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Crystalline Syndiotactic Polystyrene as Reinforcing Agent of *cis*-1,4-Polybutadiene Rubber

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ABSTRACT: Syndiotactic polystyrene (sPS), a thermoplastic polymer characterized by high crystallinity, good chemical resistance and high modulus, has been successfully tested as a reinforcing agent for *cis*-1,4-polybutadiene (PB) rubber. Blends of sPS and PB have been *in situ* synthesized using a multistep polymerization process catalyzed by monocyclopentadienyl titanium compounds activated with MAO. This procedure assures an intimate mixing of the components and homogeneous dispersion of the sPS particles having dimension from few hundreds of nanometers to micrometers. The analysis of the mechanical properties of the sPS−PB blends obtained using this process showed enhanced Young's modulus, toughness, σ_{break} and $\varepsilon_{\text{break}}$: these properties were found to be 1 order of magnitude higher than those of PB and comparable to those of PB charged with inorganic filler as carbon black or silica. A multiblock copolymer (sPSB) comprising segments of sPS and PB was successfully *in situ* synthesized with the sPS and PB homopolymers and found to be an active compatibilizer of these blends producing a novel semicrystalline phase at the interphase between the sPS particles and the PB matrix.

Introduction

Natural rubber and synthetic elastomers based on *cis*-1,4-polydienes are produced on a million tons per year scale for many practical applications in the form of composites charged with inorganic fillers as carbon black and/or silica. The presence of the filler in the range of compositions of 10−60 phr (parts per hundred of rubber by weight) improves significantly the modulus, tear resistance, abrasion resistance, tensile strength, and dynamic and static toughness of the material.[1]

Carbon black is the most effective reinforcing filler of the natural and synthetic rubber. It is typically found under the form of agglomerates of about 1 μm, consisting of primary particles on a nanometric scale.[2] The elevated specific area (80−120 m^2/g) and the van der Waals interactions with the polymer matrix, as well as the occasional covalent bonds produced under the processing, ensure good compatibility with this filler and enhanced final properties for the rubber.

Precipitated silica has been increasingly used as a reinforcing particulate filler in rubber components of tires and mechanical goods. The reason for the use of silica in tires is to improve the performance balance between wet traction and rolling resistance, snow/ice traction, and mechanical properties, such as wear performance.[3] Silica particles within a range of about 5 to about 300 nm have been employed. However, silica-loaded rubber stocks exhibited relatively poor resilience and high compound viscosity when used without any silane-coupling agent, which is somewhat expensive to be widely used in the industry.[4] Even with a certain amount of silane-coupling agent, the total balance of the foregoing performances was often not sufficient.[3]

Synthetic and natural lamellar silicates, as montmorillonites and cloisites, have been proposed as alternative nanofillers because of well designed geometry, dimension and composition. The exfoliation of the lamellar structure is necessary to increase the specific area of the inorganic compound.[5] Moreover the chemical modification of the particle surface or the use of surfactants are necessary to improve the filler−polymer interaction because of the hydrophilic properties of the filler surface that typically leads to incompatibility with hydrocarbon polymers.[6] Compared to carbon black, the use of silicates is in general limited by several problems as follows: (i) higher compound viscosity due to filler/filler interaction; (ii) hard mixing and processing; (iii) longer vulcanization time; (iv) lower network-chain density.[7] Then, a good dispersion of the filler in the polymer matrix is required to enhance all these factors and this feature is, in some cases, challenging.

Alternatively polydienes are blended and vulcanized with high performance thermoplastics such as polyethylene,[8] isotactic polypropylene,[9] and polyurethane[10] to yield thermoplastic vulcanized which find many static use applications. These reinforcing agents offer the advantage of a better mixing, less reactor fouling, and easy recycle of the material.

We have been studying since many years ago syndiospecific styrene polymerization and *cis*-1,4 specific polymerization of conjugated dienes catalyzed by monocylopentadienyl titanium compounds.[11,12] The same titanium catalysts allow copolymerization of styrene with 1,3-butadiene to yield copolymers in which stereoregular crystalline polymer segments are present. In particular, styrene-1,3-butadiene copolymerization catalyzed by $CpTiCl_3$/MAO or CpTi(MBMP)Cl/MAO (Cp = η^5-C_5H_5; MBMP = 2,2′ -methylenebis(6-*tert*-butyl-4-methylphenoxo); MAO = methylaluminoxane) yields multiblock copolymer (sPSB) in the full range of composition in which crystalline syndiotactic polystyrene segments are present at styrene molar

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Table 1. *In Situ* Blends of Syndiotactic Polystyrene (sPS), *cis*-1,4-Polybutadiene (PB) and Multiblock Copolymer (sPSB)

blend[a]	sample	$[S]_o$[b] (mol/L)	t_S[c] (h)	$[S]_o/[B]_o$[d]	t_C[c] (h)	$[B]$[e] (mol/L)	t_B[c] (h)	yield (g)	composition[h] (wt % in S)
sPS−PB	**1**	0.77	0.5			2.7	2	18	7
	2	2.12	3			1.78	1.5	88	15
	3	2.13	2			2.07	2	74	34
	4	2.80	1			1.51	2	31	46
$sPS_{80}B$−PB[f]	**5**	4.16		12	4.5	2.33	1	35	16
	6	4.16		12	4.5	3.6	1	31	34
	7	4.16		12	4.5	1.44	1	25	49
sPS−sPSB−PB[g]	**8**	0.55	2	15	0.25	1.32	2.5	112	15
	9	1.11	2	15	0.25	1.11	3	113	24

[a] Polymerization conditions: $CpTiCl_3$ (9.1×10^{-5} mol); MAO = 10 wt % in toluene, (Al/Ti molar ratio = 400); T_P = 25 °C. [b] Molar concentration of styrene in the feed. [c] Polymerization time for styrene (t_S), styrene-*co*-1,3-butadiene (t_C) and 1,3-butadiene (t_B). [d] Styrene/1,3-butadiene molar ratio in the feed during the copolymerization step. [e] Molar concentration of 1,3-butadiene in the homopolymerization step. [f] CpTi(MBMP)Cl (8.8×10^{-5}mol); MAO (Al/Ti molar ratio = 1000); T_P = 25 °C. [g] CpTi(MBMP)Cl (3.0×10^{-4}mol); MAO (Al/Ti molar ratio = 1,000); T_P = 25 °C. [h] Determined by ^{1}H NMR.

fraction higher than 0.4.[13,14] Syndiotactic polystyrene (sPS) is a thermoplastic polymer characterized by high tensile modulus (3.4 GPa),[15] excellent physical properties as high heat resistance, high crystallization rate, good electrical properties, excellent processing characteristics, outstanding dimensional stability, low moisture absorption and high chemical resistance.[16]

In view of this, we suggested that sPS synthesized *in situ* with *cis*-1,4-polybutadiene (PB) can lead to blends in which the thermoplastic polymer acts as reinforcing agent of polybutadiene rubber. This approach is particularly attractive for the further possibility of obtaining *in situ* the multiblock sPSB copolymer as compatibilizer. Finally the mixture of the polymers can be undergone to vulcanization for the anchoring of the thermoplastic polymer to the rubber matrix.

