

Study on the properties of SBR/POE blended rubber with peroxide/sulfur carrier composite vulcanization system

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Abstract: This paper employs different peroxide/sulfur carrier combinations and vulcanization systems to test the vulcanization characteristics and mechanical properties of SBR/POE blended rubber, exploring the impact of sulfur carriers on the vulcanization process and properties of the blend. The study shows that the BIPB/DTDM and BIPB/TMTD/DTDM vulcanization systems can enhance the vulcanization reaction rate of the blended rubber; the tensile strength, modulus at a given extension, hardness, and wear resistance of the BIPB/TMTD, BIPB/DTDM, and BIPB/TMTD/DTDM combination systems are all higher than those of BIPB/S, but the elongation at break is lower, and the aging properties are poorer.

Key words: peroxide; sulfur carrier; sulfurization characteristics; mechanical properties

Classification number: TQ330.7

Article number: 1009-797X(2026)04-0036-04

Document code: B

DOI: 10.13520/j.cnki.rpte.2026.04.010

Styrene-butadiene rubber (SBR) is obtained through copolymerization of butadiene and styrene monomers. Classified by polymerization method, it can be divided into emulsion-polymerized styrene-butadiene rubber (ESBR) and solution-polymerized styrene-butadiene rubber (SSBR). SBR has good processability, excellent wear resistance, and wet skid resistance, and is commonly used in tire tread rubber. However, it has poor elasticity and high heat build-up. POE generally refers to polyolefin elastomers such as ethylene-octene copolymers. The presence of polyethylene segments can endow POE with certain crystallization capabilities, thereby enhancing its load-bearing capacity. Meanwhile, the good flexibility of octene and ethylene long chains provides elasticity, exhibiting outstanding elasticity, mechanical properties, and aging resistance. When SBR is blended with POE, it can improve the elasticity of SBR, reduce heat build-up, enhance aging resistance, and expand the application scope of SBR. Therefore, exploring the properties and adjustments of SBR/POE blends holds certain research significance.

Research on the influence of peroxide and sulfur carrier

composite curing systems on rubber properties has achieved certain results. For example, Hu Weiwei and others explored the application of the BIPB/S/DTDM/CZ composite curing system in EPDM rubber hose rubber compound, and concluded that compared to sulfur curing systems and peroxide curing systems, the physical and mechanical properties and curing speed of EPDM rubber hose rubber compound in the composite curing system were significantly improved. Wu Lijuan, Luo Quankun, and others investigated the influence of peroxide/sulfur donor/composite curing system on the properties of halogen-free flame-retardant EPDM rubber, and found that the peroxide/sulfur donor composite curing system could endow EPDM with excellent physical and mechanical properties, prolong the scorch time of EPDM rubber, shorten the optimal curing time, and increase the curing rate. It can be seen that the peroxide and sulfur carrier composite curing system can improve the mechanical properties and curing efficiency of

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rubber.

This article employs BIPB and combines it with different sulfur carriers to investigate the changes in the properties of vulcanizates under different vulcanization systems, aiming to obtain the optimal composite vulcanization system. This provides valuable insights for the selection of vulcanization systems for SBR/POE blends and the exploration of the interaction between peroxides and sulfur carriers.

1 Experimental part

1.1 Raw materials

SBR 1502, Sinopec; POE 8150, DuPont Dow Chemical; SG-6, China Building Materials-Nanfeng Graphite Research Institute; N330, Tianjin Cabot Corporation; other additives are all common industrial products.

1.2 Experimental instruments and equipment

The instruments and equipment used in the experiment are shown in Table 1.

Table 1 Experimental instruments and equipment

Instrument name	Model	Manufacturer
open mill	X(S)K-160	Shanghai Shuangyi Rubber & Plastics Machinery Co., Ltd
internal mixer	XSM-1/20-80	Shanghai Kechuang Rubber and Plastic Machinery Equipment Co., Ltd
flat vulcanizing press	LCM-3C2-G03-LM	Shenzhen Jiaxin Electronic Equipment Technology Co., Ltd
Rotorless vulcanometer	GT-M2000-A	Taiwan High Speed Rail Corporation Limited
electronic tensile testing machine	I-7000S	Taiwan High Speed Rail Corporation Limited
hardness tester	Shaw's LX-A type	Shanghai Xianfeng Film Machinery Factory
DIN abrasion tester	GM-1	Yangzhou Tianfa Experimental Machinery Co., Ltd

1.3 Experimental formula

Using BIPB and varying sulfur carriers as variables, the experimental formulation is shown in Table 2.

Table 2 Test formulations of BIPB combined with different sulfur carriers

serial number	1 [#]	2 [#]	3 [#]	4 [#]
BIPB/copy	2	2	2	2
TMTD/copy	2	0	0	0.5
S/copy	0	0.5	0	0
DTDM/copy	0	0	2	0.8

The remaining components are all the same (unit: parts): SBR 1502 70, POE 8150 30, reclaimed rubber 30, N330 30, N220 20, SG-6 20, calcium hydroxide 25, C5 resin 12, stearic acid 2, zinc oxide 5, microcrystalline wax 1, RD 2, and TAIC 1. Total: 248 parts.

