

The influence of the NR/BR blend ratio on the performance of railway freight car shock-absorbing rubber compound

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Abstract: This article investigates the influence of the blending ratio of natural rubber (NR) and butadiene rubber (BR) on the performance of railway freight car damping rubber compounds, focusing on vulcanization characteristics, Mooney scorch performance, physical and mechanical properties, and thermo-oxidative aging properties. The results indicate that as the proportion of BR increases, the scorch time of the rubber compound extends, the vulcanization rate slows down, and the Mooney viscosity rises. The Shore A hardness, tear strength, tensile strength, elongation at break, and modulus at 100% deformation of the vulcanizate decrease, while the resilience and wear resistance improve. The thermo-oxidative aging properties show a downward trend. When the NR/BR ratio is 60/40, the tensile strength reaches 23.1 MPa, the modulus at 100% deformation attains 2.8 MPa, the tear strength achieves $114 \text{ kN} \cdot \text{m}^{-1}$, the Mooney viscosity is moderate, the rubber compound exhibits good fluidity, and the overall performance is optimal.

Key words: shock-absorbing rubber compound; natural rubber; butadiene rubber; blending ratio

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Natural rubber possesses excellent physical and mechanical properties as well as good processing characteristics, and is widely used as shock-absorbing material in various fields such as bridges and tunnels, engineering construction, automobile manufacturing, rail transit, aerospace, and more. However, the physical and mechanical properties of its rubber compound cannot meet the high standards required for shock absorption in certain applications, necessitating the blending with other rubber types to enhance its performance and broaden its application scope. Zhang Song et al. investigated the influence of the plasticizing process on the properties of natural rubber/brominated butyl rubber (NR/BIIR) blends with different viscosities and polarities. The results indicated that the rubber compound without undergoing specialized plasticizing and aging processes exhibited superior performance in terms of tensile strength, 100% modulus, shear modulus, 170% damping ratio, and horizontal equivalent stiffness. In terms of thermal oxidative resistance, the rubber compound that underwent specialized plasticizing and aging

processes demonstrated slightly better resistance. Cheng Anren et al. studied the effects of vulcanizing agent dosage and radiation vulcanization process on the properties of EPDM/NR vulcanizates before and after aging. The findings revealed that the radiation vulcanized rubber outperformed traditional vulcanized rubber in terms of thermal oxidative aging resistance, tensile strength, and elongation at break.

The cis-polybutadiene rubber (BR) molecular chain exhibits good flexibility, high resilience, excellent low-temperature performance, and good flex resistance, and has good compatibility with natural rubber (NR). The combination of the two can further improve the mechanical properties, thermal stability, and other properties of the rubber compound.

Biography: Hu Boyuan (1992-), a master's graduate and intermediate engineer, primarily focuses on researching damping materials for railway freight cars.

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Zhang et al. prepared NR/BR composites with a blend ratio of 80/20 using carbon nanotubes and ethanol-assisted mixing. The results showed that the tensile strength, tear strength, and thermal stability were improved after the uniform distribution of carbon nanotubes. Li et al. studied the self-heating and fatigue crack propagation behavior of reinforced NR/BR nanocomposites at different blend ratios. The results showed that when the NR/BR blend ratio was 70/30, the dissipative self-heating of the system was most pronounced; as the BR blend ratio increased, the critical tear energy (T_c) showed a downward trend.

Currently, research on rubber compound for railway freight car shock absorption mainly focuses on vulcanization process research, shock absorber life prediction, and structural improvement. There is a need to strengthen the exploration of the comprehensive performance change laws and optimization improvement of rubber compound. Therefore, this paper studies the change laws of vulcanization characteristics, Mooney scorch performance, physical and mechanical properties, and thermo-oxidative aging performance of NR/BR blends, and explores the NR/BR blend ratio that yields the best comprehensive performance of the shock absorber rubber compound.

1 Experimental part

1.1 Main raw materials

NR: Grade RSS1, Thailand; BR: Grade BR9000, Qilu Petrochemical Company; N550, N774: Qingzhou Boao Company; white carbon black (HM-6175MP): Jiangxi Black Cat Carbon Black Co., Ltd.; silane coupling agent (Crosile): Aikepu New Material Co., Ltd.; microcrystalline wax (ZT-880): Foster Rubber and Plastic Technology Co., Ltd.; zinc oxide, stearic acid (SA1801), antioxidant RD, sulfur preventer, and accelerator NOBS are all commercially available rubber industrial grade products.