In this paper we report on the *in situ* synthesis of blends of PB with sPS (sPS−PB), blends of PB with a multiblock syndiotactic polystyrene-*co*-*cis*-1,4-polybutadiene, sPS-*co*-PB (sPSB−PB) and blends of PB with a multiblock sPS-*co*-PB and sPS (sPS−sPSB−PB). The effect of the addition of the copolymer sPSB as compatibilizer in blends sPS−PB is also described (c-sPS−PB−sPSB). The mechanical, thermal and morphological properties of these blends and the use of the multiblock sPS-*co*-PB as compatibilizer have been also investigated and discussed.

Experimental Section

General Procedure and Materials. All manipulations were performed under nitrogen atmosphere using standard Schlenk techniques and a MBraun drybox. Commercial grade toluene (Carlo Erba) was predried over calcium chloride, then refluxed over sodium for 48 h and distilled before use. Polymerization grade 1,3-butadiene (≥99%, Aldrich) was dried by flowing through a column filled with activated molecular sieves (3 Å, Aldrich) and silica gel (230−400 mesh ASTM, Merck). Styrene (Aldrich) were purified by distillation over calcium hydride and stored in refrigerator at −20 °C. Methylaluminoxane (MAO, 10 wt % solution in toluene), $CpTiCl_3$, OsO_4 (4 wt % water solution), dicumyl peroxide (DCP) were purchased from Aldrich and used as received. CpTi(MBMP)Cl was synthesized according to literature procedure.[17]

Blends *in Situ* of Syndiotactic Polystyrene with *cis*-1,4-Polybutadiene (sPS−PB). The synthesis of *in situ* blends sPS−PB was carried out using the following typical procedure, described for the sample containing 34 wt % of styrene (sample **3**, Table 1). A 2 L flask equipped with a magnetic stir bar was charged with toluene (200 mL), styrene (80 mL) and MAO (25 mL, 10 wt % toluene solution, Al/Ti molar ratio = 400). After equilibration of the solution at 25 °C, the styrene polymerization was started by injection of a toluene solution of $CpTiCl_3$ (20 mg, 9.1×10^{-5} mol, 8 mL of toluene) and run for 2 h. A toluene solution of 1,3-butadiene (680 mL, 3.1M) was then added and the polymerization was stopped after 2 h by addition of ethanol acidified with aqueous solution of hydrochloric acid. The blend was coagulated with ethanol containing the antioxidant Wingstay K (0.5 phr) and hydrochloric acid, and recovered by filtration. It was then washed with fresh ethanol and dried *in vacuo* at room temperature. Yield: 74 g.

Blends *in Situ* of *cis*-1,4-Polybutadiene with a Multiblock Syndiotactic Polystyrene-*co*-*cis*-1,4-Polybutadiene (sPSB−PB). The synthesis of *in situ* blends sPSB−PB was carried out using the following typical procedure, described for the sample containing 49 wt % of styrene monomer (sample **7**, Table 1). A 1 L flask equipped with a magnetic stir bar was charged with styrene (82.5 mL), MAO (58 mL, 10 wt % in toluene, Al/Ti molar ratio = 1000), and 1,3-butadiene (25 mL, 3.6 M in toluene, styrene/1,3-butadiene molar ratio = 12). After the equilibration of the solution at 25 °C, the reaction was started by injection of a toluene solution of CpTi(MBMP)Cl (43 mg, 8.8×10^{-5} mol, 8 mL of toluene) and run for 4.5 h. A toluene solution of 1,3-butadiene (76 mL, 3.6 M) was then added and the polymerization was stopped after 1 h by addition of ethanol. The blend was coagulated in ethanol containing the antioxidant Wingstay K (0.5 phr) and an aqueous solution of hydrochloric acid. It was then recovered by filtration, washed with fresh ethanol and dried *in vacuo* at room temperature. Yield: 25 g.

Blends *in Situ* of Syndiotactic Polystyrene with Multiblock Syndiotactic Polystyrene-*co*-*cis*-1,4-Polybutadiene and *cis*-1,4-Polybutadiene (sPS−sPSB−PB). The synthesis of *in situ* blends sPS−sPSB−PB was carried out using the following typical procedure, described for the sample containing 24 wt % of styrene (sample **9**, Table 1). A 3 L flask equipped with a magnetic stir bar was charged with toluene (520 mL), styrene (100 mL), and MAO (100 mL, 10 wt % toluene solution, Al/Ti molar ratio = 400). After equilibration of the solution at 25 °C, the styrene polymerization was started by injection of a toluene solution of $CpTiCl_3$ (80 mg, 3.6×10^{-4} mol, 10 mL of toluene) and run for 2 h. A toluene solution of 1,3-butadiene (18 mL, 3.2M) and MAO (100 mL, 10 wt % toluene solution, Al/Ti molar ratio = 1000) was added and the 1,3-butadiene-styrene copolymerization started by injection of a toluene solution of CpTi(MBMP)Cl (145 mg, 3×10^{-4} mol, 10 mL of toluene). After 15 min a toluene solution of 1,3-butadiene (520 mL, 3.3 M) was added and the polymerization was stopped after 3 h by addition of ethanol. The blend was coagulated in ethanol containing the antioxidant Wingstay K (0.5 phr) and an aqueous solution of hydrochloric acid, and recovered by filtration. It was then washed with fresh ethanol and dried *in vacuo* at room temperature. Yield: 113 g.

Blends sPS−PB Compatibilized with a Multiblock Syndiotactic Polystyrene-*co*-*cis*-1,4-Polybutadiene (c-sPS−PB−sPSB). In a typical experimental procedure, 19 g of the *in situ* synthesized sPS−PB blend (sample **2**, Table 1) were dissolved at room temperature in chloroform (1 L) containing the proper amount of antioxidant (Wingstay K, 0.5 phr) and cross-linking agent (dicumyl peroxide, 2 phr). A chloroform solution of the $sPS_{80}B$ copolymer (320 mg) was added to the mixture and the blend recovered by distilling off the solvent (sample **10**, Table 2).

