Silica-Modified SBR/BR Blends

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ABSTRACT: The purpose of this article is that the silica-modified SBR/BR blend replaces natural rubber (NR) in some application fields. The styrene-butadiene rubber (SBR) and *cis*-butadiene rubber (BR) blend was modified, in which silica filler was treated with the r-Aminopropyltriethoxysilane (KH-550) as a coupling agent, to improve mechanical and thermal properties, and compatibilities. The optimum formula and cure condition were determined by testing the properties of SBR/BR blend. The properties of NR and the silica-modified SBR/BR blend were compared. The results show that the optimum formula was 80/20 SBR/BR, 2.5 phr dicumyl peroxide (DCP), 45 phr silica and 2.5 mL KH-550. The best cure condition was at 150°C for 25 min under 10 MPa. The mechanical and thermal properties of SBR/BR blend were obviously modified, in which the silica filler treated with KH-550. The compatibility of SBR/BR blend with DCP was better than those with benzoyl peroxide (BPO) and DCP/BPO. The crosslinking bonds between modified silica and rubbers were proved by Fourier transform infrared analysis, and the compatibility of SBR and BR was proved by polarized light microscopy (PLM) analysis. The silica-modified SBR/BR blend can substitute for NR in the specific application fields. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3695–3700, 2011

Key words: styrene-butadiene rubber; *cis*-butadiene rubber; blend; silica; KH-550; modification

INTRODUCTION

With the development of automobile industry, the demand of rubber is more and more all over the world, but the supply of rubber cannot satisfy the requirements so far. The prices of the rubbers have been increasing in recent years, and natural rubber (NR) price has been from 2000 to 5000 U.S. dollar per ton.[1] In addition, with rapid development of polymer science, its multiplicate uses are needed, the polymeric materials synthesized from single monomer have been unable to meet performance requirements in many fields. The synthetic rubbers blend does not only improve its physical and chemical properties, and processing method, but also reduce the product cost.[2,3]

BR as shown in Figure 1(a), is structured molecules, its elasticity is the best of all rubbers, and the glass transition temperature is −105°C, so it has good physical properties at low temperature. Its heat resistance is 120°C like NR, but the heat aging properties are superior to NR.

The styrene-butadiene rubber (SBR) as shown in Figure 1(b), is a rubber copolymer synthesized from the butadiene and styrene, its adhesivity, oil resistance, and elasticity are not as good as NR, but wear, heat aging, water resistance, and gas tightness are superior to NR.[4–6]

NR with excellent performance is widely applied in the aerospace, defence industry,[7] heavy-duty truck,[8] and medical fields.[9] However, NR price is more expensive than that of synthetic rubber, and the sources are the shortage.

On the basis of the above mentioned, the attention of the experts is focused on the synthetic rubbers replacing NR at present, such as Wu et al.[10] have studied that improved the mechanical properties of the SBR/BR by multiphase blending methods. Li and Qu[11] have investigated flame-retardant and antistatic rubber materials. But, the mechanical and heat aging properties of the SBR/BR blend are worse than NR. Therefore, the purpose of this experiment is that the SBR/BR blend is reinforced with silica. The silica surfaces were treated with r-Aminopropyltriethoxysilane (KH-550, $NH_2CH_2CH_2CH_2Si\ (OC_2H_5)_3$), which is a silane-coupling agent, to improve the mechanical and thermal properties, thus replaces NR with excellent performance.

EXPERIMENTAL

Materials

SBR (1500, styrene content 23.5 wt %, 1,2-vinyl content 20% and 1,4-cis isomer content 78% in butadiene reaction, number-average molecular weight 1.5 ×

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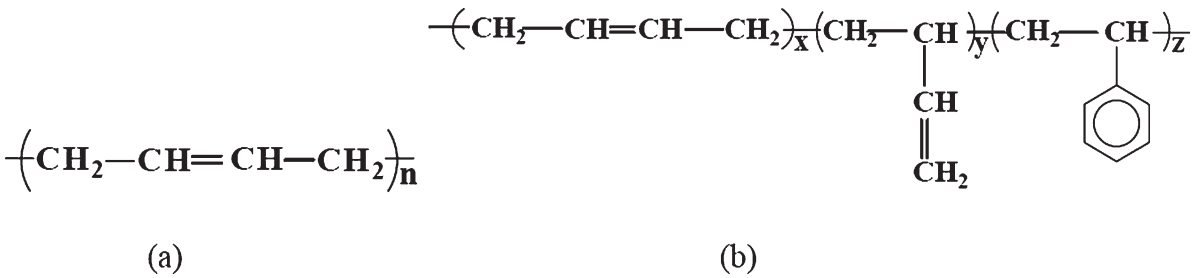

Figure 1 Chemical structures of BR (a) and SBR (b).