1.2 Instruments and equipment

SS-8060M type internal mixer: Taiwan Songshu Co., Ltd.; SS-8060K type double-roll open mill: Taiwan Songshu Co., Ltd.; MDR S3L type closed rotorless vulcanometer: Taiwan Songshu Co., Ltd.; MV S3L type Mooney viscosity tester: Taiwan Songshu Co., Ltd.; SS-5709 type hot air aging oven: Taiwan Songshu Co., Ltd.; SY-6210-A type electric air

blower: Shiyan Precision Instrument Co., Ltd.; MX-1080 type electronic tensile testing machine: Jiangsu Moxin Industrial System Co., Ltd.; JK-DIN 05 type DIN abrasion tester: Jiangsu Jiangkai Mechanical Equipment Co., Ltd.; ELB-JJ-3005 type rubber impact resilience tester: Yinglai Bo Technology (Hunan) Co., Ltd.

1.3 Test formula

The shock-absorbing rubber used is a blend of NR and BR. The basic experimental formula (in parts by mass) is: NR/BR variables (100/0, 60/40, 50/50, 40/60, 0/100), N330 22-28, N774 32-38, silica 4-10, silane coupling agent 0.4-1.0, zinc oxide 5-8, stearic acid 1-2, antioxidant 3.5, protective wax 2, naphthenic oil 4, and vulcanization system (vulcanizing agent and accelerator) 3.

1.4 Sample preparation

1.4.1 Raw rubber plasticization

Place NR in a forced-air drying oven and bake the rubber for 4 hours at 60°C. After baking, pass it through a double-roll mill for 8 to 10 times for thin-pass and set it aside for later use.

1.4.2 Raw rubber mixing

Set the feeding temperature of the internal mixer to 60~70°C, the upper ram pressure to 0.6~0.8Mpa, and the rotor speed to 60r/min. Mix the raw rubber for 2 minutes, then add zinc oxide and stearic acid and mix for 1.5 minutes; add naphthenic oil and half of the carbon black and mix for 2 minutes, continue to add the remaining carbon black, antioxidant, and protective wax and mix for 2 minutes; clean the flying powder and add it to the mixing chamber, reduce the speed to 40r/min and mix for 1.5 minutes before discharging the rubber. After cooling, add sulfur and accelerator on the open mill, mix evenly, then sheet out and place it for later use.

1.5 Performance testing

The vulcanization characteristics are tested according to GB/T 1233-2008 at 150 °C. The tensile strength, modulus at a fixed extension, and elongation at break are tested according to GB/T 528-2009, using Type 1 dumbbell-shaped samples with a thickness of 2.0 ± 0.2 mm, a width of 6~6.4 mm, and a tensile speed of (500 ± 50) mm/min. The test results are median values. The tear strength is tested according to GB/T 529-2008, using right-angle samples and a tensile speed of (500 ± 50) mm/min. The test results are median values. The Shore A hardness is tested according to GB/T 531-2008. Before testing,

ensure that the sample surface is clean and flat. Measurements are taken at different locations on the sample surface five times and the median value is recorded. The compression set is tested according to GB/T 7759.1-2015, using Type A samples. The Mooney viscosity is tested according to GB/T 1232.1-2000, using a large rotor. The samples are preheated for 1 minute and tested for 4 minutes. The same sample is tested twice and the average value is recorded. The Mooney scorch performance is tested according to GB/T 1233-2008. Other performance tests are conducted according to national standards.

2 Results and Discussion

2.1 The influence of NR/BR blend ratio on the vulcanization characteristics of shock-absorbing rubber compounds

Figure 1 illustrates the impact of the NR/BR blend ratio on the vulcanization characteristic curve of shock-absorbing rubber compound. Table 1 presents the effect of the NR/BR blend ratio on the vulcanization characteristic parameters of the shock-absorbing rubber compound. As can be seen from Figure 1 and Table 1, with an increase in the BR proportion, the minimum elastic torque M_L , maximum elastic torque M_H , and torque difference $M_H - M_L$ gradually increase, indicating an increase in the crosslinking density of the rubber compound. The vulcanization initiation time t_{s1} , process optimal vulcanization time t_{90} , and vulcanization rate slow down, while the vulcanization plateau range widens. This is because the molecular chain flexibility of BR is superior to that of NR, and its bulk viscosity and Mooney viscosity are higher