Table 2. Blends sPS−PB Compatibilized by the Multiblock Copolymer sPSB

		starting blend sPS−PB	copolymer sPSB[b]		
blend	sample	composition (wt % in S)	composition (wt % in S)	amount[c] (wt %)	final composition (wt % in S)
c-sPS−PB−sPS$_{80}$B	**10**	15[a]	80	1.6	17
	11	34[a]	80	2.1	39
c-sPS−PB−sPS$_{57}$B	**12**	17	57	1.6	18
	13	17	57	3.8	19
	14	17	57	7.4	20

[a] See Table 1. [b] Multiblock copolymer synthesized as described in Experimental Section and in ref14. [c] Amount of copolymer used as compatibilizer (wt % of the total blend).

Table 3. Mechanical Properties (Derived from Stress−Strain Curves[a]) for sPS−PB, sPSB−PB, and sPS−sPSB−PB Blends after Treatment with Dicumyl Peroxide and Curing at 180 °C for 35 min

sample		styrene composition (wt %)	Young's modulus (MPa)	toughness (MPa)	σ_{break} (MPa)	$\varepsilon_{\mathrm{break}}$ (%)	ΔH_m[c] (J/g)	crystallinity[d] (%)
PB[b]		0	3.4 ± 0.1	0.4 ± 0.2	1.0 ± 0.3	58 ± 25		
sPS−PB	**1**	7	4.1 ± 0.6	0.2 ± 0.1	0.7 ± 0.1	38 ± 11		
	2	15	11 ± 1	2.0 ± 0.5	1.8 ± 0.2	147 ± 32	18	34
	3	34	101 ± 6	4.1 ± 0.4	7.4 ± 0.7	68 ± 5	21	39
	4	46	164 ± 18	0.2 ± 0.1	2.4 ± 0.7	4.8 ± 0.8	20	38
sPS$_{80}$B−PB	**5**	16	21 ± 4	0.3 ± 0.1	1.5 ± 0.7	22 ± 8		
	6	34	29 ± 3	0.8 ± 0.2	2.6 ± 0.4	43 ± 5		
	7	49	59 ± 6	0.9 ± 0.2	4.9 ± 0.3	27 ± 3	4	8
sPS−sPSB−PB	**8**	15	24 ± 1	1.5 ± 0.2	5.0 ± 0.3	48 ± 4	30	57
	9	24	31 ± 1	2.5 ± 0.9	4.1 ± 0.8	79 ± 30	35	65
c-sPS−PB−sPS$_{80}$B	**10**	17	13 ± 1	3.9 ± 0.2	2.6 ± 0.1	200 ± 13	16	31
	11	39	175 ± 5	1.3 ± 0.1	10.4 ± 0.4	18 ± 1	20	38
c-sPS−PB−sPS$_{57}$B	**12**	18	33 ± 4	1.5 ± 0.3	4.8 ± 0.4	55 ± 9	27	51
	13	19	34 ± 6	1.8 ± 0.4	5.0 ± 0.4	55 ± 10	28	53
	14	20	48 ± 5	2.1 ± 0.5	5.9 ± 0.6	51 ± 8	27	50
c-sPS−PB[e]	**15**	17	17 ± 1	0.2 ± 0.1	1.9 ± 0.1	20 ± 2	20	37
	16	34	41 ± 4	0.4 ± 0.2	1.5 ± 0.7	26 ± 6	22	41
	17	48	182 ± 16	0.03 ± 0.01	1.8 ± 0.6	2.2 ± 0.3	22	42

[a] Average values of at least three measurements. [b] *cis*-1,4-Polybutadiene produced with $CpTiCl_3$/MAO catalyst in the same experimental conditions of the *in situ* blends. [c] Enthalpy of melting of the crystalline polystyrene domains in the samples. [d] Relative crystallinity calculated assuming the reference value of 53.2 J/g corresponding to highly crystalline sPS. [e] sPS−PB blends produced by compounding the two homopolymers in chloroform solution.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). The polymer samples were dissolved in 1,1,2,2-tetrachloethane-d_2 (TCDE) solution (20 wt %) and analyzed at 100 °C. The ^{1}H and ^{13}C chemical shifts were referenced to tetramethylsilane (TMS) using the residual isotopic impurities of the deuterated solvent. The composition of blends was determined by integration of the ^{1}H resonances in the following region (δ in ppm, TCDE, 100 °C): 6.88 and 6.38 (5H, m, $CH_2CH(C_6H_5)$; 5.51 (1H, m, $CH_2CH_2(CH{=}CH_2)$ and 5.38 (2H, m, $CH_2CH{=}CHCH_2$). Similarly, the monomer composition of the syndiotactic polystyrene-*co*-*cis*-1,4-polybutadiene was determined by integration of the ^{1}H resonances in the following region (δ in ppm, TCDE, 25 °C): 7.07 and 6.56 (5H, m, $CH_2CH(C_6H_5)$; 5.58 (1H, m, $CH_2CH_2(CH{=}CH_2)$ and 5.23 (2H, m, $CH_2CH{=}CHCH_2$).

Thermal analysis was carried out on a TA Instrument DSC 2920 calorimeter (heating rate = 10 °C/min). Molecular weight and molar mass distribution of polymers were determined by gel permeation chromatography (GPC) analysis carried out at 30 °C, using THF as solvent and narrow MWD polystyrene standards for the calibration. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four columns (range of pore size 10^3−10^6 Å).

Wide-angle X-ray diffraction patterns with nickel-filtered Cu Kα radiation were obtained, in reflection, with an automatic Bruker powder diffractometer.

Optical microscope images were obtained using a Leica DM2500P polarizing microscope equipped with a digital camera.

Mechanical Properties Measurement (Tensile Tests). Stress−strain measurements were carried out on strips die-cut from pressed sheets (width, 6 mm; average thickness, 1 mm) by means of an Instron Series IX 4301 tensile testing dynamometer. The measurements were carried out at room temperature (25 °C); the cross-head speed was 5 mm/min and the gauge length 30 mm. The specimens were prepared by dissolving 15 g of the sample in chloroform (1 L) containing the cross-linking agent (dicumyl peroxide, 2 phr) and antioxidant (Wingstay K, 0.5 phr). The solvent was distilled off and the sample dried in vacuo until constant weight. Then it was pressed at room temperature in a square frame, cured at 180 °C in oven amid two steel plates protected by Teflon sheets and quenched in water.

Atomic Force Microscopy. AFM images of spin-coated polymer films were collected in tapping mode using a Nanoscope Dimension 3100 from Digital Instruments (Santa Barbara, CA). Commercial probe tips with nominal spring constants of 20−100 N m^{-1}, resonance frequencies in the range of 200−400 kHz, and tip radius of 5−10 nm were used. Topographic and phase contrast AFM images (image size: 1 μm × 1 μm) were acquired in air at room temperature.

The samples were prepared as follow by spin-coating of two or three drops (100 μL of total volume) of a chloroform solution (0.2 wt %) on a glass surface for 15−20 s under ambient conditions at a speed of 2000 rpm. The samples were analyzed by AFM soon later their preparation. To identify the rubber domain, the spin-coated sample was exposed to OsO_4 vapors (1 wt % water solution) for 25 min and then scanned by AFM, after preliminary analysis by optical microscope.

