The impact of hexadecylamine on the desulfurization degree of waste rubber and the application of rubber asphalt

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Abstract: With the rapid development of the transportation industry, the production of waste rubber (CR) has been increasing year by year. However, there is currently a lack of environmentally friendly and efficient recycling methods. Due to the inert surface and internal three-dimensional network structure of CR, the recycling and reuse process is hindered. Therefore, the desulfurization of CR through de-crosslinking has become a highly promising research direction. This article employs a Haake internal mixer to blend waste rubber powder with a desulfurizing agent (HDA) to investigate the effects of different process parameters and HDA on the desulfurization efficiency of rubber powder. By analyzing the influence of different mixing temperatures, speeds, and desulfurizing agent contents on the degree of chloroprene rubber (CR) desulfurization through sol content, Horikx curve, and scanning electron microscopy (SEM), and applying it to modified asphalt, good results have been achieved.

Key words: hexadecylamine; rubber powder desulfurization; rubber powder modified asphalt

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With the rapid economic development in recent years, waste tires have become a derivative of economic growth. According to statistics, China produces approximately 330 million waste tires annually, with a total weight exceeding 10 million tons. These waste tires are difficult to decompose under natural conditions, and long-term storage not only releases pungent and toxic gases but also easily leads to fires. They contain harmful heavy metal elements such as lead, chromium, and cadmium, which, if not disposed of properly, can pose significant threats to human health and the natural environment. Traditional incineration and landfill disposal methods not only consume a lot of energy but also bring about a series of environmental issues. Recycling these waste tires into rubber powder and then applying it to modified asphalt can increase the consumption of these "black pollutants". This makes rubber powder modified asphalt (CMA) highly environmentally friendly, and due to the relatively low price of waste rubber powder, CMA also exhibits high economic efficiency.

The surface of ordinary rubber powder is inert and has poor compatibility with asphalt. Long-term storage can lead to phase separation between CR and asphalt, resulting in a decline in the performance of CMA, which in turn affects its widespread application. Desulfurization of rubber powder selectively breaks the S-S bond, S-C bond, and C-C bond, partially restoring the original rubber properties to enhance the compatibility of CR with asphalt and optimize the performance of CMA. Therefore, this paper combines thermomechanical

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Biography: Jin Yushi (1999-), master's degree candidate, whose main research direction is the study of green new materials and multifunctional materials.

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and chemical methods to desulfurize CR, aiming to utilize the strong shear and high temperature of the Haake mixer, as well as the selective de-crosslinking of HDA, to break the C-S bond, S-S bond, disulfide bond, and polysulfide bond in CR. By changing the temperature, speed, and HDA content of the Haake mixer, the degree of desulfurization of desulfurized rubber powder (DCR) is analyzed to determine the optimal desulfurization process. After blending DCR with SBS to produce composite modified asphalt (PMA), the influence of CR desulfurization process on asphalt performance is explored.

1 Experimental part

1.1 Raw materials

Rubber powder (CR), purchased from Jiangsu Zhonghong Environmental Protection Co., Ltd., is obtained by removing metal, textile, and other related impurities from tires, followed by crushing, grinding, and screening to obtain rubber powder below 40 mesh. Its basic composition is shown in Table 1. Hexadecylamine (HDA) and carbon disulfide (CS2), purchased from Macklin Biochemical Technology Co., Ltd. in Shanghai, China, are of HPLC 99.9% purity. Glycerol triglycidyl ether, used as a compatibilizer, is purchased from Macklin Biochemical Technology Co., Ltd. in Shanghai, with a purity of 99.9%. Waste engine oil (oil) is purchased from Shanxi Changhe Automobile Repair Factory. 90# matrix asphalt, Kunlun asphalt, has its basic properties shown in Table 2. Linear SBS (trade name YH-791H (SBS1301-1)), purchased from Sinopec Baling Petrochemical Co., Ltd., has a styrene-butadiene mass ratio of 30:70.