1.4 Sample preparation

The sample preparation process is as follows: First, weigh the raw materials according to the types and quantities specified in the formula. Then, in the internal mixer, add other compounding systems except for the curing system to the corresponding rubber of each formula. After mixing evenly, take out the rubber compound. Adjust the roller distance of the open mill to 1 mm, add the rubber compound, and thin-pass it 5 times. Add the curing agent, mix for about 5 minutes, make triangular bales 5 times after mixing evenly, take off the sheet, and let it rest for 16 hours. Use a rotorless vulcanometer to test

the curing characteristics. Adjust the molding temperature of the flat vulcanizer to 170 °C, the pressure to 10 MPa, and the time to t_{90} for curing.

1.5 Analysis and testing

(1) Vulcanization characteristic test: Conduct the test according to the GB/T 16584—1996 standard, using a vulcanometer. The test temperature is 170 °C, and the rotation angle is $\pm 1^\circ$.

(2) Breaking strength test: Conduct the test according to GB/T 528—2008 standard, using an electronic testing machine with a speed of 500mm/min, and at room temperature.

(3) Shore A hardness test: Conduct the test according to the GB/T 531.1—2008 standard, using a hardness tester, and the test temperature is room temperature.

(4) Permanent set at break: According to GB/T 528—2009, the test sample is left to rest for 3 minutes after being pulled apart, and the distance between two marked points is measured and recorded as L_1 . The permanent set at break is calculated using (1);

$$H=(L_1-L_0)/L_0 \times 100\% \quad (1)$$

Where L_0 is the initial gauge length of the specimen (mm).

(5) Tear strength test: Conducted according to GB529 standard, with the test temperature set at room temperature.

(6) Wear resistance test: The wear form adopts DIN roller wear, with a load of 10N.

(7) Hot air aging: aging conditions at 120 °C for 72 hours

(8) Crosslinking density determination: Using cyclohexane as the solvent, the equilibrium swelling method is employed to measure the vulcanized rubber V_r (the volume fraction of gel in the rubber). V_r is used to characterize the crosslinking density of the rubber, and there is a positive correlation between V_r and the crosslinking density of the rubber.

2 Results and discussion

2.1 Vulcanization characteristics

The vulcanization characteristics of SBR/POE blends using BIPB and different sulfur carrier vulcanization systems are shown in Figure 1.

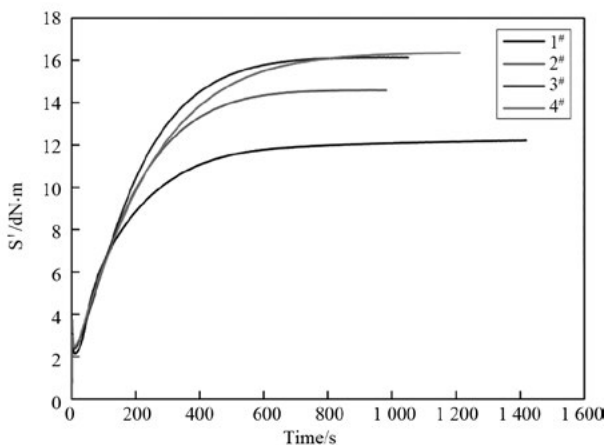


Figure 1 Vulcanization characteristic curve of BIPB with different sulfur carriers

As can be seen from Figure 1, the blending rubber in the BIPB/TMTD vulcanization system has the slowest vulcanization rate and the smallest maximum torque MH. Compared with the BIPB/TMTD vulcanization system, the BIPB/DTDM and BIPB/DTDM/TMTD vulcanization systems can significantly increase the reaction rate of the blending rubber, enhancing the MH and torque difference MH-ML of the blending rubber. The vulcanization effect of the BIPB/S vulcanization system falls between the two. Since TMTD is acidic and a tertiary amine compound, when used in combination with peroxides, it can consume the oxy-radicals generated by BIPB, forming low-activity amine radicals, thereby reducing the crosslinking of rubber macromolecules and resulting in a low torque value for the

blending rubber. When sulfur is added to the vulcanization system, due to the high vulcanization temperature of 170°C, sulfur and BIPB undergo cracking to generate sulfur radicals and alkoxy radicals, respectively. These two radicals are prone to undergo coupling termination reactions, leading to a decrease in the crosslinking density of the vulcanized rubber. DTDM and TMTD have a good mutual promoting effect, which can avoid the consumption of peroxides to some extent, thereby improving the vulcanization efficiency of peroxides. Therefore, the BIPB/DTDM/TMTD vulcanization system can play a synergistic role in enhancing the vulcanization rate and crosslinking density of the blending rubber.

2.2 Apparent crosslinking density

The apparent crosslinking density V_r of SBR/POE vulcanizates before and after aging under different BIPB/sulfur carrier composite vulcanization systems was obtained through the equilibrium swelling method, as shown in Table 3.

