Supporting Information

Interplay between compatibilization of polyethylene-*graft*-polystyrene and the composition of LLDPE/PS blends in the foaming behaviour

Guangchun Zhang,[a,b] Yuanliang Wang,[a,b] Haiping Xing,[a] Jian Qiu,*[a] Jiang Gong,[a,b] Kun Yao,[a,b] Haiying Tan,[a,b] Zhiwei Jiang,[a] Tao Tang*[a]

Materials

cis-Cyclooctene (COE) (95%, Aldrich) and chain transfer agent *cis*-4-octene (TCI, 95%) was purified by vacuum distillation before using. Grubbs' catalyst second generation (G_2) (Sigma-Aldrich), α-Bromoisobutyryl bromide (98%, Aldrich), 3-Chloroperbenzoic acid (≤77%, Aldrich), 1,5-Cyclooctadiene (≥99%, Aldrich), Lithium aluminium hydride (95%, powder, Acros) were used as received without purification. Monomer styrene was distilled on CaH_2 by vacuum. Solvents $CHCl_3$, toluene, dichloromethane were purified by a Braun System. THF was distilled from sodium/potassium alloy with benzophenone.

Synthesis of α-bromoisobutyrate functionalized cyclooctene (Br-COE)

The comonomer α-bromoisobutyrate functionalized cyclooctene (Br-COE) was synthesized by esterification of 5-hydroxy-1-cyclooctene[1] and α-Bromoisobutyryl bromide. In detail, 5-hydroxy-1-cyclooctene (1.0 equiv) and α-Bromoisobutyryl bromide (1.2 equiv) esterified in the presence of triethylamine (1.5 equiv) in anhydrous CH_2Cl_2. The resulting oil was purified by column chromatography (silica, hexane/CH_2Cl_2 = 2/1). ^{1}H-NMR ($CDCl_3$) δ 5.64 (m, 2H, $CH{=}CH$) δ 4.89 (m, 1H, CH_2CHCH_2) δ 1.51-2.43 (m, CH_3CBrCH_3, protons on the cyclooctene ring)

ROMP copolymerization of COE-Br and COE

([COE]+[Br-COE])/[*cis*-4-octene]=500, [COE]/[Br-COE]=95/5 and ([COE]+[Br-COE])/G_2=4000 $CHCl_3$ as solvent, temperature was 60 °C. The copolymer was precipitated in plenty of methanol, and the solid was isolated then dried on vacuum. The ^{1}H-NMR and ^{13}C-NMR were illustrated in Figure S1.

Hydrogenation of PCOE-Br

Based on diimide, [C=C]/[*p*-toluenesulfonylhydrozide]/[tri-*n*-propylamine]=1.0/2.0/2.2, the mixture was heated to reflux for 8 h in *o*-xylene. Followed by precipitation in methanol, the solid was filtrated and dried on vacuum. The ^{1}H-NMR spectrum was exhibited in Figure S2.

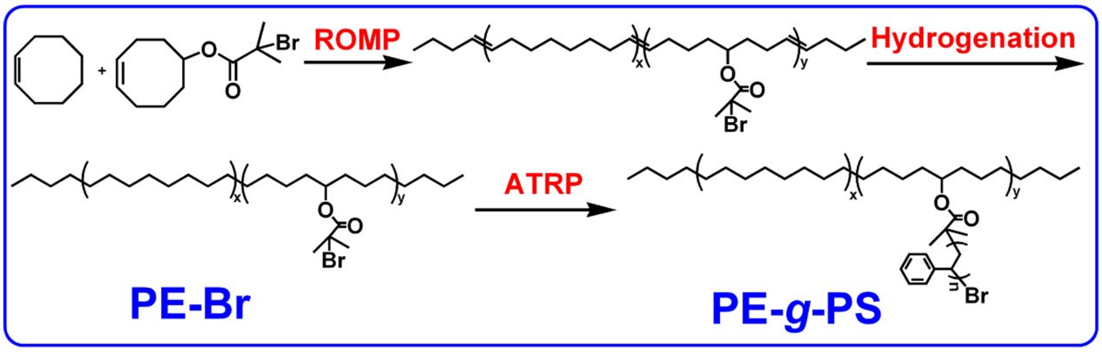
PE-*g*-PS prepared by ATRP

The polymerization work was carried out under an argon atmosphere by using standard Schlenk technique. [Br]/[CuBr]/[PMDETA]=1/2/4, toluene as solvent, freshly distilled styrene as monomer, polymerization temperature 100 °C, PE-*g*-PS graft copolymers with different length were obtained via mediating the polymerization time, 4 h, 6 h, 8 h and 10 h respectively. The ^{1}H-NMR spectrum was showed in Figure S2.

