The influence of accelerator types on the properties of chloroprene rubber/cis-polybutadiene rubber blends

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Abstract: This study, based on the ZnO/MgO–S composite vulcanization system, systematically investigated the effects of five accelerators, including sulfenamides (CZ), thiazoles (DM), thiurams (TMTD, TMTM), and tertiary amines (ACT-55), on the properties of chloroprene rubber/cis-polybutadiene rubber (CR/BR) blends. The results showed that TMTD and TMTM significantly improved the vulcanization efficiency of the blends, and the vulcanizates obtained from these systems exhibited the highest degree of vulcanization, tensile strength (reaching 18.8 MPa), abrasion resistance, and optimal low-temperature resistance (with a low-temperature brittle temperature of −44 ℃), but the retention of tensile strength after thermo-oxidative aging was poor. The blends from the CZ system exhibited the highest elongation at break, while the blends from the DM system showed the best retention of tensile strength after thermo-oxidative aging. The tertiary amine ACT-55 had the shortest scorch time and the worst tensile properties at room temperature.

Key words: CR/BR; accelerator type; blending modification; vulcanization characteristics; physical and mechanical properties

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Rubber blending is an effective means of preparing new materials, but the properties of blends are influenced by many factors, such as the type and dosage of compounding agents, blending process, etc., which have a significant impact on their processing and application properties. Chloroprene rubber (CR) exhibits excellent weather resistance, flame retardancy, and self-reinforcement, while butadiene rubber (BR) possesses outstanding elasticity and low-temperature resistance, making the blends of the two have broad application prospects in the fields of tires, hoses, conveyor belts, and sealing products. However, CR/BR blends face a technical challenge - the mismatch of the two-phase vulcanization system. BR can form a cross-linked network through a sulfur-accelerator system, while CR, due to the electron-withdrawing effect of chlorine atoms in its molecular chain on double bonds, reduces the activity of these bonds, making it difficult to achieve vulcanization using a common sulfur vulcanization system, and usually relying on metal oxides for cross-linking. The differences in vulcanization mechanisms of CR and BR lead to different cross-linked network structures in the two phases after blending, resulting in a mismatch in vulcanization rate, which in turn causes poor interfacial compatibility and decreased mechanical properties.

Research has shown that for sulfur vulcanization systems, the type and amount of accelerator play a decisive role in the vulcanization rate of rubber compound. Accelerators not only regulate the vulcanization rate but also affect the vulcanization reaction pathway and cross-linking structure type, thereby playing a key role in the degree of cross-linking between the two phases and the interfacial bonding strength in the blend system. Due to significant differences in vulcanization activity,

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induction period, type of cross-linking bond formed, and synergistic properties with metal oxides among different types of accelerators, CR/BR systems under different accelerators exhibit varying vulcanization efficiency and mechanical properties.

In this study, representative accelerators including sulfenamide (CZ), thiazole (DM), thiuram (TMTD, TMTM), and tertiary amine (ACT-55) were selected. By comparing their effects on the vulcanization characteristics and mechanical properties of CR/BR blends, the aim was to obtain an efficient accelerator system suitable for CR/BR blends with good mechanical properties.

1 Experimental part

1.1 Main raw materials and instruments

Chloroprene rubber (CR), grade CR2322, Chongqing Changshou Chemical Group Co., Ltd.; butadiene rubber (BR), grade BR9000, Sinopec Beijing Yanshan Petrochemical Co., Ltd.; fast extrusion black, grade N550, Cabot (China) Investment Co., Ltd.; high abrasion-resistant black, grade N330, Cabot (China) Investment Co., Ltd.; all other compounding agents are commercially available industrial products.

X(S)K-160 type open mill, Wuxi Chuangcheng Rubber & Plastics Machinery Co., Ltd.; XSM-1/20-80 type internal mixer, Shanghai Kechuang Rubber & Plastics Machinery Equipment Co., Ltd.; M-3000AU type rotorless curing meter, Gaotie Testing Instrument (Dongguan) Co., Ltd.; LCM-3C2-G03-LM type flat vulcanizing press, Shenzhen Jiaxin Electronic Equipment Technology Co., Ltd.; RPA 2000 type rubber processing analyzer, Alpha Technology Corporation of America; GT-7016-AR type pneumatic automatic slicer, Gaotie Testing Instrument (Dongguan) Co., Ltd.; GT-7017-M type aging oven, Gaotie Testing Instrument (Dongguan) Co., Ltd.; JDL-2500N type electronic tensile machine, Tianfa Testing Machinery Co., Ltd.; TF-2075 type low-temperature brittle temperature tester, Tianfa Testing Machinery Co., Ltd.