Results

Synthesis and Characterization of *in Situ* Blends of PB with sPS, of PB with sPS$_{80}$B, and of PB with sPSB and sPS. *In situ* blends of sPS with PB (sPS−PB; samples **1**−**4**, Table 1) were synthesized using a two step process. Styrene is polymerized first using the $CpTiCl_3$/MAO catalyst in toluene solution at 25 °C until to reach the expected monomer conversion, monitored by coagulation of aliquots of the polymerization solution. The reactor is thus fed with 1,3-butadiene in large excess and the reaction mixture left to react for the prescribed time. Under these conditions *cis*-1,4- specific polymerization of 1,3-butadiene mainly occurs because of the higher reactivity of this monomer compared to styrene (*vide infra*). The calibration in the two steps of both the monomer concentration in the feed and the polymerization time permitted to obtain sPS−PB blends with styrene concentration in the range of 7−46 wt % (samples **1**−**4**). The chemical composition of the blends was assessed by integration of the ^{1}H NMR signals diagnostic of the two monomers, namely the aromatic protons for styrene and olefinic protons for 1,3-butadiene. The average molecular weight of PB and sPS was determined by GPC analysis and found in the ranges 350−530 kDa and 30−50 kDa, respectively.

To assess the reinforcing contribution of sPS, the residual crystallinity of the polystyrene particles in the rubber matrix was evaluated by DSC (differential scanning calorimetry) analysis. The ΔH_m (enthalpy of melting) values were determined in the DSC profiles from the area of the endothermic peaks found in the temperature range of 250−270 °C. The relative crystallinity of samples **2**−**4** (see Table 3) was calculated assuming the reference value of 53.2 J g^{-1} corresponding to highly crystalline sPS.[15] The glass transition temperature T_g of polystyrene decreased from about 100 °C of the pure polystyrene to about 80 °C in the crude sPS−PB blends suggesting a penetration of the rubber in the amorphous phase of sPS.

Multiblock sPS-*co*-PB samples (sPSB) are soluble in toluene in a wide range of composition and of block lengths of crystalline polystyrene segments.[13,14] Blends of PB with sPSB are thus expected to yield phase separated materials in which the polystyrene domains are smaller and more homogeneously dispersed in the rubber matrix. A copolymer having a styrene concentration of 80 wt % ($sPS_{80}B$), styrene block length of 18, melting temperature of 247 °C and crystallinity of about 18% was chosen as test sample.

Blends of PB with variable amounts of the $sPS_{80}B$ were thus *in situ* synthesized ($sPS_{80}B$−PB, samples **5**−**7**, Table 1) by charging in sequence into the reactor the toluene solution of styrene and 1,3-butadiene in the appropriate relative concentration to yield the copolymer with the desired composition. The copolymerization reaction was started by injection of the CpTi(MBMP)Cl/MAO catalyst. This catalyst was preferred to $CpTiCl_3$ for the higher activity in styrene−1,3-butadiene copolymerization.[14] After the prescribed time a toluene solution of 1,3-butadiene was admitted to yield the PB fraction. Samples with a low styrene concentration (samples **5** and **6**) resulted completely amorphous at DSC analysis whereas the sample **7**, having a concentration of 49 wt % in styrene, showed a residual crystallinity of 8%. The melting temperature of the crystalline sPS domains was observed in this sample at 214 °C and T_g of polystyrene at 65 °C. The chemical composition of these blends, determined by the NMR method described above, are given in Table 1.

Blends of sPS and PB containing the *in situ* generated sPS-*co*-PB multiblock copolymer (sPS−sPSB−PB, samples **8** and **9**, Table 1) were synthesized using a three steps process. Styrene is polymerized for first using the titanium catalyst in toluene solution at 25 °C (Al/Ti molar ratio = 400). After the prescribed polymerization time, 1,3-butadiene was fed in such a calibrated concentration to yield the styrene-1,3-butadiene copolymer with the appropriate composition. Finally a toluene solution of 1,3-butadiene was added and the polymerization time was modulated to get the desired blend composition. The chemical composition of the samples **8** and **9** are reported in Table 1.

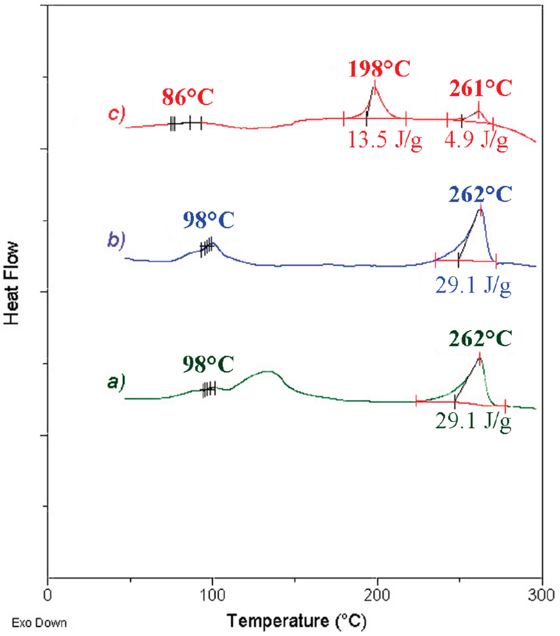

Figure 1. DSC traces showing the thermal behavior of the polymer fractions resulting from the synthesis of the sample **8**: (a) sPS from the first step; (b) mixture of sPS with sPSB copolymer from the second step; (c) mixture of sPS, sPSB, and PB at the end of the three steps polymerization.

The DSC analysis of sample **8** showed an interesting thermal behavior. Two endothermic peaks were found in the DSC curve (see Figure 1c) at 262 and 198 °C where the latter shows higher enthalpy of melting (13.5 vs 4.9 J g^{-1}). The endothermic peak at 262 °C is attributed to the melting of the δ crystalline form of sPS whereas the other one is quite unexpected. The DSC profiles of sPS and of the mixture of sPS with sPSB resulting from the first and second steps of the *in situ* polymerization process are displayed in Figures 1a,b, respectively. In this curves only the melting of the δ crystalline form of sPS is observed at 262 °C. The final product resulting from the three steps polymerization process, consisting of the two polymers compatibilized by the sPSB copolymer, exhibits the melting peak at 198 °C.

For a better understanding of the properties of the blends synthesized using the sequential process, **2** was blended with sPSB multiblock copolymers (samples **10**−**14**, c-sPS−PB−sPSB, Table 2) by mixing chloroform solutions of the polymers. This approach permits to calibrate the concentration and the composition of the copolymer sPSB used as compatibilizer. Samples of sPSB with two different compositions and monomer average block lengths were selected: (i) $sPS_{80}B$ with average styrene block length of 18, high solubility in toluene and with melting temperature of 247 °C (samples **10**−**11**); (ii) $sPS_{57}B$ containing average styrene block length of 10 and showing a melting temperature of 235 °C (samples **12**−**14**).