The molecular weight of the resultant copolymer (PCOE-Br) could be mediated using *cis*-4-octene as a chain transfer agent. When ([COE]+[Br-COE])/[*cis*-4-octene]=500, the weight-average molecular weight (M_w) of PCOE-Br was 107.7 kg/mol, M_w/M_n=1.94, according to the measurement results by room-temperature GPC. The ^{1}H-NMR spectra of PCOE-Br was shown in Figure S1 (a). The chemical shift at δ = 5.13-5.88 ppm was assigned to -C*H*=C*H*- and the characteristic chemical shift at δ = 4.92 ppm was assigned to the tertiary carbon hydrogen proton adjacent to the α-bromoisobutyrate group (-C*H*COC(CH_3)$_2$Br-). The content of Br-COE in the PCOE-Br can be calculated by the integration ratio of peak at δ = 4.92 ppm to δ = 5.13-5.88 ppm. The calculated result was 4.32 mol%, which was accorded with starting molar ratio of [Br-COE]/[COE] = 5/95. This indicated that 54 α-bromoisobutyrate groups were pended per 10000 carbon atoms along PCOE-Br backbone. Moreover, the corresponding ^{13}C-NMR spectra (Figure S1 (b)) also confirmed the microstructure of PCOE-Br. The characteristic chemical shifts at δ = 128.81-131.41 ppm corresponding to -*C*H=*C*H-, δ = 75.42 ppm corresponding to –CH_2*C*OCH_2-, δ = 171.18 ppm corresponding to –O*C*O-, and δ = 56.03 ppm corresponding to –OC*C*(CH_3)$_2$Br- appeared. A complete hydrogenation of PCOE was realized due to the disappearance of chemical shift δ = 5.13-5.88 ppm and appearance of a broad peak centered at δ = 1.32 ppm corresponded to the classic PE main chain structure (Figure S2). Furthermore, the characteristic chemical shift δ = 4.92 ppm belonged to -C*H*COC(CH_3)$_2$Br- was still present, which was indicated that the hydrogenation process did not influence the microstructure of backbone. The molecular weight of PE-Br determined by high-temperature GPC was M_w = 73.5 kg/mol and M_w/M_n = 1.82, which was approximately similar to the molecular weight and molecular weight distribution of PCOE-Br. Therefore, model PE chain with pendant 54 α-bromoisobutyrate groups per 10000 carbons along PE backbone was synthesized successfully.

The typical ^{1}H-NMR spectra of graft copolymer PE-*g*-PS is shown in Figure S2. The length of

PS chain was calculated via the peak integration area ratio at δ = 6.42-7.37 ppm assigned to the aromatic ring protons in polystyrene to that at δ = 4.92 ppm. It was indicated that the branch length varied from 0.34 kg/mol to 1.98 kg/mol. The molecular weight of the graft copolymer determined by high-temperature GPC was M_w = 74.8-85.4 kg/mol, M_w/M_n = 1.84-1.95. All the results were summarized in Table 1.



Scheme S1. The synthesis route of PE-*g*-PS graft copolymers.

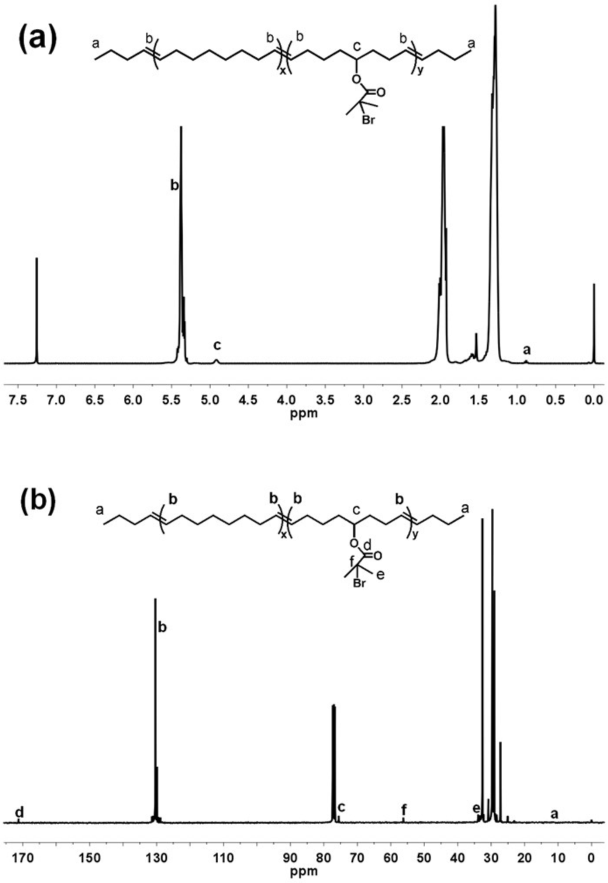


Figure S1. The ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of PCOE-Br synthesized through ROMP.