Table 1 Basic composition of 40 mesh CR

Indicator	Test Results
Operating oil/%	6.58
Rubber hydrocarbon/%	54.77
Carbon black / %	26.96
Ash content /%	11.69

Table 2 Physical properties of 90# matrix asphalt

Indicator	Test Results
Penetration/(25 ℃ ,0.1 mm)	85.7
Softening point	44.5
Ductility / (5 ℃ , cm)	0
Elastic recovery/%	8.13
Viscosity /(180 ℃ ,Pa·s)	0.12

1.2 Sample preparation

Preparation of desulfurized rubber powder: Weigh CR, HDA, and oil in a mass ratio of 20:1:3, and stir them for 10 minutes at 500/min using a mixer. Then, add them to a Haake internal mixer and mix for 10 minutes to obtain desulfurized rubber powder of different processes. The specific desulfurization conditions are shown in Table 3.

Table 3 Desulfurization conditions for desulfurized rubber powder from Hacker mixer

	Temperature T/℃	Rotational Speed R/(r.min^{-1})	HDA Content H/g
DCRT140R80H10	140	80	10
DCRT160R80H10	160	80	10
DCRT180R80H10	180	80	10
DCRT160R40H10	160	40	10
DCRT160R60H10	160	60	10
DCRT160R80H20	160	80	20
DCRT160R80H30	160	80	30

Preparation of SBS/DCR composite modified asphalt: First, mix DCR with $\omega(\mathrm{SBS})=2\%$ and $\omega(\mathrm{SBS})=40\%$ in a Haake mixer at 160℃ and 80/min for 10 minutes to obtain the SBS/DCR composite. Then, preheat 90# base asphalt in an oven at 120℃ for 30 minutes to melt it. Under an environment at 200℃, slowly add 42% (mass fraction) of the SBS/DCR composite, stir at 1200 r/min for 2 hours, and then shear at 5000 r/min for 1 hour. Finally, SBS/DCR composite modified asphalt is obtained, which is named PMAT140R80H10, PMAT160R80H10, PMAT180R80H10, PMAT160R40H10, PMAT160R60H10, PMAT160R80H20, and PMAT160R80H30.

1.3 Test method

1.3.1 Testing of DCR

(1) Sol content test

The sol content was determined by Soxhlet extraction. First, the sample (approximately 0.2 g) was extracted in boiling acetone for 12 hours, then dried in a vacuum oven at 80 ℃ to remove the solvent until reaching constant weight, and the mass was measured (w_1). Subsequently, the sample was extracted in boiling toluene for 12 hours. Finally, the sample was dried in an oven at 80 ℃ until reaching constant weight, and the mass was measured as (w_2). The sol content was calculated using equation (1):

$$\text{Sol content}(\%)=\frac{w_1-w_2}{w_1}\times 10 \qquad (1)$$

(2) Crosslinking density test

The crosslinking density was determined by the equilibrium swelling method. Initially, the sample (approximately 0.2 g) was extracted in boiling acetone for 12 hours, then dried to constant weight in an oven at 80°C, and the weight m1 was measured. The sample was immersed in toluene at room temperature for 72 hours to achieve diffusion equilibrium of swelling. Subsequently, the sample was taken out, and the solvent was quickly removed using filter paper. Then, the swelling weight was immediately measured, denoted as m_2. Finally, the sample was dried to constant weight in an oven at 80°C, and the weight was measured in units of m_3. The crosslinking density (equation (2)) is defined as:

$$V_e=\frac{\ln(1-V_r)+V_r+xV_r^2}{V_s(0.5V_r-V_r^{1/3})} \tag{2}$$

Where Ve represents the crosslinking density; Vr denotes the volume fraction of the polymer in the swollen sample; V stands for the Flory-Huggins polymer-solvent interaction parameter; and Vd signifies the molar volume of the solvent, which is 106.3 mL·mol^{-1}. The primary rubber component of CR is natural rubber, and the corresponding Flory-Huggins polymer-solvent interaction parameter, x, for the natural rubber-toluene system is 0.393.