The thermal behavior of **10** and **11** confirmed the good compatibilizing role of $sPS_{80}B$. Actually low crystallinity values were found for these samples whereas values comparable or higher than those of the sPS−PB blends with the same composition were found in the case of the samples compatibilized with $sPS_{57}B$ (samples **12**−**14**; see Table 3). Thus, the

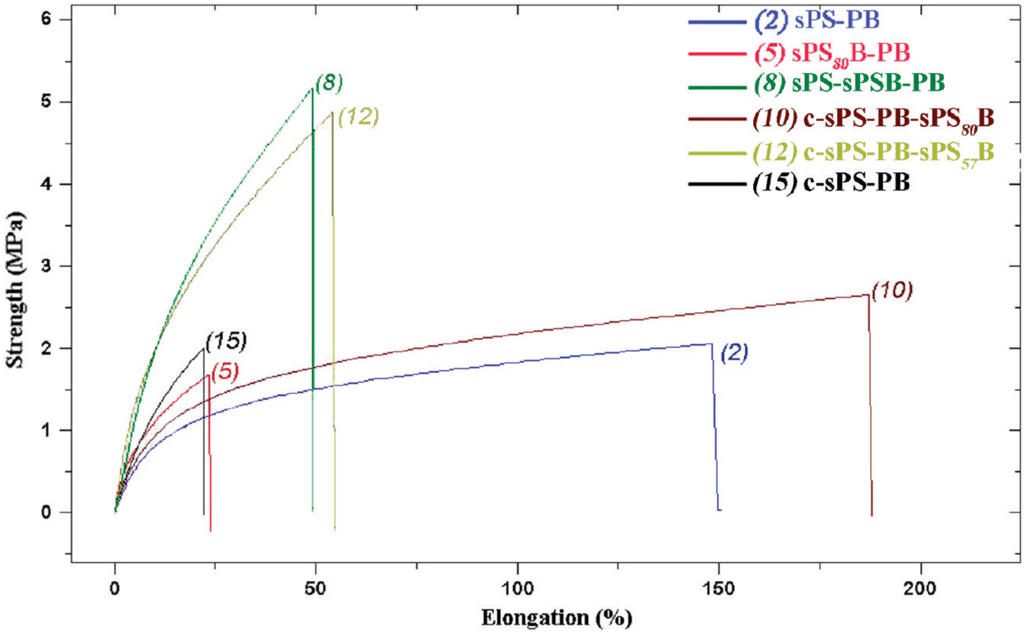

Figure 2. Stress−strain curves of the blends **2**, **5**, **8**, **10**, **12**, and **15**, cured at 180 °C for 35 min. The curves are the average value of three measurements.

sPSB copolymer containing long stereoregular styrene sequences did favor good mixing of the incompatible phases of sPS and PB.

Mechanical Properties of Blends sPS−PB, sPSB−PB, and sPS−sPSB−PB. The samples **1−14** were treated with dicumyl peroxide, cold pressed at room temperature to a thickness of 1 mm and then cured at 180 °C in oven to cross-link the polymer chains. An optimum cross-linking time of 35 min was assessed (*vide infra*) by the analysis of the stress−strain curves: longer curing time produced brittle samples as a consequence of degradation of the polymer matrix. After the thermal treatment with dicumyl peroxide, the T_g of polystyrene, determined by dynamic mechanical thermal analysis (DMTA), increased to about 120 °C suggesting that cross-linking process involves also the polystyrene phase.[18] The procedure herein described was found highly reproducible and the hot cured samples resulted completely insoluble in toluene. The polymer films were cut in rectangular strips and used for tensile tests.

Young's modulus, toughness, ultimate tensile strength (σ_{break}), and elongation at break ($\varepsilon_{\text{break}}$) of the samples **1−14** (Table 3) were compared with those of PB by $CpTiCl_3$/MAO catalyst used as reference. The mechanical properties of PB in the literature are inappropriate for a tight comparison because they are related to samples resulting from anionic polymerization catalyzed by alkyllithium compounds[19] or free radical polymerization,[20] where the stereo and regiochemistry of the monomer insertion are extremely variable and depend on the experimental conditions employed for the synthetic procedure. However, just for a comparison, typical literature values for PB are Young's modulus of 1−10 MPa, ultimate tensile strength of 1−17 MPa, and elongation at break of 50−650%.[16,21]

The Young's modulus of PB (*cis*-1,4 = 76%, *trans*-1,4 = 8%, vinyl-1,2 = 16%; M_w = 3.5 × 10^6 Da; PDI = 2.0) is rather low (3.4 MPa)[21] but increases more than 1 order of magnitude (see Table 3, samples **3** and **4**) when this polymer is *in situ* blended with sPS. Although this could be partly expected on the basis of the high modulus of sPS (3.4 GPa),[16] this effect is significantly higher than predicted on the basis of composition rule.[22] The toughness of the blends **1−4** increases of 1 order of magnitude at styrene content of 15−34 wt % but dramatically decreases at styrene concentration of 46 wt % where the blend becomes brittle likely because of the elevated concentration of the hard sPS particles. A similar trend was observed for the σ_{break}, directly depending on both modulus and toughness. The elongation at break, $\varepsilon_{\text{break}}$, reaches a maximum value that is three times greater than that of the control sample PB at styrene concentration of 15 wt % and dramatically decreases at higher concentration.

Blends of PB with sPSB (samples **5−7**) appeared macroscopically more homogeneous than samples **1−4** but the Young's modulus, toughness, σ_{break}, and $\varepsilon_{\text{break}}$ values are significantly lower at the same styrene composition.

The Young's modulus and toughness of the *in situ* blends sPS−sPSB−PB (samples **8** and **9**) are comparable to those of the *in situ* blends sPS−PB with the same composition (compare samples **2** and **8**). Despite the low styrene content, the ultimate strength was even comparable or superior to the value observed for the sPS−PB blends with higher styrene content (compare with samples **3**, **4**). This can be attributed to compatibilization of the main blend components operated by the sPSB copolymer.

To understand this role, the properties of samples of PB and sPS blended with two copolymers with different composition, namely $sPS_{80}B$ and $sPS_{57}B$, were analyzed. The blends containing $sPS_{80}B$ (samples **10** and **11**) showed an increase of the Young's modulus up to 175 MPa at styrene composition of 39 wt % and a remarkable value of σ_{break} attributed to the beneficial effect of the compatibilizer. When the styrene block length of the copolymer is reduced ($sPS_{57}B$), the Young's modulus and σ_{break} values of the corresponding blends remain still high but $\varepsilon_{\text{break}}$ is lower.

