

Preparation and characterization of grafting styrene onto LLDPE by cyclohexane compatibilization in suspension polymerization

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ABSTRACT: A novel method of grafting styrene onto linear low-density polyethylene (LLDPE) by suspension polymerization was systematically evaluated. Cyclohexane as a compatibilizer was introduced to swell and activate the surface of LLDPE molecular chain for amplifying the contact point of styrene monomer with LLDPE. A series of copolymer of grafting polystyrene (PS) onto LLDPE, known as LLDPE-g-PS, were prepared with different ratios of cyclohexane/styrene monomer and various LLDPE dosages. FTIR and ¹H NMR techniques both confirmed successful PS grafting onto the LLDPE chains. In addition, SEM images of LLDPE-g-PS particles showed that the cross-section morphology becomes smooth and dense with suitable cyclohexane dosages, indicating a better compatibility between LLDPE and PS. The highest grafting efficiency was 28.4% at 10 mL/g cyclohexane and styrene monomer when 8% LLDPE was added. In these conditions, the LLDPE-g-PS elongation at break increased by about 30 times compared with PS. Moreover, thermal gravimetric analysis (TGA) demonstrated that LLDPE-g-PS possesses much higher thermal stability than pure PS. Therefore, the optimal amount of cyclohexane as compatibilizer could increase the grafting efficiency and improve the toughness of PS. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41671.

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INTRODUCTION

Polystyrene (PS) is one of the most widely used thermoplastics, which include conductive,¹ food packaging,² biotechnology,³ antibacterial,⁴ positive temperature coefficient,^{5–7} and chemical gas sensor⁸ materials. Unfortunately, neat PS is easily brittle and has poor impact resistance because of its rigid benzene ring structure in the macromolecular side chains. However, polyethylene (PE) is a good material toughener because of its linear main chains,^{9,10} especially low-density polyethylene (LLDPE). Thus, combination of the two materials is an effective way to improve the flexibility and elongation of PS materials. Melt blending is the conventional process used for LLDPE and PS; however, the large difference in molten parameters between both products makes the simple blends to result in severe phase separation. It is widely admitted that grafting copolymerization of styrene^{11–14} in a suspension polymerization system possesses a simple and low cost technology. So, grafting copolymerization gradually becomes an outstanding approach for overcoming phase separation between polymers.^{15–17} Kim *et al.*¹⁸ have designed a novel method for PE-g-PS copolymer reactive extrusion and conducted the corresponding study. Gao *et al.*¹⁹ have

prepared blends of LLDPE and PS through free radical bulk copolymerization, using aluminum chloride (AlCl₃) as a catalyst. High-grafting blends were achieved via this method, but specific equipment for reaction and granulation was required. In addition, the viscosity of this system is severely high, which results in the instability of the polymerization system. Thus, the combination of PS and PE via *in situ* grafting polymerization holds the promise of improving the properties of the two materials. However, reports proposing this process for preparing LLDPE-g-PS beads via compatibilization process in suspension polymerization are scarce.

In this article, a novel and facile method was employed in preparing LLDPE-g-PS copolymer via the compatibilization of cyclohexane in suspension polymerization. This study aimed to improve the toughness of PS materials by selecting LLDPE as a flexibilizer. The graft polymer of styrene with LLDPE was confirmed by nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectra. Besides, the morphology and thermal behavior of copolymers were characterized by scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA), respectively. Moreover, the mechanical tests

Table I. Preparation Ingredients of LLDPE-g-PS

Sample	LLDPE (g)	BPO (g)	St (mL)	Cyclohexane (mL)	H ₂ O (mL)	PVA (mL)	Na ₂ SO ₄ (g)	TCP (g)	SDBS (mL)	PT (°C)
1	0	0.12	10	0	120	5	0.15	0.5	5	90
2	0.5	0.12	10	8	120	5	0.15	0.5	5	75
3	0.5	0.12	10	8	120	5	0.15	0.5	5	80
4	0.5	0.12	10	8	120	5	0.15	0.5	5	85
5	0.5	0.12	10	8	120	5	0.15	0.5	5	90
6	0.5	0.12	10	8	120	5	0.15	0.5	5	93
7	0.8	0.12	10	8	120	5	0.15	0.5	5	75
8	0.8	0.12	10	8	120	5	0.15	0.5	5	80
9	0.8	0.12	10	8	120	5	0.15	0.5	5	85
10	0.8	0.12	10	8	120	5	0.15	0.5	5	90
11	0.8	0.12	10	8	120	5	0.15	0.5	5	93
12	0.8	0.12	10	0	120	5	0.15	0.5	5	90
13	0.8	0.12	10	2	120	5	0.15	0.5	5	90
14	0.8	0.12	10	4	120	5	0.15	0.5	5	90
15	0.8	0.12	10	6	120	5	0.15	0.5	5	90
16	0.8	0.12	10	10	120	5	0.15	0.5	5	90
17	0.8	0.12	10	12	120	5	0.15	0.5	5	90

PT: polymerization time.

demonstrated overtly enhanced toughness for LLDPE-g-PS compared with neat PS. Finally, the grafting efficiency and granulation rate of suspension copolymerization were systematically investigated.