1.2 Experimental design

To systematically investigate the influence of accelerator types on the properties of CR/BR blends, this study selected five representative accelerators: N-cyclohexyl-2-benzothiazole sulfenamide (CZ), 2,2'-dibenzothiazole disulfide (DM), tetramethyl thiuram disulfide (TMTD), tetramethyl thiuram monosulfide (TMTM), and tertiary amine accelerator (ACT-55). Based on a unified masterbatch formula, five test rubber compounds were prepared, with the only difference being the type of accelerator used, as detailed in Table 1.

Table 1 Experimental Variables

Serial number	CZ	DM	TMTD	TMTM	ACT-55
Type of accelerator	Sulfonylureas	Thiazoles	Thiuram derivatives	Thiuram derivatives	Tertiary amines

The basic formula for CR/BR blend rubber (unit: phr) is as follows:

CR 70, BR 30, N330 48, N330 12, stearic acid (SA) 1.5, antioxidant RD 1.5, antioxidant 4010NA 1, clay 28, coumarone resin 5, ZnO 5, MgO 4, S 1.5, test variable 0.5, DOTG 0.5, total 208.

1.3 Preparation of CR/BR blend

Based on the experimental design, CR and BR masterbatches were prepared separately in the internal mixer. The initial temperature of the mixer was maintained at 65°C, and the rotor speed was 30 r/min. The compounding agents, excluding the vulcanizing agent, were added in two steps. In the first step, N330, SA, antioxidant RD, and antioxidant 4010NA were added, with a mixing interval of 2 minutes. In the second step, the remaining N330, coumarone resin, and clay were added. The total mixing time was about 15 minutes before discharging the rubber; it was then placed at room temperature for 16 hours.

Subsequently, the preparation of CR/BR rubber compound was carried out on the open mill. First, the BR masterbatch was wrapped around the roller, and CR masterbatch was added according to the CR/BR raw rubber ratio of 70/30. The rubber was cut, wrapped in a triangle shape 3 times, mixed evenly, and then divided into 5 portions. Each portion was added with ZnO, MgO, S, DOTG, and their respective accelerators according to the test formula. The rubber was wrapped in a triangle shape 8 times, rolled 3 times, and then cut into pieces and marked (CZ to ACT-55). The rubber compound was left to rest for more than 8 hours, and the test samples were vulcanized on a flat vulcanizing press under the conditions of 155 ℃×t_{90}×10 MPa.

1.4 Performance testing

(1) Vulcanization characteristics: Tested according to GB/T 9869.3—2025, the rotation angle of the rotor is ±1°, and the test conditions are 155 ℃ for 40 minutes.

(2) Shore A hardness: Tested using a Shore A durometer in accordance with GB/T 39693.4—2025.

(3) Dynamic mechanical properties: Tested according to GB/T 45159.4-2025, with a strain frequency of 1.7 Hz, a rotation angle of 0.5°, and a test temperature of 60 ℃.

(4) Tensile properties: Tested according to GB/T 528-2009, with a tensile speed of 500 mm/min and a test temperature of room temperature.

(5) Thermo-oxidative aging performance: Tested according to GB/T 3512—2014, with test conditions of 120 ℃ for 48 hours.

(6) Low-temperature brittleness temperature: Tested according to GB/T 1682—2014, using a low-temperature brittleness tester, with a testing duration of 3 minutes.

(7) Wear resistance: Tested using a rotary roller abraser according to GB/T 9867-2008, with a load of 10 N.

2 Results and Discussion

2.1 The influence of accelerator types on the vulcanization characteristics of CR/BR blends

To investigate the effects of different accelerators on the vulcanization behavior of CR/BR blends, this experiment first measured the vulcanization curves of various formulations using a rubber vulcanometer. Table 2 presents the vulcanization characteristic parameters of the blends with different accelerator systems.