To check the reinforcement role played by the copolymer, the samples **12−14** were prepared by compounding the *in situ* blend sPS−PB with a variable amount of $sPS_{57}B$ (see Table 2): a regular increase of the tensile properties was observed when the copolymer amount is increased from 1.6 wt % (**12**) to 3.2 wt % (**13**) and 6.4 wt % (**14**).

In Table 3, the mechanical properties of compounded blends c-sPS−PB (samples **15−17**), obtained by mixing

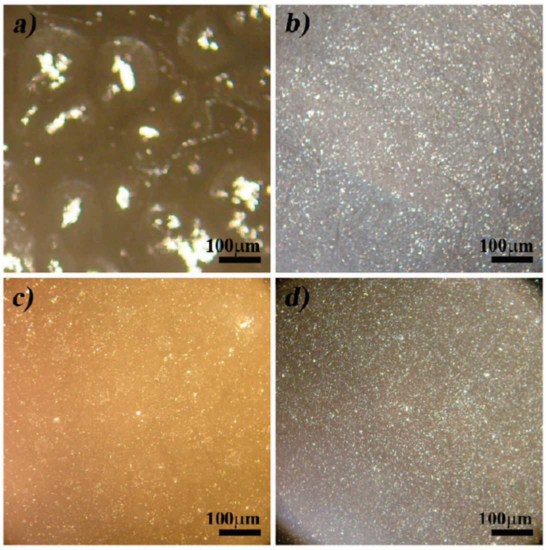

Figure 3. OM images of spin-coated film prepared from chloroform solutions (0.2 wt %) of samples **15** (a), **2** (b), **8** (c), and **10** (d).

chloroform solutions of PB and sPS, were also included for a comparison. The beneficial effect of the *in situ* synthetic procedure and the role of the sPSB copolymer as compatibilizer are somewhat immediate. The Young's modulus of the c-sPS−PB samples is the only property still high whereas all of the other properties, more depending on the dispersion of the thermoplastic additive, are rather poor. In Figure 2 a synoptical view on the mechanical performances of the investigated blends was reported.

Morphological Characterization of Blends sPS−PB, sPSB−PB, and sPS−sPSB−PB. To better understand the mechanical properties, we thoroughly characterized the morphology of the blends **1**−**17** by optical (OM) and atomic force microscopies (AFM). Staining with OsO_4 was used to enhance the image contrast between the two phases: actually, in the OM images, polybutadiene domains appeared as a dark phase in which the crystalline bright phase, consisting of polystyrene, can be easily distinguished.

The samples **2**, **8**, **10**, and **15** were preliminary analyzed by OM to check the texture of the blends (Figure 3). Thin films were prepared by spin-coating of chloroform solutions (0.2 wt %) of the polymers on glass microscope slides. A representative example of the compounded blends, namely the sample **15**, exhibits a coarse phase separated morphology consisting of sPS particles with average dimensions of about one hundred micrometers (Figure 3a). By contrast the samples **2** (Figure 3b), **8** (Figure 3c) and **10** (Figure 3d) show sPS particles with average dimensions of one micrometer or lower, homogeneously dispersed in the rubber matrix. This result proves the benefits of the *in situ* synthetic procedure and the compatibilizing effect of the multiblock copolymer sPSB.

The OM images of the blends **1**−**4** used for tensile tests exhibited, after staining with OsO_4, a phase-separated morphology consisting of hard particles of sPS appearing as white spot with average dimensions of few micrometers, homogenously dispersed in the PB matrix: a typical example is displayed in Figure 4. Unfortunately, the nanometric scale analysis by AFM was unsuccessful because of the roughness of the surface.

On the contrary AFM analysis of spin coated films of **1**−**4** showed a phase separated morphology in which the sPS particles are in nanometric scale. The topographic image in Figure 5 of the sample **2** (15 wt % in styrene) shows particles of sPS of few hundreds of nanometers. The hard nature of the small particles was confirmed by the phase image analysis. In tapping mode AFM, the shift of the cantilever oscillation phase gives information about the nature of the surface. Stiff materials produce a phase displacement and the hard domains appear in AFM phase image as a topographic prominences. Indeed the spots observed in the phase image of Figure 5b appear in Figure 5a as "*hills*" of small height.

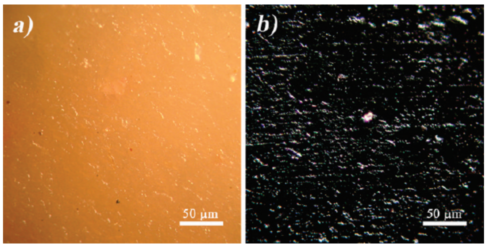

Figure 4. OM image of tensile test specimen of sample **2** (15 wt % in styrene) cut in liquid nitrogen (a) and after staining with OsO_4 (b).

In sample **10,** resulting from sample **2** compatibilized with the multiblock copolymer $sPS_{80}B$, the average dimensions of the styrene domains decrease to a few tenths of a nanometer.

The AFM phase image of the sample **8** (15 wt % in styrene) interestingly shows sPS particles of about one hundred nanometers or less, surrounded by a crown of tiny and rigid domains likely consisting of styrene-1,3-butadiene multiblock copolymer (Figure 6). Also in this case the tapping mode AFM confirms the different stiffness of the PB matrix and of the small sPS particles surrounded by a sphere of a polymer phase with intermediate properties.

The blends **5**−**7** used for tensile tests did not show any detectable phase separation between sPSB and PB also after staining with OsO_4. At styrene concentration of 49 wt % (sample **7**) a phase separation was observed, as highlighted by AFM analysis, where sPS domains of average size of about a few hundred nanometers were detected.

Discussion

A novel procedure for the *in situ* synthesis of blends of sPS and PB has been described using the $CpTiCl_3$/MAO homogeneous catalyst in a multistep polymerization process. This methodology permitted to explore for the first time the role of sPS, an engineering thermoplastic, as reinforcing agent of polybutadiene rubber. The Young's modulus of the sPS−PB samples **1**−**4** is found to be more than 1 order of magnitude higher than that of PB by the same catalyst and found to be comparable, in absolute value, to that of PB charged with carbon black or silica. The *in situ* blends **1**−**4** showed the same crystallinity and Young's modulus of the samples by solution casting with the same composition, namely **15**−**17**, but toughness is 1 order of magnitude higher as well as the elongation at break is significantly better. The modulus seems thus mainly dependent on the amount of the thermoplastic polymer added. Toughness is favored by the higher specific area of the sPS particles and good penetration of the rubber phase in the particles of the thermoplastic reinforcing agent, both resulting from in the *in situ* polymerization. Actually the sPS particles have dimensions less than a few micrometers in **1**−**4** vs tenths of micrometers in **15**−**17** and were more homogeneously dispersed in the rubber matrix. Moreover the T_g value of sPS decreased from the typical value of 105 °C for sPS to about 80 °C in the blends **1**−**4**. It is worth noting that also toughness, σ_{break}, and ε_{break} of these samples are higher than those of samples **15**−**17** with same composition produced by solution casting or hard mixing of the same polymers.