10^5, Sichuan Changshou Chemical Plant Changshou, China), BR (BR-9000, 1,4-cis-content 96%, number-average molecular weight 6.0×10^5, Jinzhou Petrochemical Ltd. Jinzhou, China). Silica (N539, Anshan Chemical Plant Anshan, China). The other ingredients are all commercial materials on the market.

Specimen preparation

Firstly, rubbers are cut into short, dried previously, and masticated on XK-160 two-roll mill (Tianjin Electrical Machinery Plant, Tianjing, China) at 45°C for 10 min, while the nip gap was about 0.5 mm. Secondly, the mixed rubber is prepared by adding various ingredients shown in Table I. The processing order is as follows: BR+SBR or NR (raw rubbers masticated) →Zinc oxide (ZnO), N-phenyl-β-naphthylamine (antioxidant D)→silica, stearic acid→mercapto- benzothiazole (accelerator M) →dicumyl peroxide (DCP), benzoyl peroxide (BPO), or sulfur, adjusted up into 50–60°C, the distance between two rolls was 4.0 mm for 30 min. At last, the mixtures of different compositions were moulded in an electrically heated hydraulic press (XLB-D350 × 350, Shanghai First Rubber Machinery, Shanghai, China) at 150°C for 20 min under 10 MPa.

In addition, the silica is mixed by adding KH-550 and stearic acid in high-mix machine at 80°C for 10min, for the silica-modified SBR/BR preparation,

Characterization

Tensile tests are performed on dumbbell-shaped specimens according to ISO 37-1994 at 300 mm/min. Shore A hardness is measured on the thickness of 6 mm according to ISO 48-1994. Wear attrition is determined according to BS903A9 by using an Akron machine (MN-74 Jiangsu Jiangdu Non-metallic Materials Manufacturer, Jiangdu, China), the specimens are made by using a wheel cutter. The cut films of the samples are observed by a polarized light microscopy (PLM) (Nanjing Dongli Industrial Ltd. Nanjing, China).

Heat aging (thermal properties) is worked out by a 401-B air aging oven at 200°C for 24 h (Jiangsu Test Mechanical Ltd. Suzhou, China) according to ISO 188-1998.

The infrared spectra of the blended samples are recorded using an IR-7685 Fourier transform infrared (FTIR) spectrometer (Shanghai Analyzer Plant, Shanghai, China) ranged from 4000 to 500 cm^{-1} at room temperature.

For each of the measurements, an average of at least five readings is taken. Errors in the measurement of mechanical and thermal properties are 10 and 11%, respectively.

RESULTS AND DISCUSSION

Effect of SBR/BR mass ratio on its properties

The effects of SBR/BR mass ratio on its properties are reported in Table II. The hardness, tensile strength, and elongation at break of SBR/BR blend are bigger than pure SBR and BR. As the amount of SBR increased in the recipe, the hardness and tensile strength are gradually increasing, whereas the elongation at break decreasing, but the wear presents the irregular change. When SBR/BR mass ratio is 80/20, the mechanical and heat aging properties are the best. It may be seen that SBR is stronger than other rubber in the mechanical properties, and SBR content in the SBR/BR composition is more than BR, so the mechanical properties of the SBR/BR 80/20 are improved.

Effect of KH-550 coupling agent on the blend properties

Because the mechanical and thermal properties of SBR/BR blend are not ideal, silica is treated with KH-550 before blending rubbers. As seen in Table III, the tensile strength, elongation at break and wear

TABLE I
Fundamental Formulation of the Mixes (phr)

SBR+BR or NR	Silica	ZnO	Stearic acid	Sulfur	Antioxidant D	Accelerator M
100	45	5	5	5	1	2.5

Phr is parts per hundred rubbers.