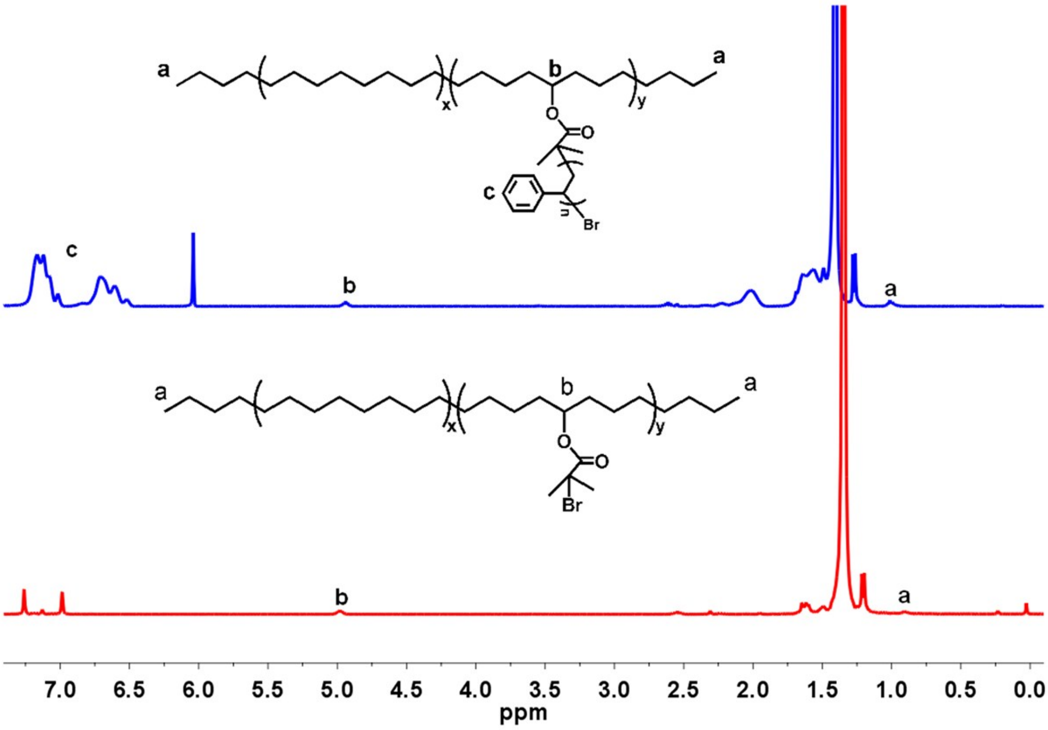


Figure S2. The ^{1}H-NMR spectra of PE-Br and graft copolymer PE-*g*-PS via ATRP.

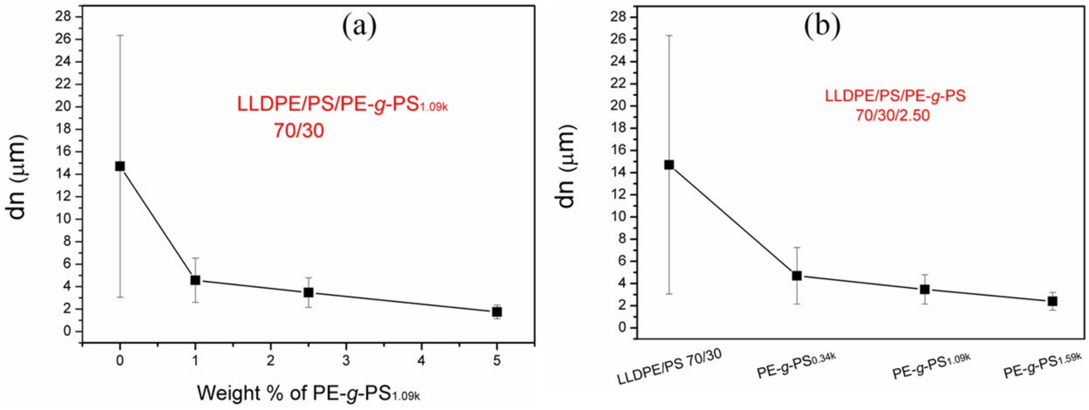


Figure S3. The statistical graph of the dependence of average size of PS particle on the concentration (a) and the branch length (b) of the compatibilizer. It should be noted that the size of the irregular dispersed particle (not spherical) was based on the longest dimension.