(3) Calculation of desulfurization degree

The desulfurization rate is calculated according to the formula specified in ASTM D6814-02 standard as follows:

$$Rd=(V_{e1}-V_{e2})/V_{e1} \tag{3}$$

Among them, V_{e1} and V_{e2} represent the crosslinking density of the rubber powder before and after desulfurization, respectively.

(4) Horikx curve

Changes in sol fraction and crosslinking density are influenced by the breakage of main chains and crosslinks during degradation. To investigate the process of bond breakage, a theoretical relationship between sol fraction and crosslinking density was established using Horikx theory . Horikx theory consists of two aspects: the relationship between crosslinking density and sol fraction can only be explained by equation (4) when main chain breakage occurs; the relationship between crosslinking density and sol fraction can only be explained by equation (5) when crosslink bond breakage occurs. Based on equations (4) and (5), and the data on sol fraction and crosslinking density tested in experiments, the Horikx curve can be determined and used to analyze the method of bond breakage.

$$1-\frac{V_f}{V_i}=1-\frac{(1-S_f^{12})^2}{(1-S_i^{12})^2} \tag{4}$$

S_i represents the sol content of untreated rubber powder; S_f represents the sol content of desulfurized rubber powder; V_i represents the crosslinking density of untreated rubber powder; V_f represents the crosslinking density of desulfurized rubber powder.

In addition, in the case of pure crosslink fracture, the soluble fraction is related to the relative decrease in crosslink density, as shown below:

$$1-\frac{V_f}{V_i}=1-\frac{\gamma_f(1-S_f^{1/2})^2}{\gamma_i(1-S_i^{1/2})^2} \tag{5}$$

Where γ_f and γ_i represent the average number of crosslinks per chain in the insoluble network after and before desulfurization, respectively (f denotes final, and i denotes initial). γ_i and γ_f are the average number of crosslink sites per chain in the insoluble network before and after desulfurization, which can be determined by the method described by Verbruggen.

(5) SEM

Scanning Electron Microscopy (SEM, ZEISS GEMINISEM 360, Carl ZEISS AG, Germany) was utilized to analyze the micromorphology of CR and SCR. Prior to testing, CR and SCR were adhered to a conductive adhesive. To obtain the conductivity of the samples, Oxford Quorum SC7620 gold spraying equipment was employed to perform 10 mA gold spraying. CR and DCR, which possess conductivity, were placed in the sample chamber of the SEM and underwent a vacuum pumping step. Once a testable vacuum level was achieved, vacuum pumping was ceased, and the micromorphology of CR and DCR samples was captured. The accelerating voltage was set at 3 kV, and images were captured at a magnification of 2,000 times.

1.3.2 Testing of PMA

According to the relevant test methods outlined in the Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering (JTG E20-2011), the physical properties of modified asphalt are measured, including softening point, needle penetration at 25℃ , ductility at 5℃ , and elastic recovery at 25℃ .

2 Results and Discussion

2.1 Analysis of Horikx curve of DCR

The fracture of the main chain and cross-linking bonds during the de-crosslinking process was analyzed, and the curve fitting of Horikx for CR and DCR is shown in Figure 1. The dashed line represents the fracture of cross-linking bonds, while the solid line represents the fracture of chemical bonds in the main chain. That is, the closer to the dashed line, the more likely there is a tendency towards S-S and C-S fracture, and the closer to the solid line, the more likely there is a tendency towards C-C fracture in the main chain. It can be observed that both excessively high temperature (sample DCRT180R80H10) and high desulfurization agent content (sample DCRT160R80H30) can lead to significant fracture of the main chain, with temperature having the greatest impact. DCRT160R40H10 and DCRT140R80H10 are close to the dashed line, indicating mainly fracture of cross-linking bonds. As the desulfurization temperature, rotational speed, and desulfurization agent content increase, the sol content increases and the cross-linking density decreases.

