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A Novel GPPS/*cis*-SB Blend with High Performance

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Summary: GPPS/*cis*-SB blends with high performance were prepared by adding 3–5 wt.-% stereoregular butadiene-styrene block copolymers (*cis*-SB) with a high *cis*-1,4 configuration of around 97% into general purpose polystyrene (GPPS). The micromorphology of the GPPS/*cis*-SB blends was characterized by transmission electron microscopy (TEM). Mechanical properties including tensile and impact properties were studied and the fracture surfaces of tensile and impact test specimens were characterized by scanning electron microscopy (SEM). PB domains of 10–30 nm with a blurry interface were tethered by continuous PS domains. The fracture surface of the tensile test piece of GPPS was relatively smooth while the fractography of patch patterns separated by river patterns was formed when the tensile specimens of GPPS/*cis*-SB blends were broken, which may be due to the nanometer-scale rubber phases with high *cis*-1,4 configuration and some partially crystalline PS segments in the *cis*-SB block copolymer. It is found that GPPS could be greatly toughened by introduction of a small amount of *cis*-SB and the tensile strength and elongation at break could also be increased.

Keywords: butadiene-styrene block copolymer; polymer blend; polystyrene; stereoregularity; toughness

Introduction

General purpose polystyrene (GPPS) possesses rigidity, good process ability, transparency, and water resistance. However, it has disadvantages such as brittleness, which limits its application. To overcome the brittleness of GPPS, the main directions have been aimed at blending GPPS and copolymerization of styrene with other polymers.[1] The polymer components blended in GPPS can be divided into two categories: homopolymers and copolymers that contain PS segments. When GPPS is blended physically with homopolymers such as polybutadiene rubber (BR), natural rubber (NR), and isoprene rubber (IR), it was observed that the impact strength increased greatly while the tensile strength of the blends decreased drastically. The negative results observed are due to the poor interfacial adhesion between the PS and rubber phases, which causes poor stress-transfer between the PS matrix and the dispersed rubber phase.[2–4] Sometimes GPPS is blended with the copolymers that contain styrene units such as styrene-butadiene rubber (SBR, styrene content of 23%), styrene-butadiene block copolymers (SBS), and chlorinated polyethylene-styrene graft copolymer (CPE-g-St).[5–8] The atactic PS segments exist in the block copolymer and the *cis*-1,4 content of butadiene unit is around 35–40%. The binding energy of the copolymer and the PS matrix is enhanced and energy from outside is easy to transmit and disperse because of PS segments in the copolymers can combine well with the PS matrix. The second method to improve the impact property of GPPS is to introduce a rubber phase via in-situ graft copolymerization with BR and SBR.[3] This impact-modified polystyrene (HIPS) consists of a PS matrix with embedded cellular rubber particles.

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The impact properties of GPPS can be improved but the tensile strength, yield strength, and tensile modulus decrease at the same time.

In our previous research work, butadiene-styrene block copolymers (*cis*-SB) with a stereospecific configuration (*cis*-1,4 content ~97%) could be synthesized by rare earth catalysis.[9,10] In this study, in order to improve the mechanical properties of GPPS, GPPS/*cis*-SB blends were prepared by adding a small amount of *cis*-SB into GPPS by a physical method.

Experimental Part

Materials and Sample Preparation

GPPS (666D) was provided by Beijing Yansan Petrochemical Corporation and HIPS (60-HR) was provided by LG Chemistry Corporation. Butadiene-styrene block copolymers with a stereospecific configuration (*cis*-SB, *cis*-1,4 content ~97%) were synthesized in our lab. The weight-average molecular weight (M_w), polydispersity (M_w/M_n), styrene content of the three *cis*-SB copolymers [SB(b), SB(c), and SB(d)] used, and the proportion of *cis*-SB in the blends have been summarized in Table 1. The blends were prepared by adding 3–5 wt.-% *cis*-SB into GPPS and then mixing the blend components in an internal mixer at 155 °C.

Mechanical Properties Testing

Tensile testing specimens were characterized using a universal tensile machine (Lloyd Instruments) and impact machine (Resil Impactor) at 23 °C, respectively, according to ASTM D1708. The specimens were prepared by an injection moulding method using an injection instrument (mass temperature 240 °C and mould temperature 90 °C). The tensile specimens had a size of $40 \times 5 \times 2$ mm^3 and the impact specimens had a size of $50 \times 3 \times 3$mm^3. At least six specimens of each sample were tested. The cross-head speed of the tensile machine was 1.2 mm/min.