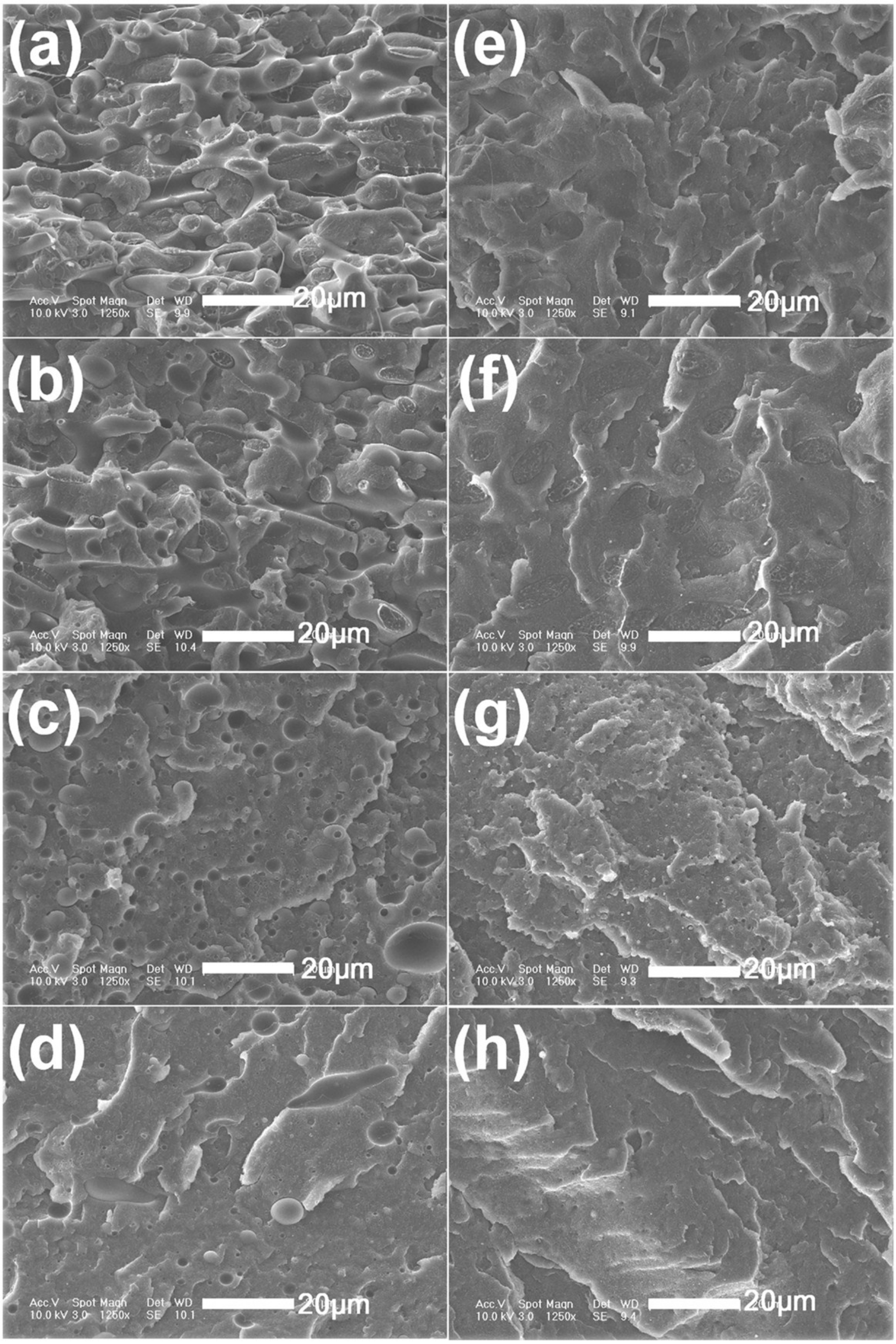


Figure S4. SEM morphology for cryogenic fractured LLDPE/PS (40/60) (a), 30/70 (b), 20/80 (c), 10/90 (d), and with PE-*g*-$PS_{1.59k}$ as compatibilizers at the same loadings 40/60/1.0 (e), 30/70/1.0 (f), 20/80/1.0 (g), and 10/90/1.0 (h).