EXPERIMENTAL

Materials

Styrene (Sigma-Aldrich, St. Louis, MO) was washed with aqueous alkali, dried over barium oxide, and distilled twice under reduced pressure before polymerization. Benzoyl peroxide (BPO, Sigma-Aldrich) as initiator was purified by recrystallization before use. LLDPE powder (0.2 mm) was provided by Longshan Chemical Plant (China). Poly(vinyl alcohol) (PVA) (degree of polymerization was 1750 ± 50 , degree of hydrolysis was 88%) and sodium dodecylbenzene sulfonate (SDBS) purchased from Sinopharm Chemical Reagent, were diluted, respectively, to 5 and 0.02 wt % aqueous solution before experiments. Calcium-trihydroxy phosphate (TCP) and sodium sulfate (Na₂SO₄) were used as regulator for system stabilization. Cyclohexane and xylene (from Sigma-Aldrich, LLC)

were dried+ through distillation before use. The water used in this work was distilled and submitted to deionization.

Preparation of LLDPE-g-PS Copolymer

The suspension polymerization of styrene (St) in the presence of LLDPE was carried out by using BPO as an oil-soluble initiator, with cyclohexane acting as a swelling agent in the system. Na₂SO₄ and TCP were used as primary and secondary dispersants, respectively. Besides, SDBS and PVA aqueous solution were employed to reduce the surface tension of the suspending medium and keep the water/oil (water/styrene) system stable.^{20–22} First, defined amounts of LLDPE, BPO, St and cyclohexane were successively introduced into a 250 mL four-necked round-bottom flask equipped with a mechanical stirrer, a condenser and drop funnel. Then, the mixture was ultrasonicated for 30 min in order to complete the swelling process of LLDPE by cyclohexane and St monomer. Then, 100 mL deionized water, 0.14 g TCP, 0.30 g Na₂SO₄, 10 mL 0.02 wt % SDBS and 10 mL 5 wt % PVA aqueous solution were added successively. The mixture was stirred at 350 rpm for 15 min at 50°C in a water bath. When the stable suspending medium was formed,

Table II. Solubility Parameter of Common Solvents and the Polymer

Sample	water	tetrahydrofuran	xylene	Acetone	cyclohexane	PS	LLDPE
σ^a	24.4	9.2	8.8	9.7	8.3	8.6	7.9
PS	No ^b	D ^c	D	D	D	-	-
LLDPE	No	No	S ^d	No	S	-	-

^a σ was solubility parameter, which represented the interaction parameter between polymer and solvent.

^b Neither dissolution nor swell in PS or LLDPE.

^c Dissolution.

^d Swell.

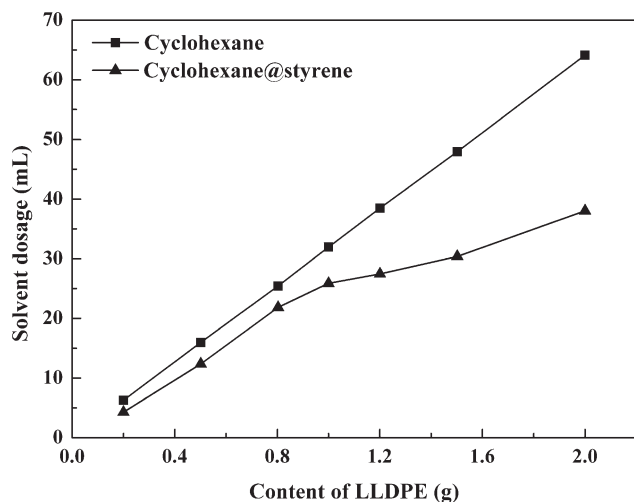


Figure 1. Dissolution curve of LLDPE in different solvents.

the system was heated to 90°C gradually. During the polymerization, TCP and Na₂SO₄ were supplemented in order to stabilize the polymerization system. The polymerization proceeded under stirring until the expected beads were achieved. Finally, the beads were separated from the system and dried at 60°C for 24 h. The detailed recipes for the synthesis of LLDPE-*g*-PS copolymer are listed in Table I.

Measuring Grafting Efficiency and Degree of Grafting

The bead-shaped particles of copolymer obtained in suspension polymerization were accurately weighed with a precision electronic balance and pulverized. The copolymer powder was wrapped with filter paper and placed in a Soxhlet extractor after labeling. The excess xylene was added into 250 mL round bottom flask and the system heated to 110°C for 30 min. The extraction residue was dried at 50°C for 24 h in a vacuum to remove the solvent. Finally, the mixture of LLDPE-*g*-PS/LLDPE was obtained after drying. According to previous studies,^{23,24} the grafting efficiency (GE) was calculated as follows.

