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Electronic Supplementary Information

Interfacial interaction modes construction of various functional SSBR–silica to high filler dispersion and excellent composites performances

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1. Synthesis of SSBR samples

SSBR was synthesized via an anionic copolymerization under dry nitrogen atmosphere at 50 °C in a 2-L stainless steel reactor. Cyclohexane, *n*-BuLi, and DMTHFA were used as solvent, initiator, and regulator, respectively. The St, Bd, and DMTHFA were dissolved in cyclohexane in the 2-L stainless steel reactor. The mass ratio of St to Bd was 25:75. After the solution was stirred for 20 min, the appropriate amount of *n*-BuLi was then added into the 2-L stainless steel reactor. The molar ratio of DMTHFA to *n*-BuLi was 0.82:1. The anionic copolymerization was carried out at 50 °C for 2 h, and then ethanol was added to the reactant solution to terminate the copolymerization.

2. Formulations of silica/F-SSBR composites

Table S1. Formulations of silica/F-SSBR composites.

Samples	Silica/SSBR	Silica/SSBR/Si69	Silica/F-SSBR
SSBR (phr[a])	100	100	0
F-SSBR (phr[a])	0	0	100
Silica (phr[a])	50	50	50
Si-69 (phr[a])	0	4	0
Zinc oxide (phr[a])	2.5	2.5	2.5
Stearic acid (phr[a])	1	1	1
Antionxidant 4020[b] (phr[a])	2	2	2
CBS[c] (phr[a])	1.4	1.4	1.4
DPG[d] (phr[a])	1.5	1.5	1.5
Sulfur (phr[a])	1.4	1.4	1.4

[a] Parts-per-hundred rubber.

[b] *N*-1,3-dimethylbutyl-*N*'-phenyl-P-phenylenediaminee.

[c] *N*-cyclohexyl-2-beozothiazole sulfonamide.

[d] 1,3-diphenylguanidine.

3. Crosslink density measurements of silica/F-SSBR vulcanizates

A square test vulcanizate was immersed into toluene. The swollen vulcanizate was weighed every 12 h until the mass was constant (i.e., swelling equilibrium). After reaching swelling equilibrium, the vulcanizate was carefully removed from the toluene, and the toluene on the vulcanizate surface was sucked away by a filter paper. Then, the vulcanizate was weighed (m_1) and dried in an oven at 80 °C for 60 h to steam off all the toluene. The final mass of the vulcanizate was recorded as m_2. The crosslink density ν_e of the vulcanizate was calculated by the Flory–Rehner equation:[1,2]

$$\nu_e = -\frac{\ln(1-\nu_r) + \nu_r + \chi\nu_r^2}{V_s(\nu_r^{1/3} - 0.5\,\nu_r)} \quad \text{(S1)}$$

where ν_r, χ, and V_S are the volume fraction of the polymer, interaction parameter between SSBR and toluene, and the molar volume of the toluene (105.7 cm^3/mol), respectively. v_r was determined by the equation:[3]

$$v_r = \frac{(m_2 - m_{ins})/\rho_r}{(m_1 - m_2)/\rho_s + (m_2 - m_{ins})/\rho_r}$$

(S2)

where m_{ins} is the weight of the insoluble components in the test vulcanizate, ρ_r is the density of rubber, and ρ_s is the density of toluene (0.867 g/cm^3).

The χ was determined by the equation:[4,5]

$$\chi = \frac{V_s\,(\delta_r - \delta_s)^2}{R\,T} + 0.34$$

(S3)

where V_S is the molar volume of the toluene (105.7 cm^3/mol), δ_r is the solubility parameters of the rubber, and δ_S is the solubility parameters of the toluene.

4. Synthesis of F-SSBRs

Table S2. Characteristics of SSBR and F-SSBRs.