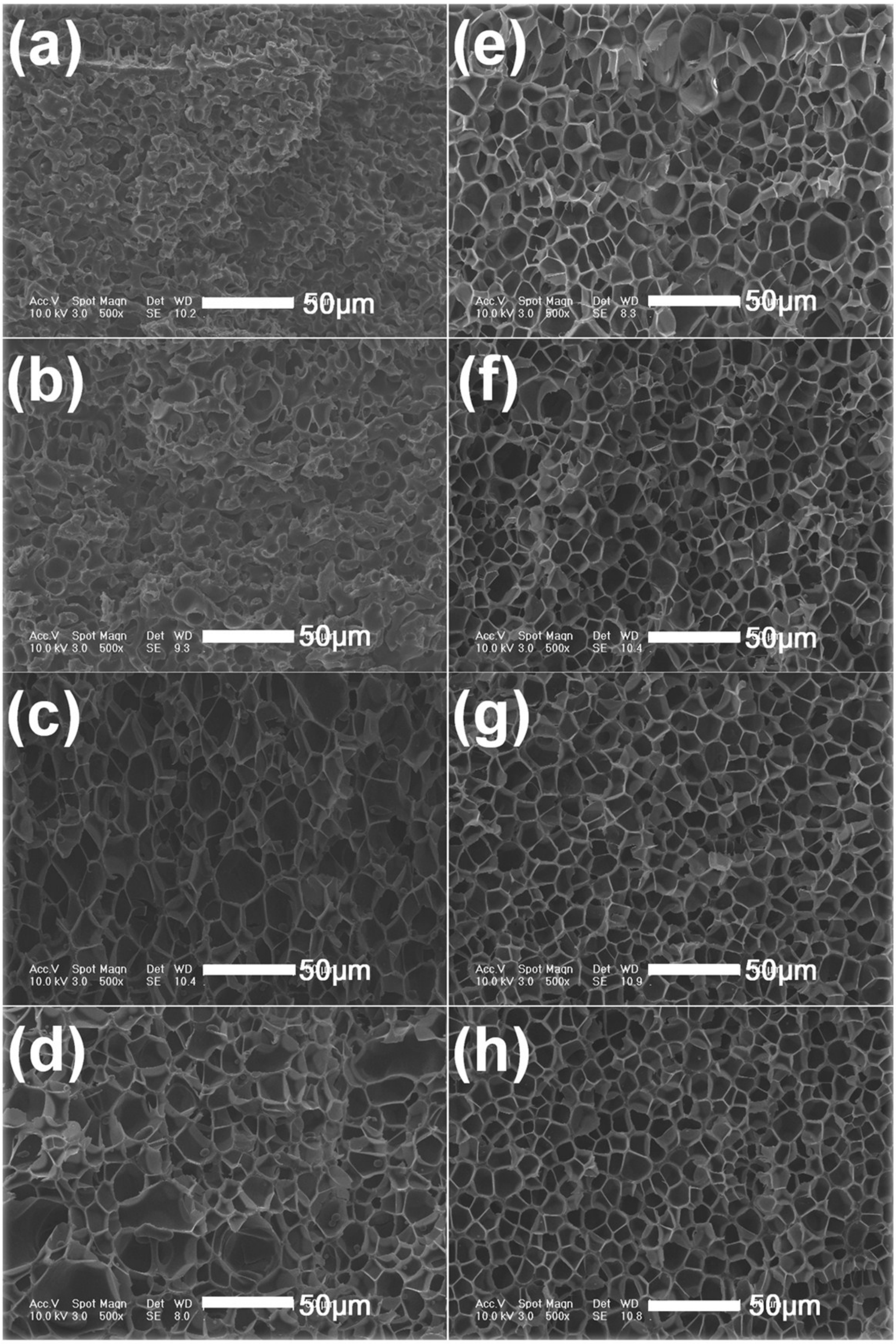


Figure S5. The cell morphology of LLDPE/PS blends at different ratio 40/60 (a), 30/70 (b), 20/80 (c) and 10/90 (d), with PE-*g*-PS$_{1.59k}$ as compatibilizers at 1.0wt% 40/60/1.0 (e), 30/70/1.0 (f), 20/80/1.0 (g), and 10/90/1.0 (h). Foaming temperature: 113 ^{o}C; CO_2 saturation pressure: 13.3 MPa.