TABLE II
Effects of the SBR/BR Mass Ratio on the Vulcanizate Properties

	Shore A hardness		Tensile strength (MPa)		Elongation at break (%)		Wear (cm^3/1.61 km)	
SBR/BR	B	A	B	A	B	A	B	A
0/100	57	81	4.91	3.32	144	24	0.04	0.26
20/80	64	84	4.84	3.68	395	26	0.12	0.25
25/75	75	87	5.11	3.58	202	28	0.11	0.25
30/70	76	87	5.68	3.97	197	27	0.06	0.24
70/30	67	87	5.92	3.64	195	27	0.07	0.21
75/25	68	89	7.80	4.02	172	28	0.03	0.15
80/20	82	89	7.80	4.02	172	28	0.03	0.15
85/15	80	87	6.51	3.08	156	27	0.05	0.15
100/0	61	88	3.17	3.64	40	26	0.05	0.25

B: Physical properties before heat ageing.
A: Physical properties after heat ageing.

of the blend with KH-550 are better than those without, Shore A hardness does not vary considerably before and after heat aging, it can be thought that the mechanical and thermal properties of SBR/BR blend have markedly improved by adding KH-550. The best dosage of coupling agent is 2.5 mL. The modified silica,[12–16] the reaction mechanism of which is shown in Figure 2, can easily form physical entanglement and chemical crosslinking between rubbers and silica. But the blend remains lower mechanical properties, especially thermal properties.

Effect of crosslinking agents on the SBR/BR properties

As mentioned above, DCP and BPO are used as the crosslinking agents to improve SBR and BR compatibility, aimed at improving the performance of SBR/BR blend. The experimental results are shown in Table IV, tensile strength, elongation at break and wear are distinctly improved except the hardness. It can be thought that DCP and BPO make rubbers crosslink, so that the intermolecular action is increased, and the mechanical thermal properties improved. In addition, the SBR/BR performances with BPO and DCP/BPO are inferior to those with DCP, and the results are not any regularity. With two kinds of materials' compatibility principle, the construction and polarity of DCP are more similar than BPO for SBR and BR, so the compatibility of SBR/BR blend with DCP is better than that with BPO and BPO/DCP. By overall evaluating, when crosslinking agent DCP is added 2.5 phr, the mechanical and thermal properties of SBR/BR blend are the best, and the optimum formula of SBR/BR blend is SBR 80, BR 20, sulfur 5, zinc oxide 5, stearic acid 5, antioxidant D 1, silica 45, accelerant M 2.5, DCP 2.5 phr, and KH-550 2.5mL.

Effect of cure condition on the SBR/BR properties

The vulcanization is a process, during which the mixed rubbers are crosslinked, and chemical reactions are occurred under certain temperature and pressure. Three essential factors of the vulcanization are the cure temperature, pressure and time, of which temperature is the most important. Enhancing temperature can shorten cure time, and increase productivity. But the rubber is a poor heat conductor. For thick rubber products, the higher temperature will increase the difference between the inside and outside temperature of the mixed rubber, which

TABLE III
Effect of the KH-550 Content on the SBR/BR Properties

	Shore A hardness		Tensile strength (MPa)		Elongation at break (%)		Wear (cm^3/1.61 km)	
KH-550 (mL)	B	A	B	A	B	A	B	A
0	82	89	7.80	4.02	172	25	0.03	0.15
2.0	85	83	8.62	4.53	728	382	0.05	0.07
2.5	82	88	9.16	6.94	765	507	0.04	0.05
3.0	84	79	8.37	6.79	733	488	0.05	0.06
3.5	80	85	9.55	6.22	733	336	0.05	0.08
4.0	88	86	7.78	6.51	723	444	0.05	0.07

SBR/BR is 80/20.