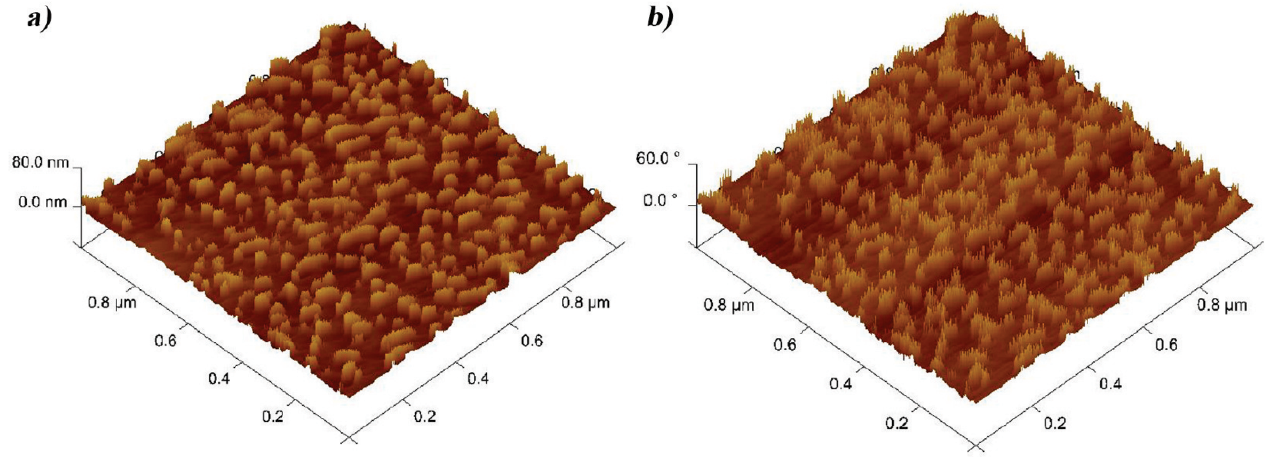

Figure 5. 3D tapping mode AFM height image (a) and phase image (b) of spin-coated film of sample **2** (scan size, 1 μm; z-scale, 80 nm).

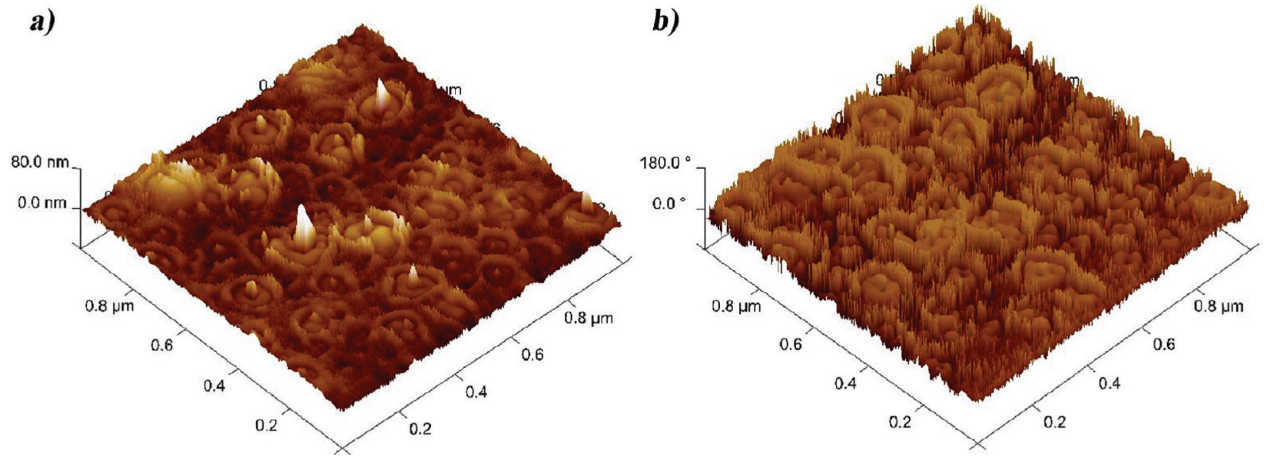

Figure 6. 3D tapping mode AFM height image (a) and phase image (b) of spin-coated film of sample **8** (scan size, 1 μm; z-scale, 80 nm).

In the present discussion we assumed that the samples **1**−**4** produced in the *in situ* process mainly consist of an intimate mixing of PB and sPS. However a trace amount of sPSB could be additionally produced after feeding with 1,3-butadiene in presence of unreacted styrene. We have previously shown that the block copolymer sPSB is synthesized only when the styrene/1,3-butadiene molar ratio in the feed is in the range of 5−14.[13,14] The presence of high concentration of 1,3-butadiene in the polymerization solution and the difference in the reactivity ratios of the two monomers ensure the formation of a blend containing mainly of the two polymers.

To understand the role of the sPSB copolymer, *in situ* blends of PB with $sPS_{80}B$ (samples **5**−**7**) were prepared using the same two steps process. The comparison of the mechanical properties for the sample **6** and **3** (styrene concentration of 34 wt %) shows a lower Young's modulus and toughness for the former due to good dispersion of the sPS phase in the rubber matrix. This is supported by the lower crystallinity detected by p-WAXS analysis of **5**−**7** samples and AFM analysis, in which sPS particles of few hundred of nanometers were detected. The mechanical properties of **5**−**7** are comparable if not better than those of polybutadiene samples blended with SSBR:[23] the segments of sPS in sPSB seem to be unable to form rigid domains and consequently their stiffening efficiency is lower than observed with sPS homopolymer.

The samples **8**−**9** consist of *in situ* blends of sPS, PB and sPSB synthesized using a three-step process. They appear macroscopically very homogeneous. A good compromise of the mechanical properties has been reached in these two samples. Young's modulus is comparable to that of **1**−**4** and **5**−**7** as well as toughness, σ_{break}, and ε_{break}. Interestingly, the compatibilizing role of the sPSB copolymer was highlighted by the AFM analysis, in which one can observe sPS particles of about 100 nm surrounded by a region consisting of tiny and rigid domains lying at the interface between the thermoplastic phase and the rubber matrix. In the DSC curve of the sample **8** an additional crystalline phase was detected showing lower melting temperature and ΔH of melting higher than that of δ phase of sPS. Attempts to characterize this crystalline phase were thus carried out. The p-WAXS analysis of the native sample **8** showed the presence of the δ crystalline form of sPS in which toluene molecules resulting from the polymerization solution are clathrated in the voids of the crystalline phase.[24] When this sample was heated at 120 °C the endothermic peak at 198 °C disappears while the peak at 262 °C persists, suggesting that the novel crystalline phase is thermally unstable above the T_g of sPS. Low melting temperature values in the range 205−230 °C were previously observed in the DSC profiles of the sPSB copolymers with styrene molar fraction of 0.40−0.98.[13,14] This phenomenon is typically observed when domains of sPS are intimately mixed with PB. The low crystallinity degree of these samples did not permit a full characterization of the crystalline phase by X-ray diffraction. Studies on this issue are currently in progress and will be reported elsewhere.