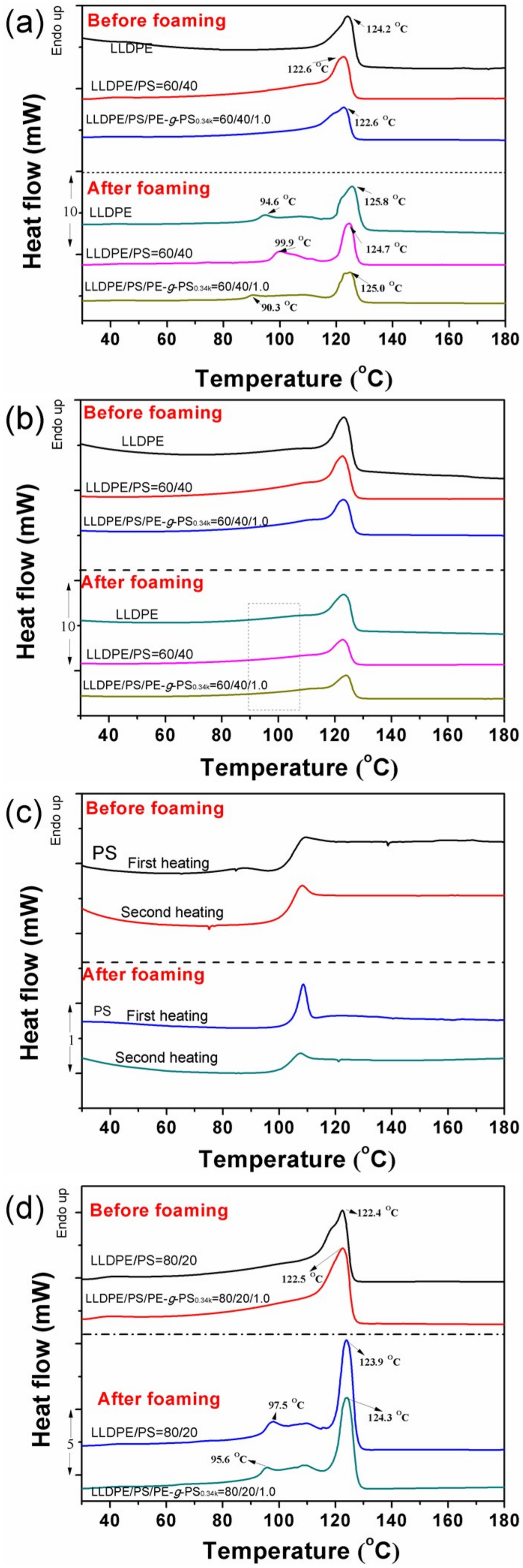
(a)
Endo up
Before foaming
124.2 °C
LLDPE
122.6 °C
LLDPE/PS=60/40
LLDPE/PS/PE-g-PS0.34k=60/40/1.0
122.6 °C
After foaming
94.6 °C
125.8 °C
10
LLDPE
99.9 °C
124.7 °C
LLDPE/PS=60/40
LLDPE/PS/PE-g-PS0.34k=60/40/1.0
125.0 °C
90.3 °C
Heat flow (mW)
40
60
80
100
120
140
160
180
Temperature (°C)
(b)
Endo up
Before foaming
LLDPE
LLDPE/PS=60/40
LLDPE/PS/PE-g-PS0.34k=60/40/1.0
After foaming
10
LLDPE
LLDPE/PS=60/40
LLDPE/PS/PE-g-PS0.34k=60/40/1.0
Heat flow (mW)
40
60
80
100
120
140
160
180
Temperature (°C)
(c)
Endo up
Before foaming
PS
First heating
Second heating
After foaming
PS
First heating
1
Second heating
Heat flow (mW)
40
60
80
100
120
140
160
180
Temperature (°C)
(d)
Endo up
Before foaming
122.4 °C
LLDPE/PS=80/20
122.5 °C
LLDPE/PS/PE-g-PS0.34k=80/20/1.0
123.9 °C
After foaming
97.5 °C
124.3 °C
LLDPE/PS=80/20
5
95.6 °C
LLDPE/PS/PE-g-PS0.34k=80/20/1.0
Heat flow (mW)
40
60
80
100
120
140
160
180
Temperature (°C)

Figure S6. (a) The first heating scan curves of LLDPE, LLDPE/PS=60/40 and LLDPE/PS/PE-*g*-PS$_{0.34k}$=60/40/1.0 samples before foaming process vs after foaming process; (b) the second heating scan curves; (c) the first and second heating curves of PS samples before foaming process and after foaming process; (d) the first and second heating curves of LLDPE/PS=80/20, LLDPE/PS/PE-*g*-PS$_{0.34k}$=80/20/1.0 samples before and after foaming process. Here "before foaming" means the measured samples did not undergo batch foaming, and "after foaming" means the measured samples had undergone batch foaming. All the samples were measured using DSC (Mettler Toledo Star system (DSCI)) under a nitrogen atmosphere, operating at a heating rate of 10 °C /min from 25 to 200 °C, held at 200 °C for 5 min, subsequently cooled at a rate of 10 °C/min and heated again at a rate of 10 °C/min. The crystallinities were calculated based on the heat of fusion of crystallites. The heat of fusion for perfect PE crystal is 293 J/g.

