa)	BE (%)
PS	18.79	6.2
LDPE	13.62	400
LDPE/PS interpolymer	15.10	193

The content of PS in LDPE/PS interpolymer is 55%.
TS – tensile strength; BE – elongation at break.

particles was 438.6°C, which shifted to higher temperature compared with neat PS.

3.7 Mechanical properties

The mechanical properties of the LDPE, PS, and LDPE/PS interpolymer resin are shown in Table 3. The tensile strength

of LDPE/PS interpolymer resin was 15.10 MPa, while the elongation at break of the resin was 193%. The tensile strength of LDPE/PS interpolymer resin increased as compared to PE; however, the elongation at break considerably decreased. Due to the presence of LDPE-g-PS, the compatibility of PE and PS improved, and the composites exhibited higher tensile strength compared to LDPE, indicating the reinforcement effect of rigid PS particles.

4 Conclusions

The PS was successfully incorporated into LDPE matrices through swelling suspension polymerization, providing means for preparation of the LDPE/PS interpolymer resin particles. The polymerization temperature of 90°C, polymerization time of 9 h, and BPO concentration of 1% (weight percent of St) were the optimal conditions for polymerization. The cross-sectional SEM analysis indicated that PS was dispersed in LDPE and co-continuous or interlocking structure was formed. In addition, FTIR analysis demonstrated that PS-g-PE existed in the LDPE matrix. The mechanical properties of LDPE/PS interpolymer resin were intermediate between PS and LDPE, which expands the application of the two polymers.

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