Samples	Compositions[a] (wt%)				$M_n \times 10^{-4}$ (g·mol^{-1})	M_w/M_n
	Styrene units	Butadiene units		Grafted mercaptans +reacted 1,2-Polybutadiene units		
		1,2-Polybutadiene units	1,4-Polybutadiene units			
SSBR	22.5	42.7	34.8	0	18.1	1.11
SSBR-*g*-MPL70	23.0	40.1	31.4	5.5	18.5	1.15
SSBR-*g*-MUA70	20.9	39.5	29.6	10.0	18.6	1.11
SSBR-*g*-MPTES13	18.4	47.8	31.7	2.1	18.6	1.10
SSBR-*g*-MPTES42	17.9	45.0	30.4	6.7	18.7	1.16
SSBR-*g*-MPTES70	21.1	38.7	29.6	10.6	19.6	1.11

[a] The compositions of SSBR and F-SSBRs were calculated through the analysis of ^{1}H NMR by using Eqs. (S4)–(S8).

The compositions of SSBR and F-SSBRs were estimated from the ^{1}H NMR spectra by using Eqs. (S4)−(S8):

$$\frac{2N_{Bd1,4}+N_{Bd1,2}}{2N_{Bd1,2}}=\frac{A_{5.10-5.90}}{A_{4.45-5.10}}$$

(S4)

$$N_{Bd1,4}+N_{Bd1,2}=1 \qquad \text{(S5)}$$

$$\frac{xN_{Mercaptan}}{2N_{Bd1,2}}=\frac{A_{Methylene-H}}{A_{4.45-5.10}}$$

(S6)

$$\frac{5N_{St}}{2N_{Bd1,2}}=\frac{A_{6.70-7.23}}{A_{4.45-5.10}}$$

(S7)

$$M_{Bd}\times N_{Bd1,4}+M_{Bd}\times N_{Bd1,2}+M_{St}\times N_{St}+M_{Mercaptan}\times N_{Mercaptan}+M_{Bd}\times N_{Mercaptan}=M_n \qquad \text{(S8)}$$

where $N_{\mathrm{Bd1,2}}$, $N_{\mathrm{Bd1,4}}$, N_{St}, and $N_{\mathrm{Mercaptan}}$ represent the molar numbers of 1,2-polybutadiene units, 1,4-polybutadiene units, styrene units, and mercaptan units in the F-SSBR, respectively. $A_{4.45–5.10}$, $A_{5.10–5.90}$, and $A_{6.70–7.23}$ represent the NMR peak areas in the ranges of δ = 4.45–5.10, 5.10–5.90, and 6.70–7.23 ppm, respectively. $A_{\mathrm{Methylene\text{-}H}}$ represents the NMR peak areas of methylene protons in -C$\boldsymbol{H}_2$OH, -C$\boldsymbol{H}_2$COOH, and -Si-(OC$\boldsymbol{H}_2$CH$_3$)$_3$, respectively. The "x" denotes, respectively, the hydrogen atom numbers of methylene protons in -C$\boldsymbol{H}_2$OH, -C$\boldsymbol{H}_2$COOH, and -Si-(OC$\boldsymbol{H}_2$CH$_3$)$_3$. For SSBR-*g*-MPL, $A_{\mathrm{Methylene\text{-}H}}$ is the NMR peak areas in the range of δ = 3.70–3.85, and "x" is "2". For SSBR-*g*-MUA, $A_{\mathrm{Methylene\text{-}H}}$ denotes the NMR peak areas in the range of δ = 2.30–2.40, and "x" is "2". For SSBR-*g*-MPTES, $A_{\mathrm{Methylene\text{-}H}}$ represents the NMR peak areas in the range of δ = 3.80–3.92, and "x" is "6".

The grafting percentage (GP) of mercaptan based on SSBR was calculated from ^{1}H NMR spectra by using Eq. (S9).

$$GP\%=\frac{M_{Mercaptan}\times N_{Mercaptan}}{M_{Bd}\times N_{Bd1,4}+M_{Bd}\times N_{Bd1,2}+M_{St}\times N_{St}+M_{Bd}\times N_{Mercaptan}}\times 100\%$$

(S9)

5. Torque values of SSBR, F-SSBRs and their compounds

Table S3. Torque values of SSBR, F-SSBRs and their compounds.