Table 2 Vulcanization characteristics of CR/BR blends under different accelerator systems

serial number	CZ	DM	TMTD	TMTM	ACT−55
M_H/dN·m	20.03	19.10	23.10	21.33	21.07
M_L/dN·m	3.19	3.17	3.16	2.89	3.05
M_H−M_L/dN·m	16.84	15.94	19.94	18.44	18.02
t_{10}/min	1:42	1:14	1:16	1:47	0:51
t_{90}/min	21:51	22:09	12:51	12:17	24:01

As can be seen from Table 2, the M_L of TMTM rubber compound is the lowest, while the M_L s of the other four rubber compounds are not significantly different; the order of M_H and M_H-M_L for the rubber compounds is TMTD > TMTM > ACT-55 > CZ > DM, indicating that the vulcanization degree and crosslinking density of TMTD rubber compound are higher; the scorch time t10 of the rubber compound using ACT-55 is the shortest, at 51 s; both accelerators TMTM and TMTD can significantly shorten the t_{90} of the rubber compound, accelerating vulcanization.

Experimental phenomena indicate that thiuram-type accelerators can significantly enhance the vulcanization rate and degree of vulcanization of blend rubber. This is attributed to the fact that both TMTD and TMTM contain two accelerating groups and two reactive groups, which can effectively activate the vulcanization system and promote group reactions. Specifically, TMTD contains ⩾ 2 sulfur atoms, which can precipitate active sulfur atoms during vulcanization, further enhancing the degree of crosslinking. Therefore, the use of TMTD and TMTM can impart greater vulcanization degree to CR/BR blend rubber.

2.2 Effect of accelerator type on the physical and mechanical properties of CR/BR blends

To further investigate the impact of different accelerators on the overall mechanical properties of CR/BR vulcanizates, the physical and mechanical properties of each blend vulcanized at 155℃ are presented in Table 3, and their corresponding tensile stress-strain curves are shown in Figure 1.

Table 3 Physical and mechanical properties of CR/BR blends under different accelerator systems

serial number	CZ	DM	TMTD	TMTM	ACT−55
Shore A hardness /°	73	73	76	76	74
Tensile strength/MPa	15.1	14.0	18.6	18.8	12.7
Elongation at break, %	338	314	316	298	274
50% modulus at fixed extension/MPa	2.1	2.2	2.5	2.8	2.1
100% modulus at fixed extension/MPa	3.5	3.8	4.3	4.8	3.7
200% modulus/MPa	8.2	8.5	10.8	11.8	8.9
300% modulus/MPa	13.5	13.4	17.8	/	/
Permanent deformation upon breakage /%	10	10	10	10	10

Based on Table 3 and Figure 1, it can be seen that the use of thiuram-based accelerators (TMTD or TMTM) significantly enhances the comprehensive mechanical properties of CR/BR blends. The corresponding vulcanizates exhibit the highest hardness, tensile strength, and modulus at various extension rates, with tensile strength approaching 19 MPa. In comparison, the mechanical properties of vulcanizates prepared with the sulfenamide-based CZ and thiazole-based DM are at a medium level, with the CZ system showing the highest elongation at break (338%). The vulcanizates from the tertiary amine-based ACT-55 system have the worst comprehensive mechanical properties, with the lowest tensile strength and elongation at break. The above results indicate that to obtain CR/BR blended vulcanizates with high modulus and high strength, it is more effective to choose thiuram-based accelerators (such as TMTD or TMTM) as accelerators.

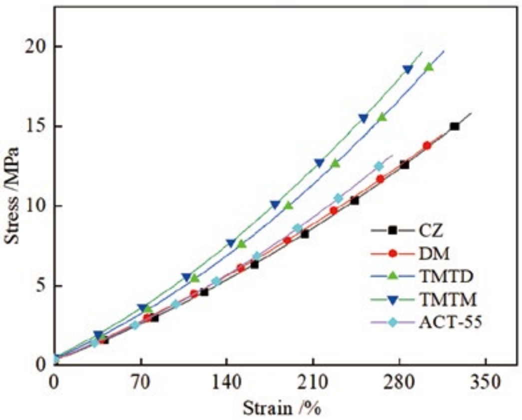

Figure 1 Stress-strain curves of CR/BR blends under different accelerator systems

2.3 Effect of accelerator type on the dynamic mechanical properties of CR/BR blends

Rubber products are often subjected to periodic stress deformation in practical use, and their dynamic mechanical properties are crucial for evaluating the comprehensive application value of materials. To reveal the mechanical characteristics of the crosslinked networks constructed with different accelerators under dynamic loading, this study investigated the storage modulus (*G*), loss modulus (*G*'), and loss tangent (tan*δ*) of CR/BR blended vulcanizates at 60℃, as shown in Figures 2 and 3.