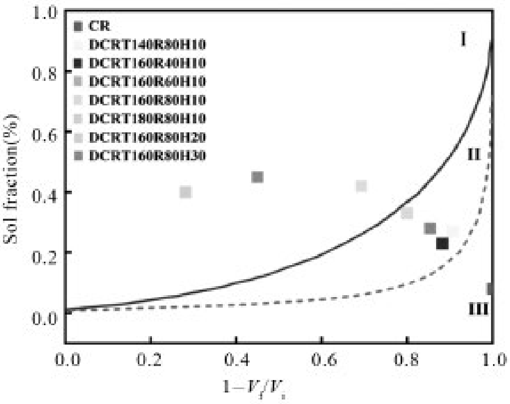


Figure 1 Horikx curve of CR and DCR

2.2 Microscopic morphology of DCR

As shown in Figure 2(a), the apparent morphology of CR is characterized by particles that are separated from each other without bonding, presenting a granular appearance. This is due to the interconnected network structure of the rubber powder, which leads to a compact structure and low bonding energy, resulting in a granular distribution of CR. The remaining

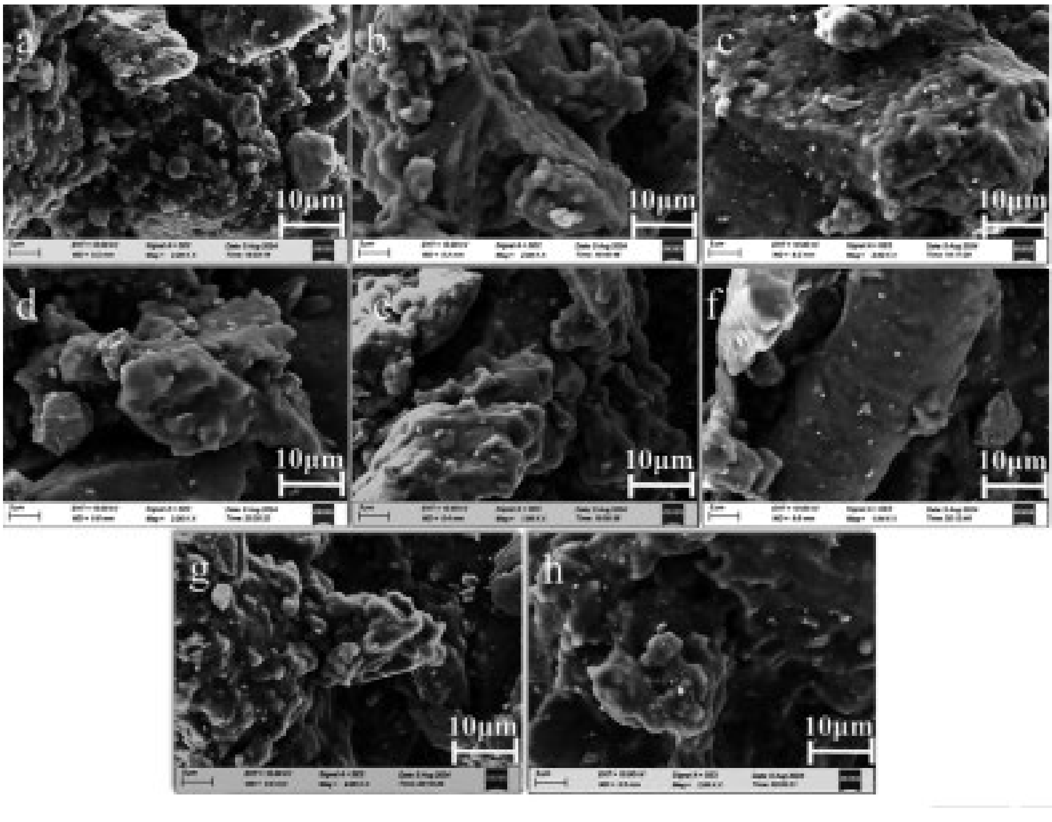


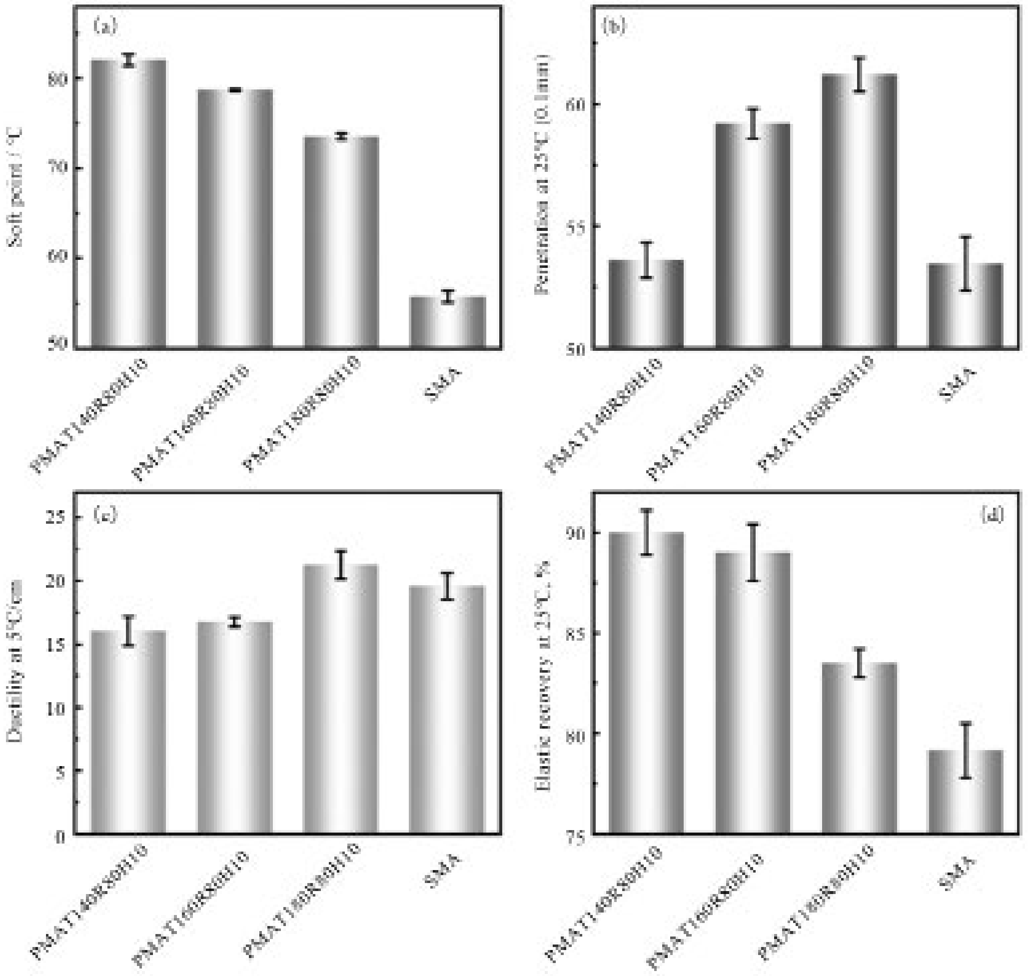
Figure 2 SEM Microscopic Morphology of CR and DCR: (a) CR, (b) DCRT140R80H10, (c) DCRT160R40H10, (d) DCRT160R60H10, (e) DCRT160R80H10, (f) DCRT180R80H10, (g) DCRT160R80H20, (h) DCRT160R80H30