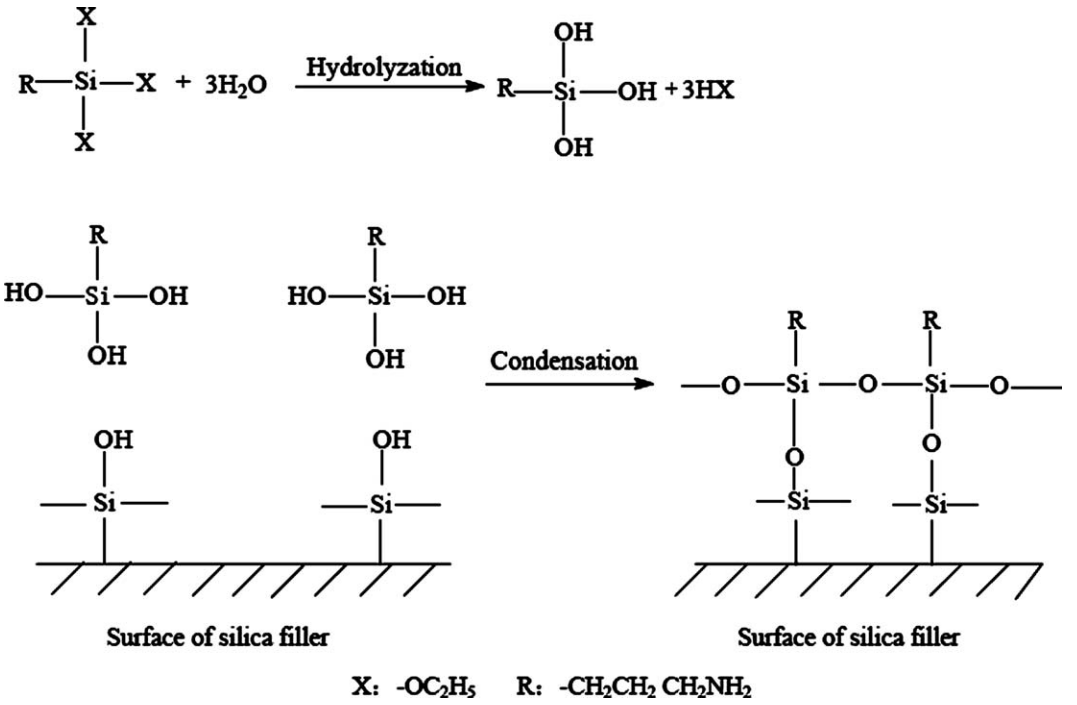

Figure 2 The reaction mechanism of silica modified with KH-550.

leads the inconsistency of cure degree, while thin product is on the contrary. The mixed rubbers are generally cured under a certain pressure, which depends on the nature of the rubber, processing conditions, the product properties and so on.

As can be seen in Table V, when the cure temperature is low or high, the tensile strength, hardness and wear are worse such as they are over 160°C or less than 130°C, but the mechanical and thermal properties of the vulcanizate are the best at 150°C. It can be seen that the cure temperature is less than 130°C, the sample are in a lack of vulcanization, and SBR and BR do not crosslink fully. When the cure temperature is more than160°C, over cure occurs, and crosslinking networks break down, so the blends properties decrease.

TABLE IV
Effect of the Crosslinking Agents on the SBR/BR Properties

	Shore A hardness		Tensile strength (MPa)		Elongation at break (%)		Wear (cm^3/1.61 km)	
Crosslinking agent	B	A	B	A	B	A	B	A
DCP (phr)								
0	82	88	9.16	6.94	765	507	0.04	0.05
2.0	89	88	9.55	6.74	792	556	0.03	0.05
2.5	86	88	9.66	7.35	724	588	0.03	0.04
3.0	84	87	9.48	7.08	721	514	0.04	0.04
3.5	83	86	9.56	7.39	715	509	0.04	0.04
BPO (phr)								
2.0	83	85	8.24	6.95	639	549	0.04	0.05
2.5	84	86	8.88	7.57	698	557	0.03	0.05
3.0	82	85	8.95	7.54	749	526	0.04	0.05
3.5	81	81	8.96	7.84	738	491	0.05	0.06
DCP/BPO								
1/1	82	82	9.19	7.32	768	521	0.04	0.05
1/2	79	84	9.08	7.08	722	525	0.03	0.04
1/3	84	79	9.29	6.94	744	550	0.03	0.05
2/1	85	86	9.65	6.99	747	514	0.04	0.04
3/1	82	85	9.38	7.29	775	578	0.05	0.05

SBR/BR is 80/20, KH-550 is 2.5 mL.