Samples	M_H/dN.m	M_L/dN.m	M_H-M_L/dN.m
SSBR	15.29	11.27	4.02
Silica/SSBR	20.47	17.67	2.80
SSBR-*g*-MPL70	14.01	13.90	0.11
Silica/SSBR-*g*-MPL70	16.77	15.15	1.62
SSBR-*g*-MUA70	8.73	8.66	0.07
Silica/SSBR-*g*-MUA70	42.65	29.84	12.81
SSBR-*g*-MPTES70	13.44	13.05	0.39
Silica/SSBR-*g*-MPTES70	83.94	32.88	51.06

6. Dispersion of silica in F-SSBR matrix

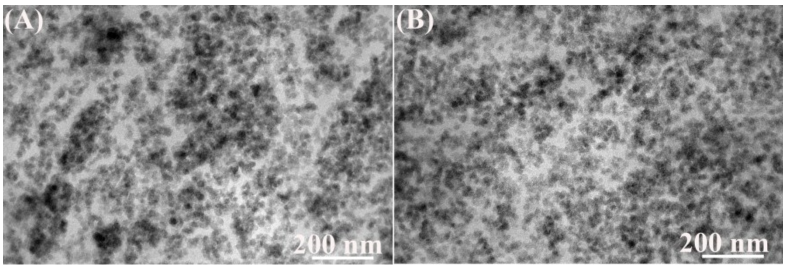

Fig. S1. TEM micrographs of (A) silica/SSBR-*g*-MPTES13 and (B) silica/SSBR-*g*-MPTES42 vulcanizates.

7. Tan δ values at 7% strain of all vulcanizates

Table S4. Tan δ values at 7% strain of silica/SSBR, silica/SSBR/Si69, and silica/F-SSBR vulcanizates.

Samples	Tan δ values at 7% strain
Silica/SSBR	0.132
Silica/SSBR/Si69	0.112
Silica/SSBR-*g*-MPL70	0.104

Silica/SSBR-*g*-MUA70	0.096
Silica/SSBR-*g*-MPTES13	0.110
Silica/SSBR-*g*-MPTES42	0.086
Silica/SSBR-*g*-MPTES70	0.065

8. Mechanical properties of all vulcanizates

Table S5. Mechanical properties of silica/SSBR, silica/SSBR/Si69, and silica/F-SSBR vulcanizates.

Samples	Modulus at 100% strain (MPa)	Modulus at 300% strain (MPa)	Elongation at break (%)	Tensile strength (MPa)
Silica/SSBR	1.5	9.0	452	15.0
Silica/SSBR/Si69	2.6	12.8	406	21.0
Silica/SSBR-*g*-MPL70	4.2	N/A[a]	200	14.2
Silica/SSBR-*g*-MUA70	6.3	23.3	340	26.0
Silica/SSBR-*g*-MPTES13	2.8	N/A[a]	275	18.2
Silica/SSBR-*g*-MPTES42	3.2	N/A[a]	248	12.8
Silica/SSBR-*g*-MPTES70	11.0	N/A[a]	105	11.9

[a] Not available because of the low elongation at break.

9. Dynamic property parameters of all vulcanizates

Table S6. Dynamic property parameters of silica/SSBR, silica/SSBR/Si69, and silica/F-SSBR vulcanizates.

Samples	Tan δ_{max}	T*g*/°C	Tan δ (0 °C)
Silica/SSBR	0.640	-9.0	0.472
Silica/SSBR/Si69	0.727	-9.2	0.514
Silica/SSBR-*g*-MPL70	1.010	-0.9	1.004
Silica/SSBR-*g*-MUA70	1.284	-2.1	1.233
Silica/SSB-*g*-MPTES13	1.335	-8.9	0.886
Silica/SSB-*g*-MPTES42	1.353	-3.9	1.210
Silica/SSB-*g*-MPTES70	1.360	-1.1	1.342

References

1 P. J. Flory and J. Rehner, *J. Chem. Phys.*, 1943, **11**, 521–526.

2 P. J. Flory and J. Rehner, *J. Chem. Phys.*, 1943, **11**, 512–520.

3 W. Salgueiro, A. Somoza, A. J. Marzocca, I. Torriani and M. A. Mansilla, *J. Polym. Sci., Part B: Polym. Phys.*, 2009, **47**, 2320–2327.

4 A. J. Marzocca, *Eur. Polym. J.*, 2007, **43**, 2682-2689.

5 C. J. Sheehan and A. L. Bisio, *Rubber Chem. Technol.*, 1966, **39**, 149-192.