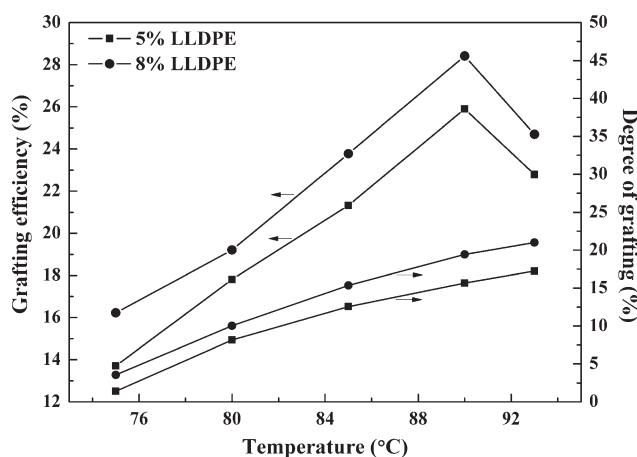


Figure 2. Effect of polymerization temperature on the efficiency and degree of grafting.

$$GE \% = (W_g - W_{LLDPE}) / W_{PS} \times 100 \quad (1)$$

Where W_g is the weight of polymer ($W_{LLDPE} + LLDPE-g-PS$) purified by Soxhlet extraction, W_{PS} the weight of styrene monomer, and W_{LLDPE} the weight of LLDPE raw material.

The degree of grafting (GD) was obtained by analyzing the FTIR spectra of a series of samples with different LLDPE/PS weight ratios.²⁵ The peaks at 1527–1404 cm⁻¹ (A_1) and 702–678 cm⁻¹ (A_2) were analyzed. The 1527–1404 cm⁻¹ peak region was due to overlapping absorption of the -CH₂ group on PE and the benzene group on PS. The 702–678 cm⁻¹ peak region was attributed to the benzene group on PS. Ratios of A_1 to A_2 for LLDPE-*g*-PS were plotted against grafting samples. By linear fit, the degree of grafting was calculated by the calibration eq. (2)

$$GD\% = 3.168 / (A_1/A_2 - 1.579) \times 100 \quad (2)$$

Scanning Electron Microscope (SEM)

The copolymer particles were broken at low (liquid nitrogen) temperature to ensure a brittle fracture. The crispy section was labeled and sprayed with gold to release the polymer surface charge for increased contrast. The cross-section morphology of the copolymer was imaged on a SHIMADZU SSX-550 scanning electron microscope (SEM) to analyze the compatibility of LLDPE and PS. The accelerated voltage was 15 KV.

Fourier Transform Infrared (FTIR) Spectroscopy

The absorption spectra of copolymer particles between 4000 and 400 cm⁻¹ were recorded with a FTIR-8400S SHIMADZU spectrometer at a resolution of 2 cm⁻¹.

Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H NMR spectra were obtained on an FT-80A NMR (400 MHz) using d₆-DMSO as solvent and internal standard.

Thermal Gravimetric Analysis (TGA)

All samples were dried overnight before measurement. The TGA curves were recorded on a Pyris Diamond TG/DTA (Perkin Elmer) under nitrogen flow at 50 mL/min and heating at 10°C/min from 50°C to 850°C. Sample weights were 5–10 mg.

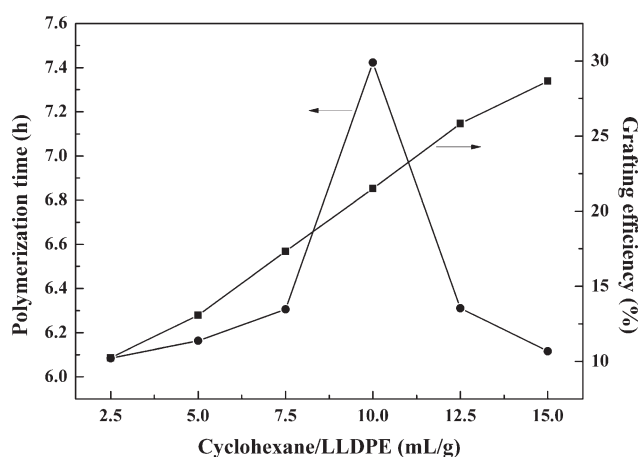


Figure 3. Effect of cyclohexane/LLDPE ratio on polymerization time and grafting efficiency.