TABLE V
Effect of the Cure Condition on the SBR/BR Properties

	Shore A hardness		Tensile strength (MPa)		Elongation at break (%)		Wear (cm^3/1.61km)	
Cure conditions	B	A	B	A	B	A	B	A
Temperature (°C, 10 Mpa × 20 min)								
130	58	61	6.66	5.35	321	378	0.09	0.13
140	67	72	7.73	6.08	406	378	0.05	0.07
150	86	88	9.66	7.35	724	588	0.03	0.04
155	85	84	9.34	8.43	657	509	0.05	0.06
160	78	68	8.87	7.92	626	461	0.06	0.07
Pressure(MPa, 150°C × 20 min)								
8	58	61	6.74	5.59	670	548	0.05	0.06
9	71	75	7.47	6.88	711	562	0.04	0.06
10	86	88	9.66	7.35	724	588	0.03	0.04
11	85	89	8.80	6.90	684	495	0.04	0.05
Time (min, 150°C × 10 MPa)								
10	41	39	4.13	3.63	603	293	0.07	0.06
15	76	79	7.27	6.11	695	410	0.05	0.05
20	86	88	9.66	7.35	724	588	0.03	0.04
25	89	91	10.67	8.09	762	620	0.03	0.05
30	73	74	7.18	7.31	681	487	0.04	0.05

It is optimum formula that SBR: BR: sulphur: zinc oxide: stearic acid: antioxidant D: silica accelerant M: DCP is 80: 20: 5: 5: 5: 1: 45: 2.5: 2.5, and KH-550 2.5 mL.

TABLE VI
Comparison of the Vulcanizate Properties of SBR/BR and NR

	Shore A hardness		Tensile strength (MPa)		Elongation at break (%)		Wear (cm^3/1.61 km)	
Rubbers	B	A	B	A	B	A	B	A
SBR/BR[a]	89	91	10.67	8.09	762	620	0.03	0.05
NR[b]	62	75	12.50	7.20	747	491	0.21	0.32

[a] It is the optimum formula. The cure conditions are 150°C for 25 min under 10 MPa.
[b] The formula is shown in TableI. The cure conditions are 150°C for 25 min under 10 MPa.

The results appear turning point under the cure pressure 10 MPa except that wear little change, and are the worst under 8 MPa because the samples are not pressed fully lead to delaminate. But the over pressure would accelerate sample breaking down under 11 MPa, and affect mechanical properties of the SBR/BR blends.

However, the results are bad when the cure time is 10 or 30 min, because the blend cannot crosslink for 10 min in a lack of time. When the cure time is more than 30 min, the crosslinked blends are broken down, and the blends appear over curing phenomena. All properties integrated, the best cure condition is 150°C for 25 min under 10 MPa.

Comparison of the vulcanizate properties of SBR/BR and NR

The comparison of the properties of NR and SBR/BR blend is shown in Table VI. It can be seen that the mechanical and thermal properties of silica-modified SBR/BR blend are better than those of NR except tensile strength before heat aging. Therefore, the SBR/BR blend can substitute for NR in the

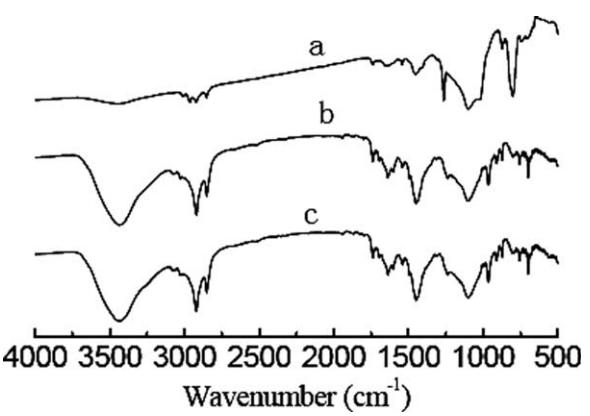

Figure 3 The FT-IR spectra of (a) SBR/BR, (b) SBR and (c) BR, in which SBR/BR is in the optimum formula and cure condition.