than those of NR. As the BR blend ratio increases, the melt viscosity of the rubber compound increases, corresponding to an increase in the minimum torque during the initial stage of the vulcanizer test. Secondly, the NR molecular chain contains a large number of double bonds and side groups with methyl groups, exhibiting high reactivity; the BR molecular chain is high cis-1,4-polybutadiene, with lower reactivity of double bonds than BR, resulting in a longer vulcanization induction period and reaction cycle. As the BR blend ratio increases, the vulcanization reaction rate decreases, and t_{s1} and T_{c90} prolong. Finally, as the BR blend ratio increases, the distribution of vulcanizing agents and accelerators in the two phases tends to favor the low reactivity phase, leading to an amplified difference in vulcanization rates between the two phases. The torque increase process is slower, with no obvious steep step segment.

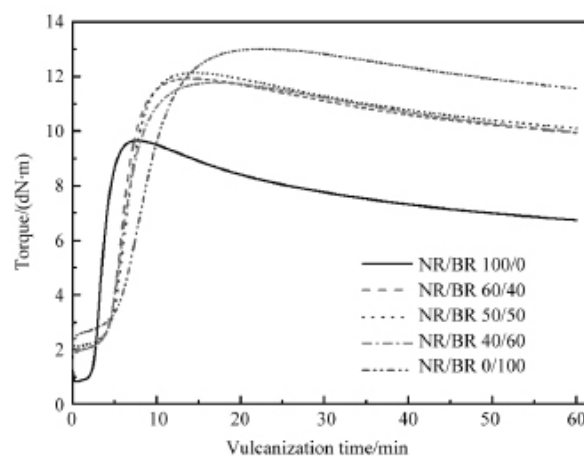


Figure 1 Vulcanization characteristic curve of NR/BR with different blending ratios at 150 °C

Table 1 Changes in vulcanization characteristic parameters with NR/BR blend ratio

Blended ratio	M_L /dN·m	M_H /dN·m	$M_H - M_L$ /dN·m	t_{s1} /min	t_{10} /min	t_{90} /min	Sulfidation plateau period/min
100/0	0.819	9.665	8.846	2.67	2.63	5.15	5.15~16.19
60/40	1.960	11.944	9.984	4.43	4.43	8.70	8.70~32.79
50/50	2.075	12.145	10.07	4.65	4.65	9.28	9.28~32.54
40/60	1.859	11.796	9.937	4.30	4.28	9.82	9.82~37.80
0/100	2.356	13.025	10.669	5.03	5.17	13.55	13.55~48.63

2.2 The influence of NR/BR blend ratio on the Mooney scorch performance of shock-absorbing rubber compounds

Table 2 shows the influence of the NR/BR blend ratio on the Mooney scorch performance parameters of the shock-absorbing rubber compound, and Figure 2 illustrates the effect of the NR/BR blend ratio on the Mooney scorch performance

of the shock-absorbing rubber compound. From Figure 2 and Table 2, it can be observed that as the BR proportion increases, the minimum Mooney value (L_M), maximum Mooney value (M_1), and Mooney viscosity (M_v) increase. The Mooney scorch time (t_s) and Mooney vulcanization time (t_{35}) are prolonged, and the Mooney vulcanization rate ($t_{35} - t_s$) slows down. This indicates that an increase in the BR proportion leads to

an increase in the viscosity of the shock-absorbing rubber compound, a slower Mooney vulcanization rate, and a delayed vulcanization effect.

Figure 2 The influence of NR/BR blend ratio on the Mooney scorch performance of shock-absorbing rubber compound

Table 2 Changes in Mooney scorch performance parameters of shock-absorbing rubber compounds with varying NR/BR blend ratios

Serial number	ratio	L_M	M_I	t_5	t_{35}	$t_{35}-t_5$	M_V
1	100/0	19.518	31.871	20:56	24:51	03:55	28.866
2	60/40	39.260	57.771	29:36	36:47	07:10	43.097
3	50/50	41.892	66.415	31:26	39:01	07:35	33.672
4	40/60	37.384	54.563	31:43	39:02	07:19	50.876
5	0/100	50.728	80.402	32:34	41:22	08:48	60.652