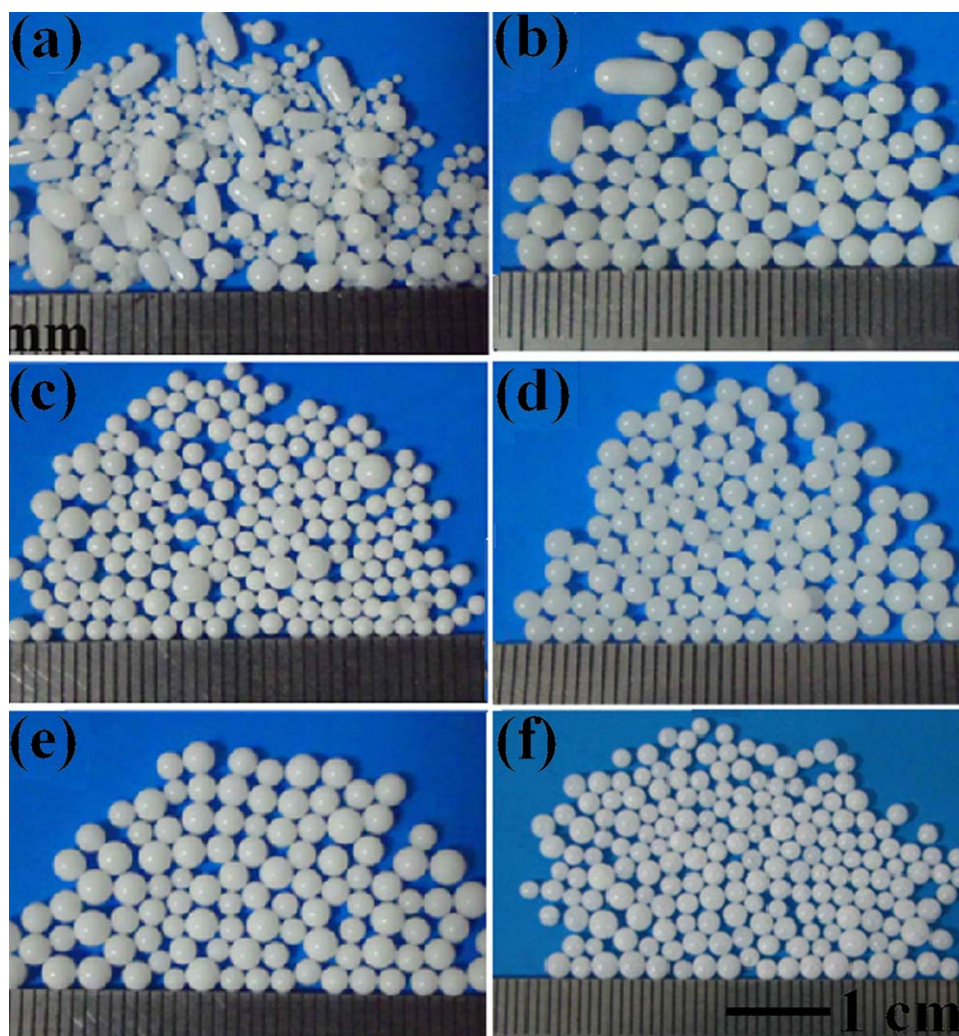


Figure 4. Morphology of polymer particles (LLDPE/St = 0.8 g/10 g) at different cyclohexane/LLDPE ratio, (a) 0 mL/g, (b) 2.5 mL/g, (c) 5 mL/g, (d) 7.5 mL/g, (e) 10.0 mL/g, (f) 12.5 mL/g. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Tensile Performance Tests

The LLDPE-g-PS and LLDPE polymer particles were heated slowly to 140°C on an H-X608 tablet rheometer detection instrument (China) and templates of $80 \times 40 \times 1 \text{ mm}^3$ were made. Tensile properties were assessed by using the HS-30-type testing machine (China). The testing standard was GB/T1040-1992.

RESULTS AND DISCUSSION

Selection of the Compatibilizer

How to increase the compatibility of PS and PE has been a challenge for affecting the preparation of PE-g-PS. In this work, a compatibilizer was used to swell and etch the surface of LLDPE's molecular chain, which increased the contact between LLDPE and the styrene monomer. Precisely, this provided more grafting points to increase the compatibility of LLDPE and PS and improve the toughness of PS. The solubility parameter (σ) of common solvents and the polymer material as well as dissolving or swelling conditions of LLDPE and PS are shown in Table II. According to similar compatible principle and experimental results, xylene and cyclohexane could swell LLDPE.

Owing to xylene's high boiling point and toxicity, cyclohexane with a low-boiling point was selected as compatibilizer.

Figure 1 shows the dissolution curve of LLDPE in cyclohexane and the cyclohexane and styrene mixture. Styrene was used at 10 g in all experiments. As shown in Figure 1, the solubility of LLDPE in cyclohexane was 1 g/33 mL, whereas this value was 1 g/25 mL in the cyclohexane and styrene mixture. This indicated that LLDPE has better dissolution effect in the styrene and cyclohexane mixture because of the swelling of styrene monomers to LLDPE.