Table 3 Crosslinking density of BIPB combined with different sulfur carriers in vulcanizates

Serial number	1 [#]	2 [#]	3 [#]	4 [#]
V_r before aging /%	32.43	35.60	39.82	40.71
V_r after aging /%	44.93	50.71	42.51	47.71

The experiment utilizes V_r to characterize the crosslinking density of SBR/POE vulcanizates, with a higher V_r indicating a greater degree of crosslinking in the vulcanizate. Table 3 reveals that before aging, the SBR/POE vulcanizate in the BIPB/DTDM/TMTD vulcanization system exhibits the highest V_r , indicating the highest crosslinking density. This is followed by the BIPB/DTDM and BIPB/S vulcanization systems. Conversely, the SBR/POE vulcanizate in the BIPB/TMTD vulcanization system has the lowest V_r , indicating the lowest crosslinking density.

The V_r of the vulcanized rubber after aging is increased compared to that before aging, which is due to the further crosslinking of the vulcanized rubber during the aging process, leading to an increase in the crosslinking network density of the SBR/POE vulcanized rubber.

2.3 Physical and mechanical properties

The experimental results of the influence of BIPB and different sulfur carriers on the physical and mechanical properties of SBR/POE vulcanizate before and after aging are presented in Table 4.

Table 4 Effect of BIPB combined with different sulfur carriers on the physical and mechanical properties of SBR/POE vulcanizate

Formula Number		1 [#]	2 [#]	3 [#]	4 [#]
Hardness / Shore A	before aging	76	75	78	77
	after aging	87	89	90	91
Tensile strength / MPa	before aging	13.0	10.4	14.3	14.7
	after aging	10.7	9.1	—	9.4
Elongation at break / %	before aging	542	630	474	459
	after aging	190	112	—	57
50% modulus at fixed extension/MPa	before aging	2.1	2.0	2.4	2.4
	after aging	5.2	6.2	—	9.1
100% modulus/MPa	before aging	3.0	2.6	3.5	3.6
	after aging	7.5	8.6	—	—
200% modulus at fixed extension/MPa	before aging	5.5	4.0	6.4	6.7
	after aging	—	—	—	—
300% modulus/MPa	before aging	7.9	5.5	9.6	10.0
	after aging	—	—	—	—
Permanent deformation upon breakage /%	before aging	48	75	43	40
	after aging	25	20	—	5
Tear strength / (kN·m ⁻¹)	before aging	45.7	46.4	48.0	47.6
	after aging	30.00	28.5	25.2	31.2

According to Table 4, under the BIPB/DTDM and BIPB/DTDM/TMTD vulcanization systems, the tensile strength, hardness, tear strength, and modulus at a given extension of SBR/POE vulcanizate are higher than those of the BIPB/TMTD and BIPB/S vulcanization systems. However, the elongation at break is lower. This is because the cross-linking network of the vulcanizate under the BIPB/DTDM and BIPB/DTDM/TMTD vulcanization systems is denser, with stronger intermolecular forces, greater rigidity, and higher tensile strength, resulting in a lower elongation at break.

As can be seen from Table 4, after hot air aging, the hardness of SBR/POE vulcanizate increases compared to before aging, but its mechanical properties decrease. Among them, the performance retention rates of vulcanizates under BIPB/TMTD and BIPB/S vulcanization systems after aging are superior to that of the BIPB/DTDM vulcanization system.

2.4 DIN abrasion

According to Figure 2, the wear resistance of SBR/POE vulcanizates in the BIPB/TMTD, BIPB/TMTD, and BIPB/TMTD/DTDM systems is higher than that in the BIPB/S system, but there is little difference in wear resistance among the three systems.

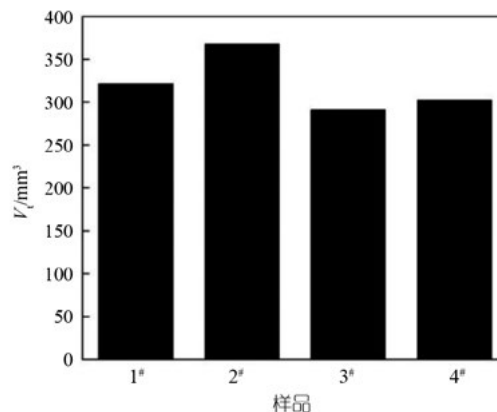


Figure 2 Effect of BIPB combined with different sulfur carriers on the wear resistance of SBR/POE vulcanizate

3 Conclusion

(1) Compared with the BIPB/TMTD and BIPB/S vulcanization systems, the BIPB/DTDM and BIPB/TMTD/DTDM vulcanization systems can significantly enhance the vulcanization reaction rate and crosslinking degree of the blended rubber.

(2) Compared to the BIPB/TMTD and BIPB/S vulcanization systems, the BIPB/DTDM and BIPB/TMTD/DTDM vulcanization systems exhibit higher tensile strength, modulus at a given extension, hardness, and abrasion resistance in the vulcanizates, but lower elongation at break and poorer aging properties.

(3) For SBR/POE blends, the vulcanizate obtained under the BIPB/TMTD/DTDM composite vulcanization system exhibits superior comprehensive properties.