figures in Figure 2 demonstrate the disappearance of loose particles in DCR, with surface adhesion and the appearance of holes and gaps. This is due to the destruction of the internal cross-linking network of DCR. Figures 2(b)(e)(f) show the apparent morphology of DCR at different desulfurization temperatures. From Figure 2(b) to (e), it can be observed that the surface of DCR becomes increasingly rough, and the particle size decreases. When the desulfurization temperature is increased from 140℃ to 160℃, it accelerates the chemical reaction between HDA and CR, allowing the desulfurizing agent to fully contact and react with the sulfur cross-linking bonds on the rubber molecular chains, thereby accelerating the breakage of the cross-linking bonds. On the other hand, high temperatures intensify the thermal motion of rubber molecules, increasing the flexibility of the molecular chains, making them more prone to breakage and rearrangement. Simultaneously, the mechanical shearing effect of the internal mixer becomes more effective at high temperatures, further promoting the breakage of rubber molecular chains and the refinement of rubber powder particles. From Figure 2(e) to (f), it can be observed that the surface of DCR tends to become smoother. When the desulfurization temperature is increased from 160℃ to 180℃, it may be due to the excessively high temperature inside the internal mixer, leading to a more thorough desulfurization reaction. At the same time, a large number of cross-linking bonds in the rubber molecular chains break, becoming smaller and more uniform, rearranging on the surface of the rubber powder, thus presenting a smooth appearance. Figures 2(c)(d)(e) show the apparent morphology of DCR at different desulfurization speeds. It can be observed that as the speed increases, the surface of DCR becomes increasingly rough, with more and more holes and gaps appearing. This is due to the increased mechanical shearing effect caused by the higher speed of the internal mixer, which subjects DCR to greater shearing and friction inside the chamber, leading to more wear and tear on the surface of the rubber powder, forming more irregularities, holes, and cracks, and significantly increasing surface roughness. Figures 2(e)(g)(h) show the apparent morphology of DCR with different contents of desulfurizing agent HDA. It can be observed that as the content of desulfurizing agent increases, the pores inside the rubber powder become more abundant and connected, and the surface becomes rougher. This is because HDA interacts with the rubber molecular chains, gradually destroying the cross-linking network, making the originally compact structure looser, and thus forming more pores. The increase in HDA content is accompanied by a deeper degree of desulfurization reaction, leading to more severe breakage of rubber molecular chains. This makes DCR particles more prone to crushing under the shear force of the internal mixer, resulting in particles with blurred and irregular edges, unlike CR which has a clearer outline and regular shape.

2.3 The impact of desulfurization process on the conventional physical properties of PMA

The impact of the desulfurization process on the conventional physical properties of PMA is illustrated in Figures 3 and 4. It can be observed that as the desulfurization temperature and rotational speed increase, both ductility and penetration increase, but the softening point and elastic recovery decrease, indicating a strong correlation with its degree of desulfurization. When the degree of desulfurization is low, the interaction between rubber powder and asphalt is weak, with little impact on the softening point. As the degree of desulfurization increases, the rubber powder disperses and swells better in the asphalt, reducing the high-temperature stability of the asphalt, and the softening point tends to decrease. The softening point represents the temperature at which asphalt transitions from a solid state to a paste with certain fluidity. After desulfurization of rubber powder, the crosslinking density decreases, weakening its ability to absorb light components in asphalt. This results in a relative increase in light components in asphalt, making it more prone to flow at high temperatures, leading to a decrease in softening point.