The styrene block length and the crystallinity in the sPSB copolymer were found both to affect the compatibilizing properties of the sPS−PB blends. When the sample **2** was blended with $sPS_{80}B$ (samples **10**, **11**) and $sPS_{57}B$ (samples **12**−**14**) the $sPS_{80}B$ copolymer, having higher styrene block lengths and crystallinity, well compatibilizes sPS and PB as documented by the lower crystallinity of samples **10** and **11**. At styrene concentration of 17 wt % (sample **10**) good elongation at break was found whereas sample **11** exhibits Young's modulus significantly higher than sPS−PB blends **1**−**4**. The high crystallinity of sPS domains in samples **12**−**14** produce high values of Young's modulus and σ_{break}. The overall performances of these blends appear very similar to that of the not compatibilized samples **1**−**4**.

Conclusions

Blends *in situ* of sPS with PB were synthesized in a two-step process using $CpTiCl_3$/MAO catalyst in toluene at 25 °C. The sPS−PB samples were cured with dicumyl peroxide at 180 °C in a range of cross-linking time before being undergone to the analysis of the mechanical properties.

The presence of crystalline sPS produced an increase of the Young's modulus of PB of 1 order of magnitude or more at styrene concentration of 34 and 46 wt %. Young's modulus, toughness and properties at break of these blends are remarkably higher than those of PB or the corresponding samples produced by mechanical mixing or solution casting of the two polymers. The sPSB multiblock copolymer *in situ* generated (2 wt %) acts as compatibilizer of the sPS−PB blends. The sPS particles dimension decreased in these samples to about one hundred nanometers and a novel phase was detected by AFM at the interface of sPS particles and PB matrix characterized. Moreover an additional melting temperature at 198 °C was observed in the DSC profile of the compatibilized blend samples.

The dimensions of the sPS particles decreased from few hundred of nanometers in the *in situ* synthesized blends sPS−PB to few tenths of nanometers in the compounded blends c-sPS−PB−sPSB. Enhanced Young's modulus up to 175 MPa at styrene concentration of 39 wt % were found for the latter as a consequence of the reduced dimension of sPS domains and enhanced hydrodynamic effect of the sPS particles. The toughness takes also advantage from this morphology determining propagation of the fractures more difficult.

These results highlight the role of sPS as reinforcing agent of PB rubber and the ability of the *in situ* multistep polymerization process to yield high performance materials with tunable properties.

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Supporting Information Available: Text discussing and figures showing AFM micrographs of samples **7** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ashby, M. F. *Material selection in mechanical design*; Butterworth-Heinemann: Oxford, U.K., 1999.
(2) Koga, T.; Hashimoto, T.; Takenaka, M.; Aizawa, K.; Amino, N.; Nakamura, M.; Yamaguchi, D.; Koizumi, S. *Macromolecules* **2008**, *41*, 453.
(3) Halasa, A. F.; Hsu, W.-L.; Armstrong, S. K. *Method of making alkoxy functionalized rubbery polymers*. U.S. Patent 11,682,050, **2007**.
(4) Colvin, H. A.; Chen, S. L. *Reinforced silica/elastomer composite*, U.S. Patent 10,021,200, **2001**.
(5) Paul, D. R.; Robeson, L. M. *Polymer* **2008**, *48*, 3187.
(6) Alexandre, M.; Dubois, P. *Mater. Sci. Eng., R: Rep.* **2000**, *28*, 1.
(7) Ciesielski, A. *An Introduction to Rubber Technology*; Rapra Technology Ltd: Shawbury, U.K., 1999.
(8) Muraki, T.; Tajima, M. *Improvements in rubber for medical or pharmaceutical articles*. EP 324554 A1 19890719, **1989**.
(9) Weng, W.; Jacob, S.; Jiang, P.; Dekmezian, A. H.; Mehta, A. K.; Ayers, J. R.; Lohse, D. J.; Manders, P. W.; Arjunan, P. *Processes for preparing thermoplastic vulcanizates and articles*. PCT WO 2007142742 A1, **2007**.
(10) Higuchi, H.; Nagasawa, H. *Solid golf ball comprising polybutadiene rubber core and thermoplastic polyurethane cover*. U.S. Patent 293,226, **2008**
(11) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 271.
(12) Oliva, L.; Longo, P.; Grassi, A.; Ammendola, P.; Pellecchia, P. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 519.
(13) Caprio, M.; Serra, M. C.; Bowen, D. E.; Grassi, A. *Macromolecules* **2002**, *35*, 9315.
(14) Cuomo, C.; Serra, M. C.; González-Maupoey, M.; Grassi, A. *Macromolecules* **2007**, *40*, 7089.
(15) Malanga, M. *Adv. Mater.* **2000**, *12*, 1869.
(16) Mark, J. E. *Polymer Data Handbook*; Oxford University Press: New York, 1999.
(17) González-Maupoey, M.; Cuenca, T.; Frutos, L. M.; Castaño, O.; Herdtweck, H. *Organometallics* **2003**, *22*, 2694.
(18) The DSC analysis of the specimens used for tensile tests did not permit us to evaluate the T_g of polystyrene because of an overlap with the exothermic peak due to the cross-linking. For this reason the T_g was determined by DMTA analysis in bending mode.
(19) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization principles and practical applications*; Marcel Dekker, Inc.: New York, 1996.
(20) Moad, G.; Solomon, D. H. *The Chemistry of free radical polymerization*, 1st ed.; Elsevier Science Ltd.: New York, 1995.
(21) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*; John Wiley & Sons, Inc.: New York, 1999.
(22) Lipatov, Y. S. *Polymer Reinforcement*: ChemTech Publishing: Toronto, Canada, 1995.
(23) Kwang, G.; Kim, P.; Han, S.; Lee, S.; Choi, H.; Kim, S. *J. Appl. Polym. Sci.* **2007**, *105*, 477.
(24) (a) D'Aniello, C.; Rizzo, P.; Guerra, G. *Polymer* **2005**, *46*, 11435. (b) Milano, G.; Guerra, G. *Prog. Mater. Sci.* **2009**, *54*, 68.