As can be seen from the figure, at 60℃, the CR/BR blend corresponding to thiuram-type accelerators (TMTM and TMTD) exhibits superior dynamic mechanical properties: its G can reach up to 11.37 kPa, while G can drop as low as 1.83 kPa and tanδ can reach a minimum of 0.16. A higher G indicates that the elastic response of the blended vulcanizate dominates during dynamic deformation, indicating a denser cross-linking network; a lower tanδ reflects a smaller internal friction in

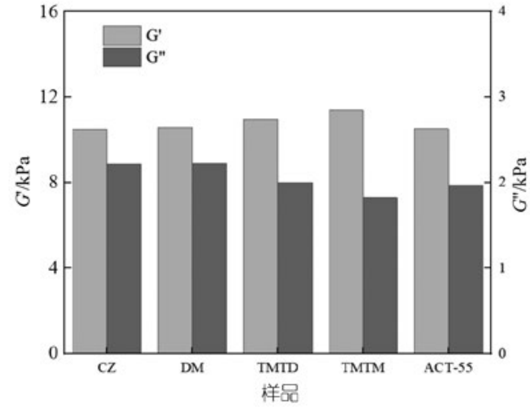

Figure 2 G′and G″of CR/BR blends with different accelerator systems at 60℃

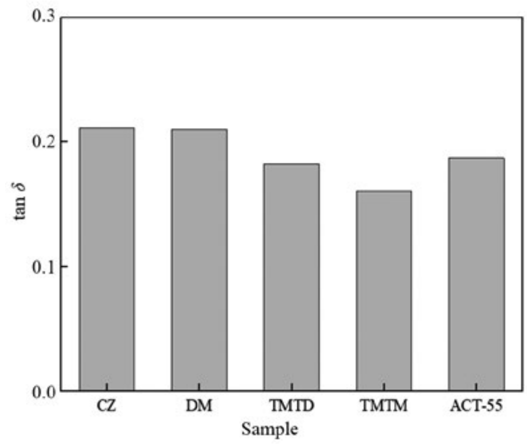

Figure 3 tanδ of CR/BR blends with different accelerator systems at 60℃

the blended vulcanizate, resulting in lower energy loss during dynamic deformation. The above results suggest that the sulfur-accelerator system constructed with thiuram-type accelerators enables the blended vulcanizate to exhibit both superior creep resistance and lower dynamic heat build-up under dynamic conditions.

2.4 Effect of accelerator type on the mechanical properties of CR/BR blends after thermo-oxidative aging

After undergoing thermal-oxidative aging at 120℃ for 48 hours, the physical and mechanical properties and their changes of CR/BR blended vulcanizates under different accelerator systems are presented in Table 4.

Based on the analysis of Table 3, it can be seen that compared to the CR/BR vulcanizate before aging, the vulcanizate after aging under all accelerator systems exhibits increased hardness, higher modulus, and decreased elongation at break. This is due to the dual effects of heat and oxygen during the thermo-oxidative aging process, where the CR phase molecular chains undergo further crosslinking reactions to form—C—C—crosslinks, resulting in a denser crosslinking network. Therefore, the vulcanizate macroscopically exhibits an increase in hardness and modulus.

Table 4 Physical and mechanical properties and change rates of CR/BR blends after thermo-oxidative aging

Serial number	CZ	DM	TMTD	TMTM	ACT−55
Shaw A hardness /°	86	87	87	87	88
Tensile strength / MPa	17.9	16.4	14.7	14.7	16.6
Change rate of tensile strength /%	18	17	−21	−22	30
Elongation at break /%	162	164	123	128	142
Rate of change of breaking elongation /%	−52	−48	−61	−57	−48
50% modulus at fixed extension / MPa	5.5	5.1	5.9	5.7	5.4
100% modulus at fixed extension / MPa	10.5	9.6	11.5	10.9	10.3
Permanent set at break /%	5	0	0	0	0

However, different accelerators exhibit significant differences in the retention rate of the tensile properties of vulcanizates: the tensile strength of vulcanizates using CZ, DM, and ACT-55 increased by approximately 17% to 30% compared to before aging; the tensile strength of vulcanizates using TMTD and TMTM decreased by 21% and 22%, respectively. This difference is related to the accelerating effect of accelerators on the vulcanization efficiency of sulfur: TMTD and TMTM, as super-accelerators, can significantly enhance the crosslinking reaction efficiency of sulfur, forming a sulfur bond network with high crosslinking density. Although this characteristic endows the unaged blend with higher modulus, it also leads to insufficient flexibility in the crosslinking network, making it more prone to stress concentration effects due to excessive crosslinking of the blend after thermal-oxidative aging, resulting in brittle fracture. Therefore, it exhibits the lowest elongation at break and tensile strength after thermal-oxidative aging.