Primary Factors

Figure 2 depicts the influence of polymerization temperature on the efficiency and degree of LLDPE-g-PS grafting. The grafting efficiency in the 5% and 8% LLDPE reaction systems increased before 90°C, but dropped thereafter. This was due to the competitive relation between grafting and homopolymerization reaction, which persisted during the reaction process. When the temperature exceeded 90°C (temperature of PS polymerization), the styrene homopolymerization reaction was dominant in the system, resulting in lower grafting efficiency. When the

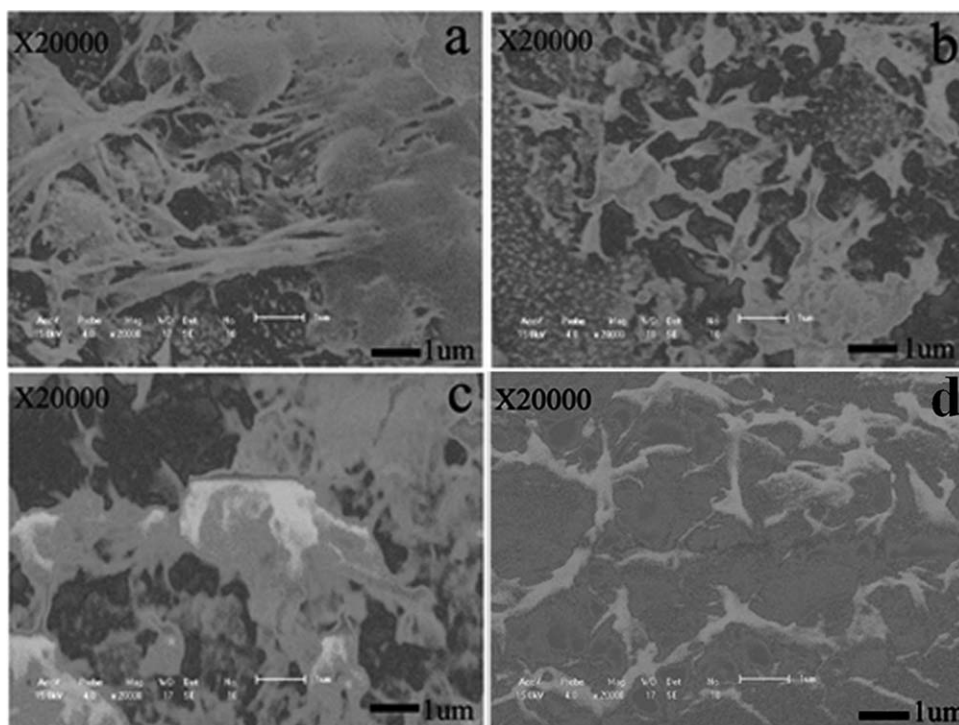


Figure 5. SEM images of cross-section morphology of the graft copolymer using different cyclohexane/LLDPE ratios, (a) 2.5 mL/g, (b) 5 mL/g, (c) 7.5 mL/g, (d) 10 mL/g.

polymerization temperature was 90°C, the grafting efficiency for the 5% and 8% LLDPE systems were 25.1% and 28.4%, respectively. The degree of grafting slowly increased with the polymerization temperature. The degree of grafting with 5% and 8% LLDPE at 90°C were 15.67% and 19.44%, respectively.

Figure 3 shows the effect of cyclohexane/LLDPE ratio and polymerization time on grafting efficiency. In this article, the LLDPE-*g*-PS polymerization time elapsed from charging the styrene monomer and BPO initiator to achieving the expected

composite beads. As seen in Figure 3, the suitable volume of cyclohexane promoted grafting efficiency. Indeed, the grafting efficiency of products were rapidly increased from 9.5% to 25.9% when the cyclohexane/LLDPE ratio changed from 2.5 to 10.0 mL/g. However, the grafting efficiency decreased at cyclohexane/LLDPE ratios over 10.0 mL/g. This phenomenon could be explained by the reduced colliding chance between LLDPE and the styrene monomer due to excess cyclohexane. Meanwhile, the polymerization time was extended with increased cyclohexane/LLDPE volume. This was because cyclohexane

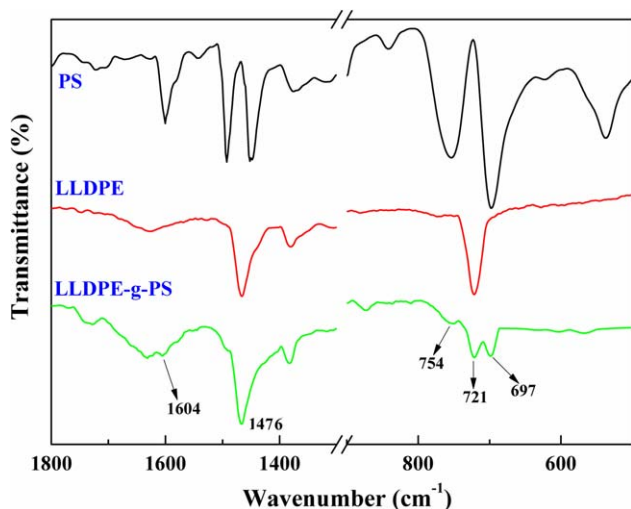


Figure 6. FTIR spectra of PS, LLDPE and LLDPE-*g*-PS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