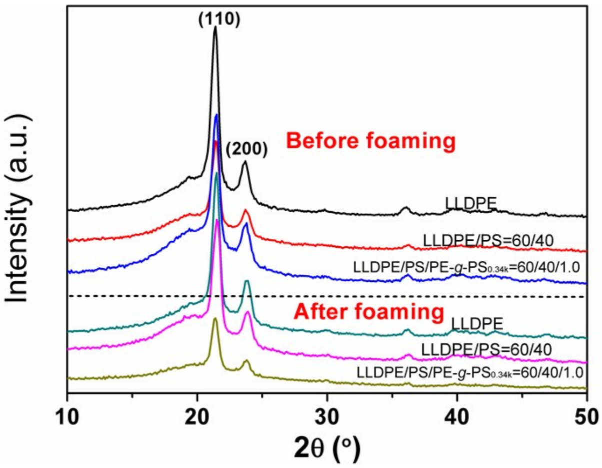


Figure S7. WAXD patterns of LLDPE, LLDPE/PS=60/40, LLDPE/PS/PE-*g*-PS$_{0.34k}$=60/40/1.0 samples before foaming process and after foaming process. Wide-angle X-ray diffraction (WAXD) measurements were performed on a Bruker D8 ADVANCE diffractometer with a Cu Kα radiation (λ = 0.154 nm) operating at 40 kV and 40 mA from 10 to 50° at a scanning rate of 2 °/min.

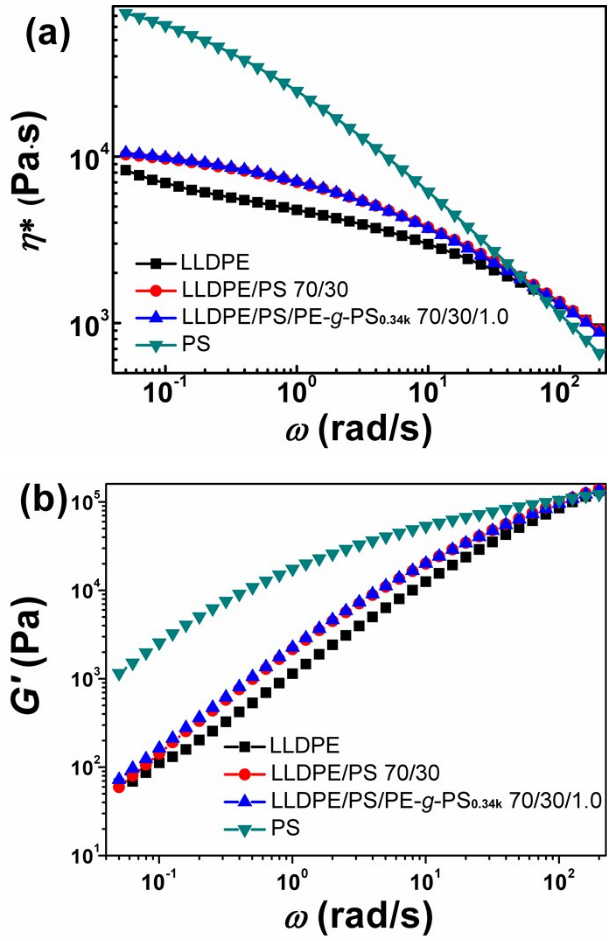


Figure S8. (a) The complex viscosity (η^*) versus angular frequency (ω) and (b) storage modulus (G') versus angular frequency (ω) at 180 $^{\circ}$C for LLDPE, PS, LLDPE/PS 70/30 and LLDPE/PS/PE-g-PS$_{0.34k}$ 70/30/1.0.

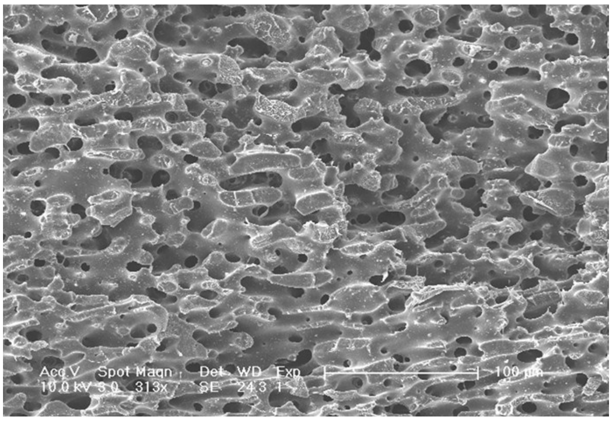


Figure S9. SEM morphology for the treated LLDPE/PS 50/50 blends. A 10×10×1 mm sample was suspended in THF then stirred for 48 h. Afterwards the treated sample was dried in vacuum for 24 h. The mass of the dried sample was half of untreated sample via weighing.