GPC Analysis

The copolymer sample was dissolved in tetrahydrofuran (THF) to a concentration of 10 mg/mL. M_n, M_w, and M_w/M_n of the copolymer were determined at 25 °C with a Waters 515–2410 GPC System equipped with Waters 996 PAD, RI 2410 detectors and three Waters styragel HT3-5-6E columns. THF was the carrier solvent used with a flow rate of 1.0 mL/min. The calibration was established with polystyrene standards.

SEM Analysis

Examination of the fracture surface of the tensile specimen was carried out using a scanning electron microscope (SEM) (Cambridge-S250MK3). The fracture ends were cut off and mounted on the aluminum stubs, then coated with a thin layer of gold.

TEM Analysis

The copolymer sample (20 mg) was dissolved in toluene (10 mL). The copolymer film was formed after the evaporation of toluene, supported on 3 mm copper grids, and stained with osmium tetroxide (OsO_4). The sample was then examined with a HITACHI-800 transmission electron microscope operating at 150 kV.

Polar Optical Microscopy Analysis

The copolymer sample (20 mg) was dissolved in toluene (10 ml). The copolymer film was formed after the evaporation of toluene. The sample was examined with a

Table 1.
Characteristics of *cis*-SB used in the experiments.

Samples	M_w	M_w/M_n	St content (wt.-%)	SB in blends (%)
SB(b)	363 000	6.2	35.9	5
SB(c)	473 000	5.4	33.0	3
SB(d)	590 000	8.7	14.3	3

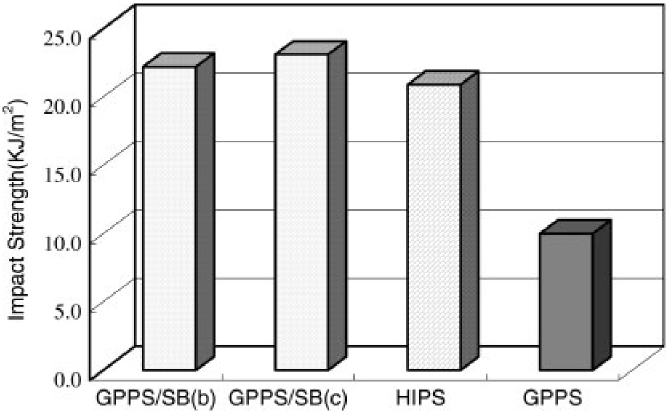


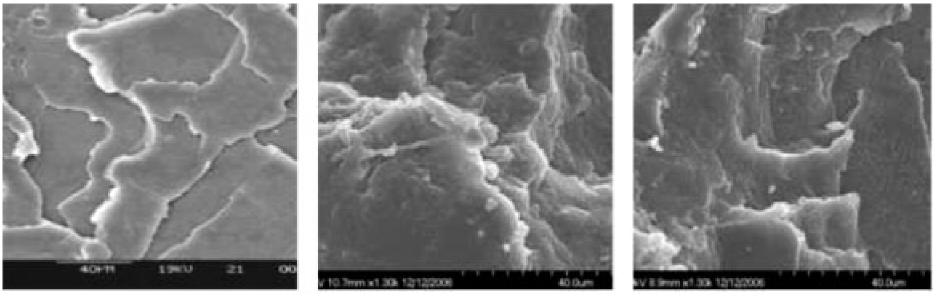
Figure 1.
Impact strength of GPPS/SB, GPPS, and HIPS.

XSZ-H polar optical microscope (POM) (Chongqing Optical & Electrical Instrument Co., Ltd.).

Results and Discussion

A comparison of the different impact strengths of the GPPS/*cis*-SB blends, GPPS, and HIPS is shown in Figure 1.