2.5 Effect of accelerator type on the wear resistance of CR/BR blends

To investigate the influence of accelerator types on the wear resistance of CR/BR blends, DIN abrasion tests were conducted on CR/BR vulcanizates. The wear volume of blends with different accelerator systems is shown in Figure 4.

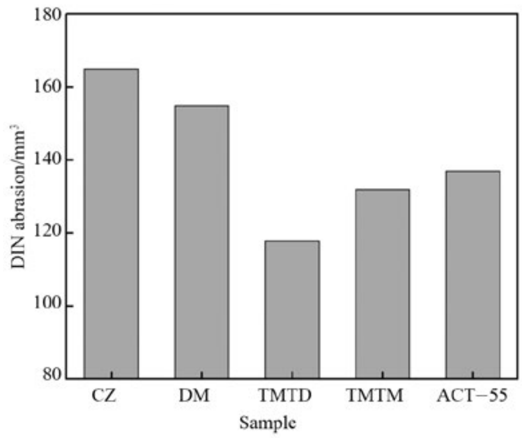

Figure 4 Wear volume of CR/BR blend under different accelerator systems

The results in Figure 4 indicate significant differences in the DIN abrasion resistance of CR/BR vulcanizates under different accelerator systems. The DIN abrasion volume, from highest to lowest, is as follows: CZ > DM > ACT-55 > TMTM > TMTD. Combined with the vulcanization characteristics data of the blends in Table 2, it can be seen that the blends corresponding to TMTD and TMTM have a higher degree of vulcanization, indicating a higher crosslinking density and a denser crosslinking network, which effectively resists loss during abrasion and exhibits the best wear resistance.

2.6 Effect of accelerator type on the low temperature resistance of CR/BR blends

Figure 5 shows the low-temperature brittle temperature of CR/BR blend vulcanizates under different accelerator systems. It can be seen from the figure that the blend using TMTD has the best low−temperature resistance (with the lowest brittle temperature of −44℃), while the blend using ACT−55 has the worst low-temperature resistance (with the highest brittle temperature of −39℃).

3 Conclusion

This work investigates the effects of different accelerators on the properties of CR/BR blends, revealing the role of

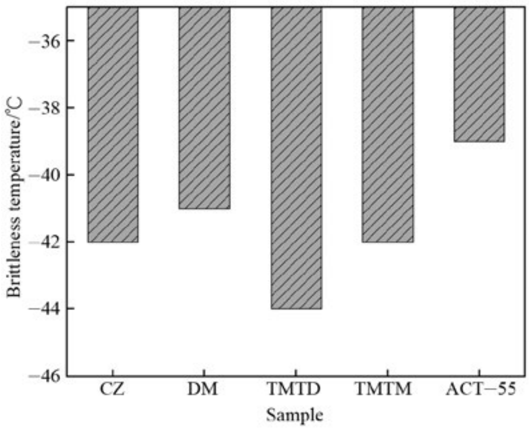

Figure 5 Low-temperature brittle temperature of CR/BR blends under different accelerator systems

accelerator types in regulating the vulcanization characteristics, mechanical properties, and service performance of the blends. The experimental conclusions are as follows:

(1)The thiuram accelerators TMTD and TMTM can significantly enhance the vulcanization efficiency and crosslinking density of CR/BR blends. The vulcanizates produced exhibit the highest Mooney viscosity (MH) and the shortest process positive vulcanization time t90. The corresponding vulcanizates in their systems also possess the highest tensile strength (up to 18.8 MPa), modulus at a fixed extension, and storage modulus, and demonstrate the best wear resistance and low-temperature resistance.

(2)The sulfenamide accelerator CZ can impart the vulcanizate with the highest tensile elongation at break and the longest scorch time t10; the vulcanizate using the thiazole accelerator DM exhibits tensile properties similar to those of CZ; the vulcanizate using the tertiary amine accelerator ACT-55 has the shortest scorch time, only 51 seconds.

(3)Under thermal oxidative aging conditions, the tensile strength retention of vulcanizates from the CZ and DM systems is higher; the modulus of vulcanizates from the thiuram accelerator system is the highest after aging, but the tensile strength is the lowest.