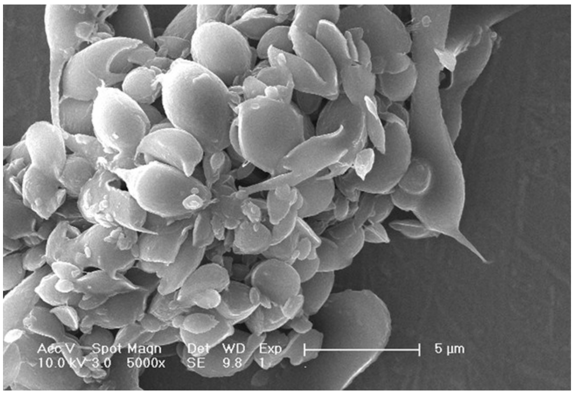


Figure S10. SEM micrographs of the etched products of LLDPE/PS 20/80 foam by THF at room temperature. Most of the foam is dissolved in THF under stirring, and then the obtained suspension is subjected to centrifugation 3 times using THF. The resulting solid is dried in vacuum for 24 h.

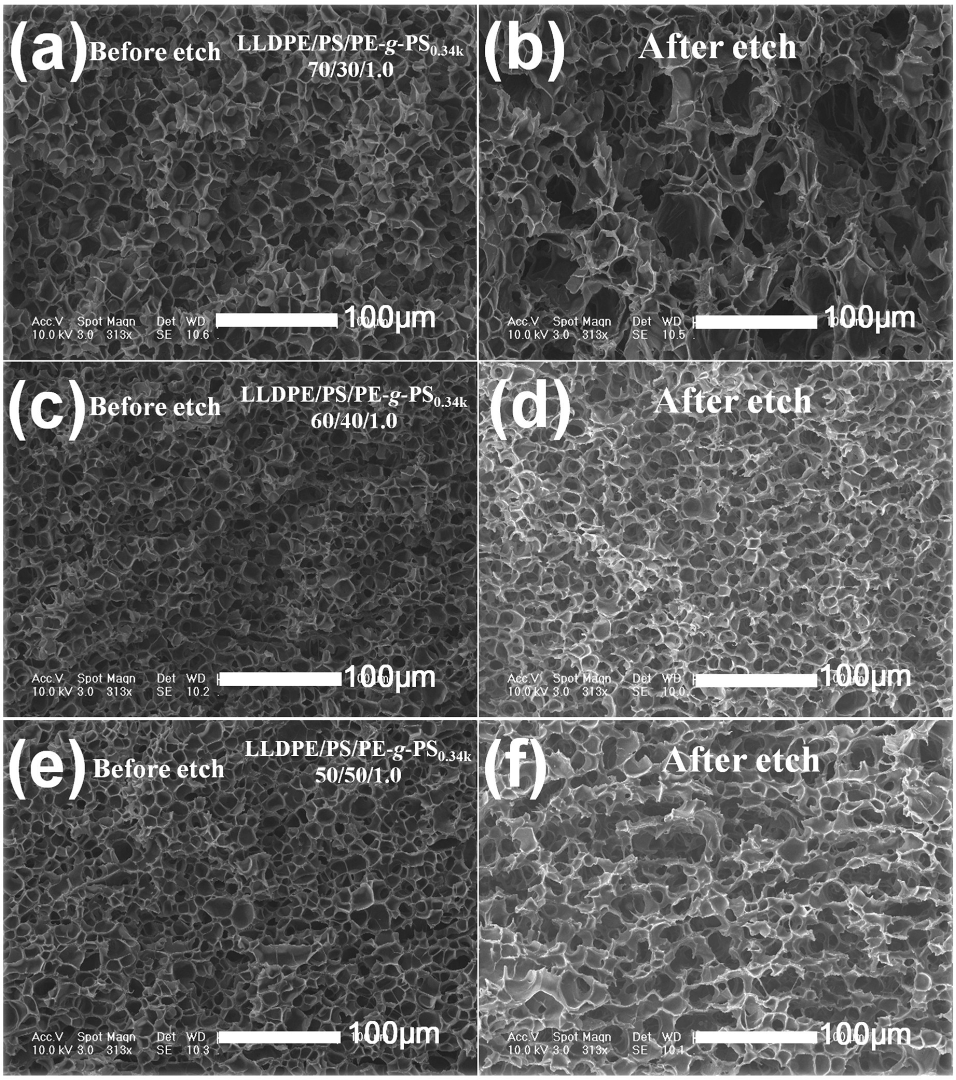


Figure S11. SEM micrographs for foamed morphology of LLDPE/PS blends with PE-*g*-PS$_{0.34k}$ 70/30/1.0 (a), 60/40/1.0 (c) and 50/50/1.0 (e), and corresponding etched morphology (b), (d), (f) by THF respectively.

References

1. M. A. Hillmyer, W. R. Laredo and R. H. Grubbs, *Macromolecules*, 1995, **28**, 6311.