As shown in Figure 1, the impact strength of GPPS was near 10 kJ/m^2, while the impact strength of HIPS, GPPS/SB(b), and GPPS/SB(c) were 20.9, 22.2, and 23.1 kJ/m^2 respectively. The impact strength of HIPS was increased to 20.9 kJ/m^2 by introducing a relatively high content of butadiene rubber in the range of 8–10 wt.-%. Comparatively, the impact strength of the GPPS/SB could be increased to around 23 kJ/m^2 by introducing only 3 wt.-% of cis-1,4 (~97%) SB block copolymer. Thus, the impact property of GPPS could be obviously improved by adding 3 wt.-% *cis*-SB(c) with a high molecular weight (M_w) of 473 000 or 5 wt.-% *cis*-SB(b) with a relatively low molecular weight (M_w) of 363 000 at similar styrene content in the block copolymers. Figure 2 shows the SEM micrographs of the fracture surface of the impact strength testing specimens. As shown in Figure 2(a), the fracture surface of the impact strength testing specimen from GPPS was relatively smooth, thereby indicating a brittle fracture. As shown in Figure 2(b) and



(a) GPPS (b) HIPS (c) GPPS/SB(b)

Figure 2.
SEM images of the fracture surface of impact strength test specimens.

Figure 2(c), both the fracture surfaces of the GPPS/*cis*-SB(b) blend and the HIPS were relatively rough and had multiple crazing in the vicinity. The overlapping layers of different extent were formed when the specimens of the GPPS/SB blend were broken and the tough fracture feature was presented.

The tensile strength and elongation at break of GPPS, HIPS, and GPPS/*cis*-SB are shown in Figure 3 and the curves of stress–strain are shown in Figure 4. It can be seen from Figure 3(a) that the tensile strength of GPPS was around 38.0 MPa and that of HIPS decreased to 20.3 MPa. Very interestingly, the tensile strengths of the three GPPS/*cis*-SB(b, c and d) blends increased to 34.5, 31.9, and 44.1 MPa, respectively. It can be seen that not only the impact strength was improved as shown in Figure 1 but also the tensile strength decreased slightly to 34.5 or 31.9 MPa, and even improved to 44.1 MPa by adding small amount of *cis*-SB block copolymers into GPPS. The high molecular weight of around 590 000 of the cis-PB segment in the SB(d) copolymer made a great contribution to the improvement of tensile strength. Moreover, it can be seen from Figure 3(b) and Figure 4 that GPPS exhibited a typically brittle fracture and the elongation at break was only 2.4%. The elongation at break of HIPS was 23% and those of the three GPPS/*cis*-SB blends reached 21.7%, 18.9%, and 38.9% respectively. Comparing the mechanical properties of GPPS/*cis*-SB

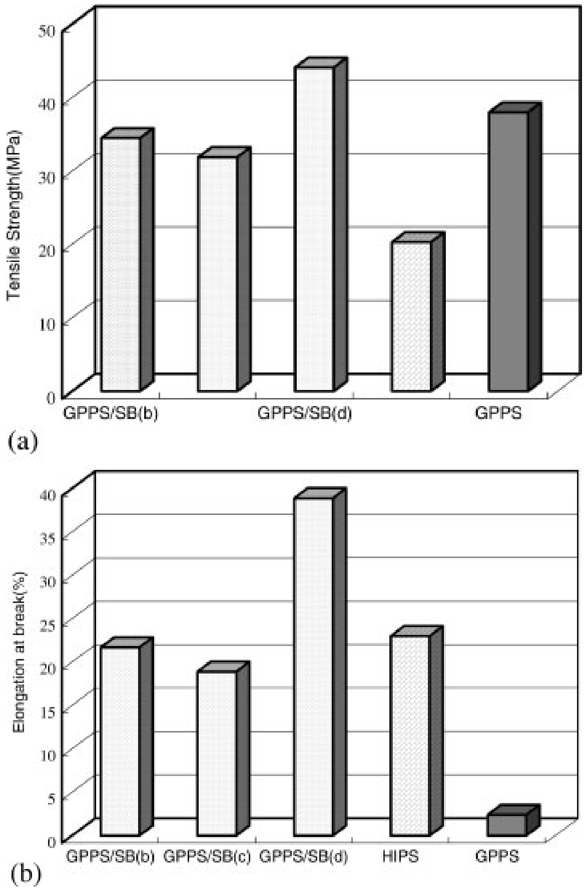


Figure 3.
Tensile strength and elongation at break of GPPS, HIPS and GPPS/SB blends.