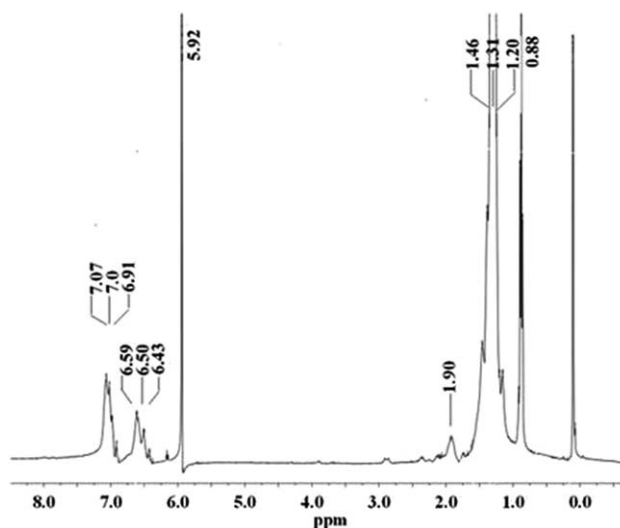
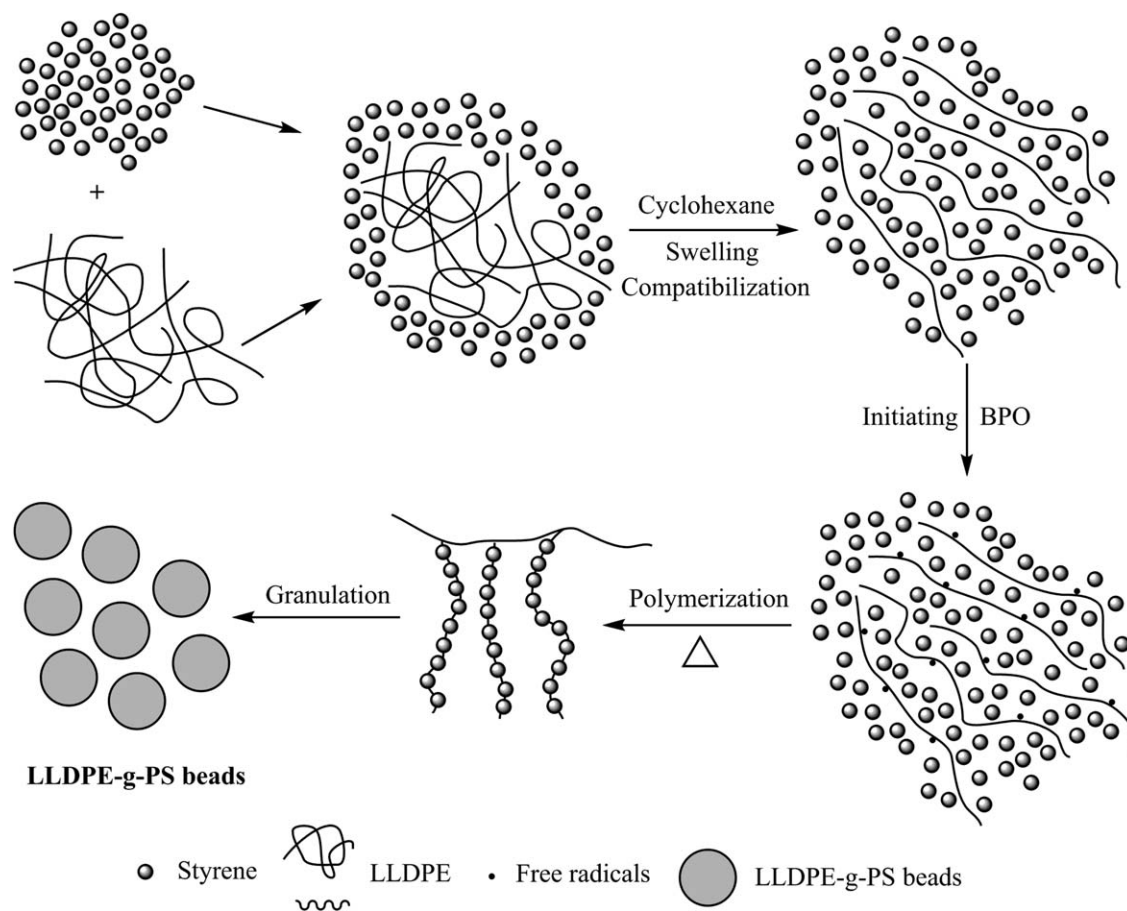


Figure 7. $^1\text{H-NMR}$ spectrum of LLDPE-*g*-PS copolymer.



Scheme 1. Mechanism of graft copolymerization in presence of cyclohexane.

could swell copolymer particles during reaction, which extended the hardening time of particles.