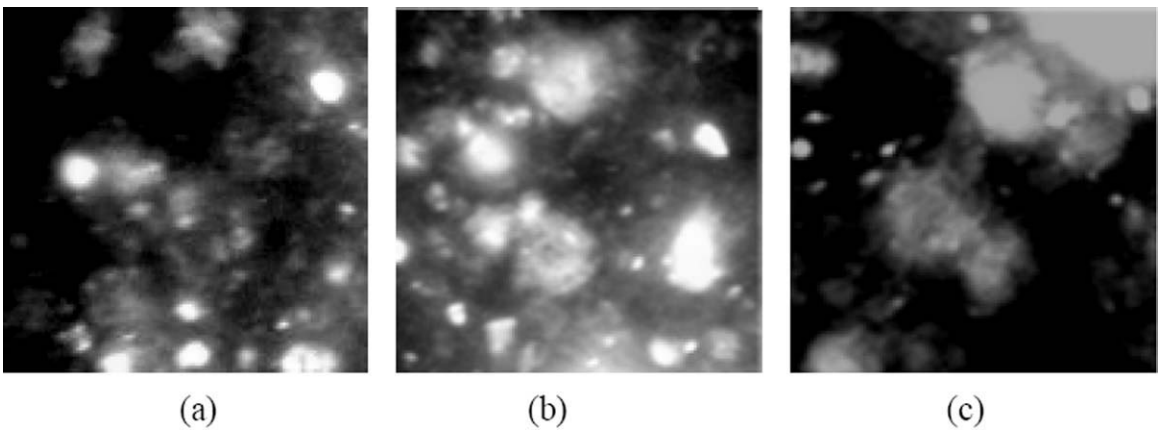

Figure 4 The polarizing microscope photographs of (a) SBR, (b) BR and (c) SBR/BR for magnification 400, in which SBR/BR is in the optimum formula and cure condition.

specific application fields such as flexibility, wear, thermal properties and so on.

IR analysis of SBR/BR blend

FTIR spectra of SBR/BR blend (a), SBR (b), and BR (c) are shown in Figure 3. The spectra of SBR and BR not only remains H—O stretching vibration peak at 3434 cm^{-1}, CH_2 absorption peak at 2919 and 1449 cm^{-1}, COO stretching vibration peak 1739 and 1237 cm^{-1}, and C=C absorption peak 1639 cm^{-1}, but the spectrum of SBR/BR blend also presents Si—O—Si and Si-CH_3 characteristic peaks at 1300 and 1260 cm^{-1} separately. It suggests that the crosslinking bonds between modified silica and SBR/BR blend are formed, so the mechanical and thermal properties of the silica-modified SBR/BR blend are better than those of pure SBR or BR.

Polarizing microscope analysis of SBR/BR blend

As shown in Figure 4, SBR and BR show the obvious spherulite growth, the average diameter is about 200 μm, the crystal morphology has changed after two rubbers blended as shown in Figure 4(c). It makes spherulites extrude and impact each other, so the formation of spherulite is difficult. The silica-modified SBR/BR blend can be not seen the intact spherulite morphology, only seen the crystal string. It suggests that the blend of SBR and BR can not only affect the crystal nucleation, but also changes the crystal growth way, and results in the improvement of their performances. In terms of the crystal morphology of the blend, the compatibility between SBR and BR is improved.

CONCLUSIONS

In summary, SBR and BR were blended by the adjustment of the SBR/BR formulation and the control of the cure condition. The mechanical and thermal properties of the silica-modified SBR/BR blend were improved. The optimum formula was 80/20 SBR/BR, 2.5 phr DCP, 45 phr silica, and 2.5 mL KH-550. The best cure condition was at 150°C for 25 min under 10 MPa. The mechanical and thermal properties of SBR/BR blend were obviously modified, in which the silica filler treated with KH-550. The compatibility of SBR/BR blend with DCP was better than those with BPO and DCP/BPO. The crosslinking bonds between modified silica and rubbers were proved by FTIR analysis, and the compatibility of SBR and BR was proved by PLM analysis. The silica-modified SBR/BR blend can substitute for NR in the specific application fields.

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