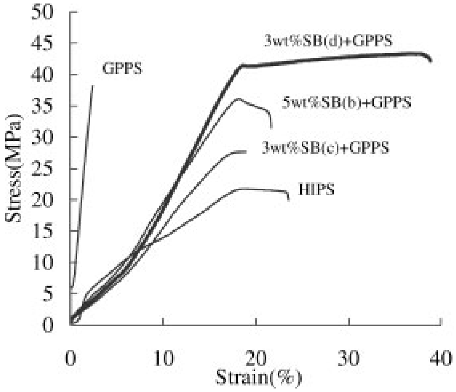
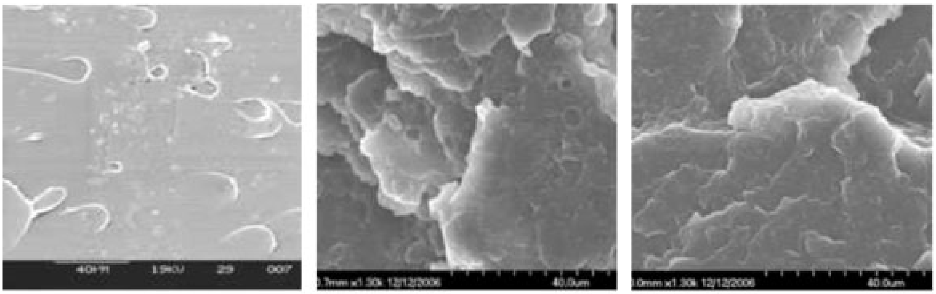


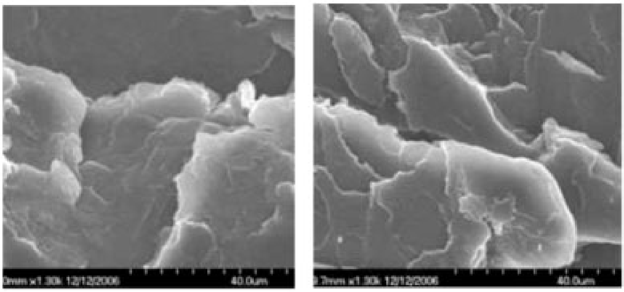
Figure 4.
Curves of stress–strain of GPPS, HIPS and GPPS/SB blends.

blends, it can also be found that the characteristics of *cis*-SB including molecular weight and its distribution were the key factors to influence the mechanical properties of the blends. The *cis*-SB with high molecular weight and relatively broad molecular weight distribution could provide superior tensile properties to the blends.

It can be seen from Figure 5 that the fracture surface of the tensile strength test specimen of GPPS was relatively smooth and a brittle fracture feature was presented, while those of HIPS and GPPS/*cis*-SB blends were relatively rough. A fractography of patch patterns separated by river patterns was formed when the tensile specimens of HIPS and GPPS/*cis*-SB blends were broken.[11] Comparing the fracture surfaces of HIPS and the GPPS/*cis*-SB blends, it can be observed that some microvoids with a size of 1–5 μm were formed in the HIPS matrix. The formation of these microvoids may be due to the function of pulling out of rubber particles from the matrix of HIPS during the process of tensile testing. Therefore, the elongation at break was improved while the tensile strength obviously decreased. However, it can be seen from Figure 5(c–e) that the fracture surfaces of the tensile strength test specimens of GPPS/*cis*-SB blends were

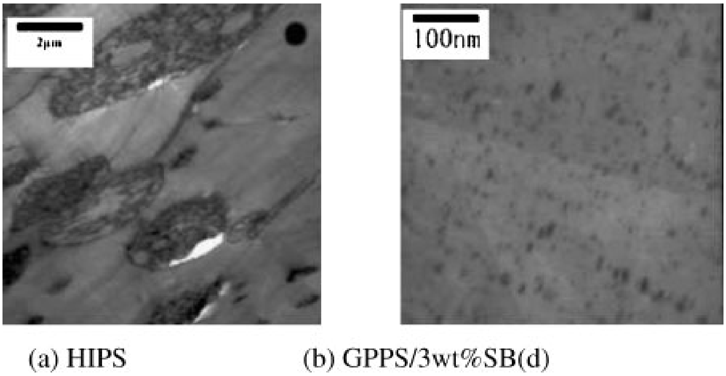


(a) GPPS (b) HIPS (c) GPPS/5wt%SB(b)



(d) GPPS/3wt%SB(c) (e) GPPS/3wt%SB(d)

Figure 5.
SEM micrographs of the fracture surface of tensile strength test specimens.