Optical and SEM Images of LLDPE-g-PS Beads

Figure 4 shows the morphology of LLDPE-g-PS (8% LLDPE) polymer particles in different cyclohexane volumes. As shown

in Figure 4, the polymer particles were irregular with rod-like particles. This phenomenon was improved with increased cyclohexane volume, and the polymer particles started to become well-distributed after 7.5 mL/g of cyclohexane. In view of grafting efficiency, the best ratio of cyclohexane/LLDPE was 10 mL/g.

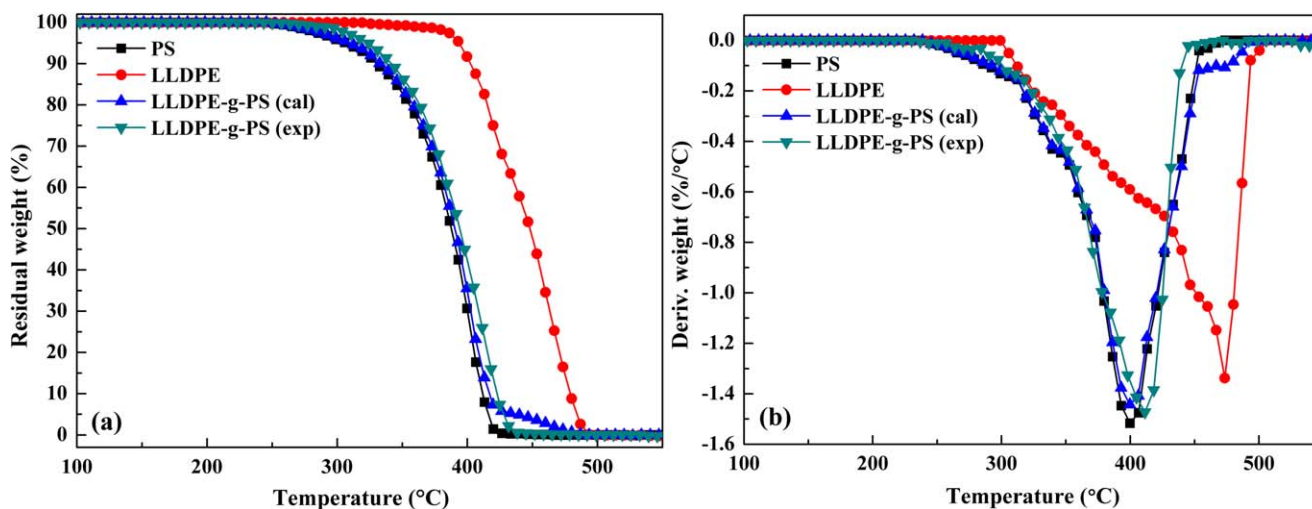


Figure 8. Thermal behavior of PS, LLDPE and LLDPE-g-PS in nitrogen atmosphere, (a) TGA curves, (b) DTG curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. TGA Data of PS, LLDPE, and LLDPE-g-PS in Nitrogen Atmosphere

Sample code	T_{on} (°C)	T_{max} (°C)	R_{max} (%/°C)
PS	305.7	399.8	-1.52
LLDPE	393.9	473.7	-1.34
LLDPE-g-PS (cal) ^a	309.8	400.5	-1.44
LLDPE-g-PS (exp) ^b	324.1	411.7	-1.47

^aCalculated TGA sample, data calculated by adding the data of the two components.

^bThe content of LLDPE in St is 8 wt % in the preparation process of LLDPE-g-PS.

Figure 5 represents the SEM images of cross-section morphology of LLDPE-g-PS particles from different grafting systems. As shown in Figure 5, the fracture surface of LLDPE-g-PS particles becomes smooth with increasing ratios of cyclohexane/LLDPE, which indicated a better compatibility of LLDPE and PS in the suitable volume of cyclohexane. Moreover, the grafting efficiency in 10 mL/g of the cyclohexane/LLDPE system was highest in Figure 3. Therefore, cyclohexane plays a compatibilization role for LLDPE chain in the polymerization process that increased the compatibility of LLDPE and PS as well as the grafting efficiency.

Characterization of LLDPE-g-PS

Figure 6 depicts the FTIR spectra of LLDPE, PS and LLDPE-g-PS (8% LLDPE) after Soxhlet extraction. As shown in Figure 6, a peak for the CH bond of benzene ring vibration was found at 697, 754 and 1476 cm^{-1} and the stretching vibration of a carbon-carbon double bond was found at 1604 cm^{-1} in LLDPE-g-PS. This revealed the existence of PS in the LLDPE-g-PS copolymer. Meanwhile, the characteristic peak of the methyl stretching vibration in LLDPE was found at 721 cm^{-1} . All above data confirmed that PS was successfully grafted to LLDPE.