2.3 Effect of NR/BR blending ratio on the physical and mechanical properties of shock-absorbing rubber compound

The influence of the NR/BR blend ratio on the physical and mechanical properties of the shock-absorbing rubber compound is shown in Table 3. Table 3 reveals that as the proportion of BR increases, the Shore A hardness, tear strength, tensile strength, elongation at break, and modulus at 100% of the vulcanizate decrease, while the resilience and wear resistance increase. When the blend ratio of the two is 60/40, the comprehensive performance of the rubber compound is optimal. At this point, the tear strength reaches 114 kN·m⁻¹, and the tensile strength and modulus at 100% are 23.1 MPa and 2.8 MPa, respectively. This is primarily due to the more regular and flexible molecular chains of butadiene rubber, which easily return to their normal state after being stressed. Additionally, the internal friction (tanδ) is lower when stressed, resulting in less energy loss and better stress dispersion, thus resisting mechanical damage during wear. Natural rubber molecular chains have pendant groups, which form a denser cross-linked network after vulcanization, effectively transmitting stress when stressed and preventing local tear propagation. However, the cross-linked network of butadiene rubber is relatively loose, making it prone to chain breakage when stress is concentrated.

2.4 The influence of NR/BR blend ratio on the thermo-oxidative aging properties of shock-absorbing rubber compound

Table 4 shows the impact of the NR/BR blend ratio on

Table 3 Effect of NR/BR blending ratio on the physical and mechanical properties of shock-absorbing rubber compound

Performance	NR/BR blend ratio				
	100/0	60/40	50/50	40/60	0/100
Shore A hardness	65	64	62	61	58
Tear strength / (kN·m ⁻¹)	118	114	112	109	75
Resilience /%	70.5	71.4	72.0	73.1	74.8
Wear resistance (volume reduction) / mm ³	166	141	140	138	105
Tensile strength / MPa	24.8	23.1	21.5	18.9	14.7
Elongation at break, %	469	505	488	512	417
100% modulus/MPa	3.1	2.8	2.7	2.4	1.8

the thermo-oxidative aging properties of shock-absorbing rubber compounds. The evaluation was conducted from four aspects: changes in Shore A hardness, tensile strength, elongation at break, and compression set. The results indicate that as the proportion of BR increases, the thermo-oxidative aging properties of the rubber compound show a downward trend, indicating that the thermo-oxidative aging properties of BR are inferior to those of NR. The main reason is the difference in reaction activity of unsaturated double bonds and intermolecular forces in their molecular structures. The BR molecular chain has a regular -CH₂-CH=CH-CH₂ structure, and the methylene-CH₂-hydrogen atoms adjacent to the double bonds are more active and more prone to undergo hydrogen abstraction reactions under the influence of heat and oxygen, leading to molecular chain breakage or crosslinking. However, the NR molecular chain contains pendant methyl groups, which form steric hindrance to the double bonds and adjacent hydrogen atoms, reducing their reaction activity towards oxidation. In addition, the pendant methyl groups in the NR molecular chain increase intermolecular forces, causing the molecular chains to pack more tightly, which to some extent hinders the diffusion of oxygen molecules into the rubber. On the other hand, the BR molecular chain lacks pendant groups, resulting in weak intermolecular forces, making it easier for oxygen molecules to penetrate and accelerating the thermo-oxidative aging process.

4 Conclusion

(1) As the BR ratio increases, M_L , M_H , and M_H-M_L gradually increase, t_{s1} and t_{90} are prolonged, the vulcanization rate slows down, and the range of the vulcanization plateau widens. L_M , M_I , and M_V increase, t_5 and t_{35} are prolonged, and

Table 4 The influence of NR/BR blend ratio on the thermo-oxidative aging properties of shock-absorbing rubber compound

Thermo-oxidative aging performance		NR/BR blend ratio				
		100/0	60/40	50/50	40/60	0/100
70 °C ×24h	"Shao A hardness change"	0	1	1	1	2
	Change in tensile strength /%	-1.28	-2.43	-2.88	-2.97	-3.58
	Change in elongation at break, %	-5.1	-8.9	-9.8	-10.7	-13.4
Compression set/%		19.1	22.4	23.7	23.9	26.6

t_{35} - t_5 slows down.

(2) With the increase in BR ratio, the Shore A hardness, tear strength, tensile strength, elongation at break, and modulus at 100% increase, while the resilience and wear resistance

improve, and the thermo-oxidative aging performance tends to decrease. When the NR/BR ratio is 60/40, the comprehensive performance of the rubber compound is the best.