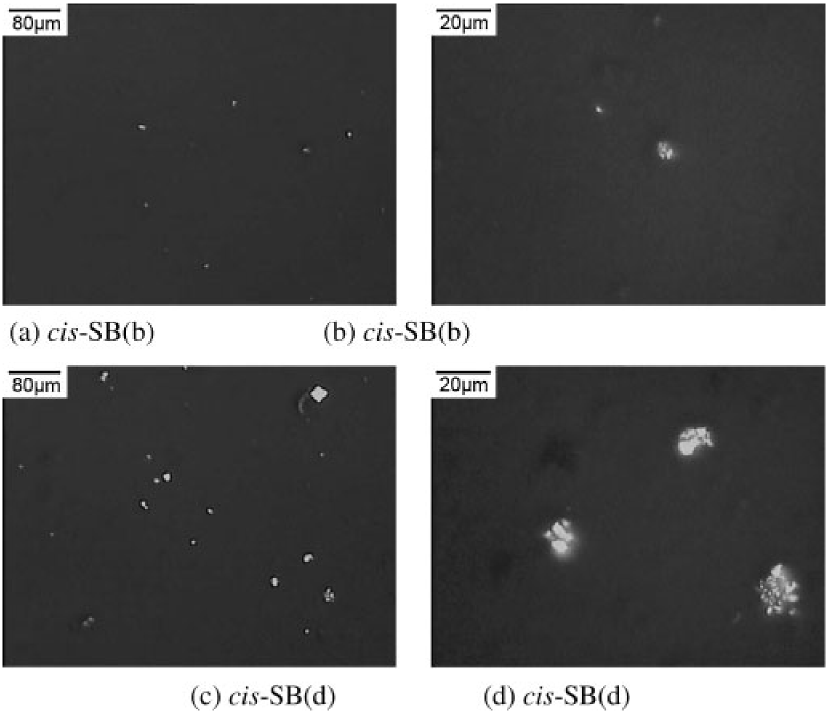
(a) HIPS (b) GPPS/3wt%SB(d)

Figure 6.
TEM images of HIPS and the GPPS/SB(d) blend.

similar to that of HIPS while the microvoids were not detected in GPPS/*cis*-SB blends, which perhaps leads to the improvement of tensile strength to some degree.

In order to further investigate the high performance of GPPS/*cis*-SB in both impact and tensile strength, the micromorphology of HIPS and GPPS/*cis*-SB was characterized by TEM.

Figure 6 shows TEM micrographs of HIPS and a GPPS/*cis*-SB blend. The darker region is the PB phase stained by OsO_4. It can be seen that there is an obvious difference between HIPS and GPPS/*cis*-SB



(c) *cis*-SB(d) (d) *cis*-SB(d)

Figure 7.
POM images of *cis*-SB block copolymers.

blend. A configuration of interpenetrating polymer networks (IPN) was formed due to the existence of graft copolymer in HIPS. Rubber phases with a size of around 2 μm were distributed in the PS matrix, and the size of the rubber phase was almost consistent with the size of holes that exist on the fracture surface of the tensile test specimen. The morphology of the GPPS/*cis*-SB blend shows dark PB phases with sizes of 10–30 nm distributed in light PS matrix, and the boundary of the two phases was blurry. Therefore, the toughness and rigidity of the GPPS could be improved at the same time. Furthermore, the *cis*-SB block copolymers were characterized by POM and the corresponding POM micrographs are shown in Figure 7.

As shown in Figure 7, the crystalline phase with size of 2–20 μm was formed in the *cis*-SB block copolymers, which supports the increase of tensile strength of the GPPS/SB(d) blend. It is found that the addition of some crystalline *cis*-SB block copolymer into GPPS leads to the improvement of toughness and rigidity of GPPS at the same time.

Conclusions

A novel GPPS/*cis*-SB blend with high performance could be obtained by adding 3–5 wt.-% stereoregular butadiene-styrene block copolymers with high *cis*-1,4 configuration of around 97% into GPPS. GPPS could be greatly toughened, the tensile strength could also be improved, and elongation at break increased as well. The simultaneous improvement of toughness and rigidity of GPPS was due to the function of PB phases with a nanometer-scale in the blends, the high *cis*-1,4 PB segments, and partially crystalline PS segments in the *cis*-SB block copolymer.

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