Figure 7 represents the ¹H-NMR spectrum of LLDPE-g-PS. A solvent (1,1,2,2-tetrachloroethane-d₂) peak was obtained at 5.29 ppm. The three peaks near 7.0 ppm represented the hydrogens in the benzene ring from PS. The three peaks near 6.50 ppm could be explained as follows: when the grafting reaction occurred between styrene and LLDPE, the carbon-carbon double bond in LLDPE was broken and the hydrogen electron cloud

density in the double bond was increased, resulting in chemical displacement toward high magnetic field. The chemical shifts at 1.20–1.3 and 0.88 ppm corresponded to CH₂ and CH₃ protons in LLDPE side chains. The chemical shifts at 1.46 and 2.0 ppm represented CH₂ and CH in PS. The chemical displacement of hydrocarbon in LLDPE and hydrogen in the benzene ring from polystyrene appeared simultaneously in the LLDPE-g-PS copolymer after soxhlet extraction, further indicating that LLDPE was successfully grafted on the PS.

The suspension polymerization of styrene was a free radical polymerization process. BPO as initiator was decomposed and produced a number of free radicals that could induce polymerization. The mechanism of graft copolymerization in presence of cyclohexane is shown in scheme 1. First, LLDPE molecular chain was swelled by cyclohexane and styrene. Then, more initiator styrene monomers entered into the twining LLDPE molecular chains, which increased the contact points between LLDPE and the styrene monomer. The main chain of therein. The styrene monomer was grafted onto the LLDPE molecular chains by free radical reaction and LLDPE-g-PS beads were finally formed.

Thermal Behavior of PS, LLDPE, and LLDPE-g-PS

TGA is a method of great significance for evaluating the degradation procedure, thermal stability, and char residue weight of materials. The thermal behavior of PS, LLDPE, and LLDPE-g-PS in nitrogen atmosphere was investigated by thermogravimetric analysis (TGA), and the results are exhibited in Figure 8(a). Besides, the corresponding differential thermal gravity (DTG) curves were also presented in Figure 8(b). The detailed TGA data, including initial decomposition temperature (T_{on} , 5 wt % weight loss), maximum weight loss temperature (T_{max}), and maximum weight loss rate (R_{max}) are listed in Table III. As shown in Figure 8 and Table III, the initial degradation temperatures of pure PS, LLDPE, and LLDPE-g-PS were 305.7, 393.9, and 324.1°C, respectively. In order to investigate the thermal behavior of LLDPE-g-PS, the thermal degradation curve of a LLDPE/PS mixture was derived by the linear combination of the two components, based on mass percentages, assuming that the compounds do not affect each other.²⁶ Interestingly, the actual thermal decomposition process of LLDPE-g-PS was overtly different from what obtained from the calculated curve. Compared with LLDPE-g-PS (cal),

Table IV. Mechanical Properties of PS, LLDPE, and LLDPE-g-PS

Sample	BP (N)	TS (MPa)	BS (MPa)	BE (%)	GE (%)	RSD (%)
PS	820.7	19.89	18.42	6.2	-	-
LLDPE	213.8	13.72	5.10	400	-	-
1	819.2	19.6	18.42	6.0	6.28	0.5
2	788.9	19.79	17.24	80.0	7.60	3.3
3	775.2	18.5	14.71	109.0	9.81	3.1
4	575.3	16.77	13.92	195.0	25.9	1.5

BP: breaking power; TS: tensile strength; BS: breaking strength; BE: break elongation; GE: grafting efficiency; RSD: relative standard deviation of grafting efficiency.

both the T_{on} and T_{max} values of LLDPE-g-PS (exp) shifted to higher temperatures. This demonstrated that grafting styrene onto LLDPE occurred and produced the LLDPE-g-PS copolymer.

Mechanical Properties of LLDPE-g-PS

The mechanical properties of the LLDPE-g-PS copolymer are shown in Table IV (samples 1, 2, 3, and 4 correspond to a, b, c, and d, respectively, in Figure 5). The break elongation increased about 30 times after addition of 8% LLDPE and 10 mL/g of cyclohexane compared with that of PS. However, the breaking power, tensile strength, and breaking strength decreased with increased cyclohexane compatibilizer.²⁷ Therefore, the right amount of cyclohexane as compatibilizer could increase the grafting efficiency and improve the toughness of PS.

CONCLUSIONS

On the basis of similar compatibility principle, cyclohexane as a compatibilizer was used to swell and etch the surface of LLDPE, which provided more grafting points to increase the compatibility between PS and LLDPE molecular chain. The optimal experimental condition for preparing the LLDPE-g-PS copolymer was 8% LLDPE and the ratio of cyclohexane/LLDPE was 10 mL/g. In this condition, the highest grafting efficiency of 28.4% was achieved. The cross-sectional SEM images of the graft copolymer particles showed that the right amount of cyclohexane could improve the compatibility of LLDPE and PS. In addition, the compatibility of LLDPE and PS increased with the grafting efficiency. The tensile properties of polymer materials indicated that the break elongation increased, while the tensile strength, breaking power and breaking strength decreased with increased LLDPE. This suggested that the right amount of cyclohexane as compatibilizer could increase the grafting efficiency and improve the toughness of PS.

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