Generally, when the degree of desulfurization is low, due to less damage to the CR cross-linked structure, its dispersibility in asphalt is poor, and its impact on the penetration of asphalt is small. As the degree of desulfurization increases, the cross-linked structure is largely destroyed, CR swells fully in asphalt, and the plasticizing effect of organic small molecules in DCR on asphalt is enhanced, resulting in an increase in the penetration of asphalt. Penetration reflects the hardness and consistency of asphalt. DCR's ability to absorb light components in asphalt weakens, and the content of organic small molecules increases, playing a plasticizing role,

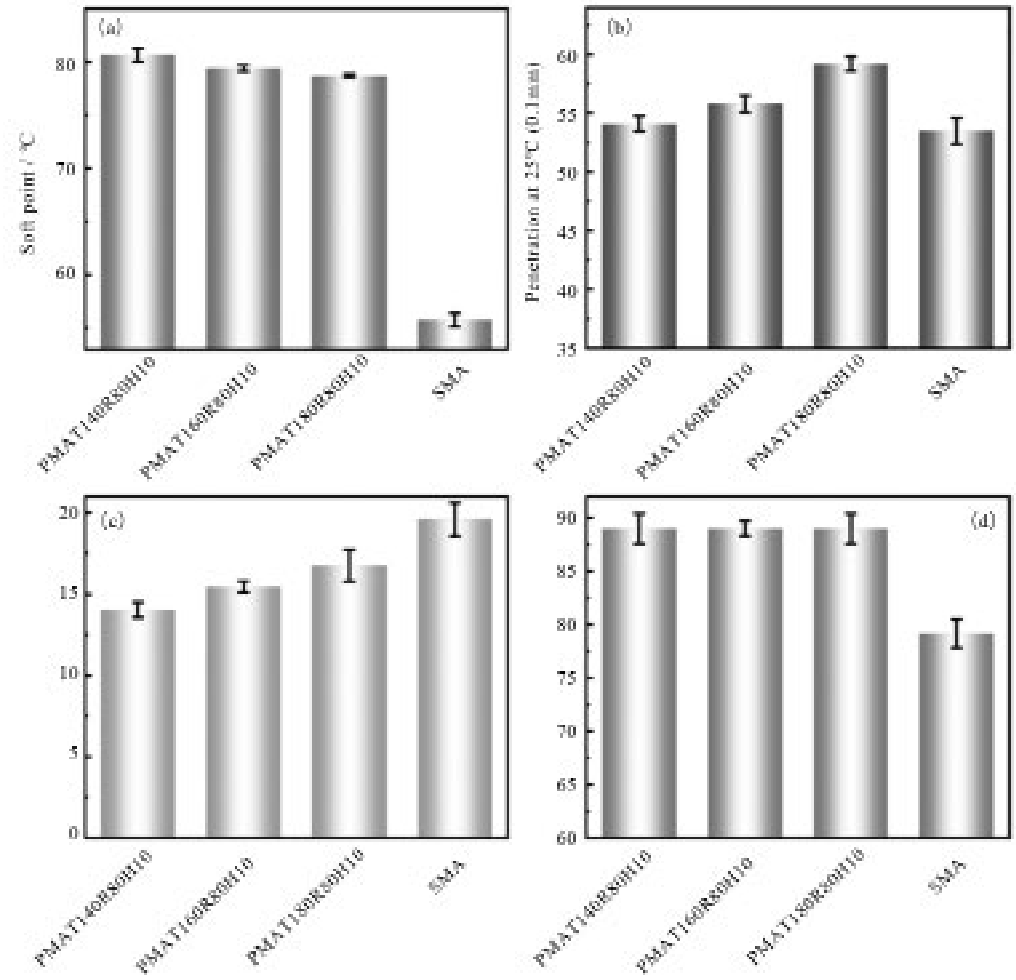


(a) Softening point; (b) Penetration; (c) Ductility; (d) Elastic recovery

Figure 3 Conventional physical properties of PMA and SMA at different desulfurization temperatures

softening the asphalt, and increasing its penetration. Within a certain range of desulfurization degree, as the degree of desulfurization increases, the dispersibility and compatibility of CR in asphalt improve, and CR's improvement effect on the flexibility and deformability of asphalt is enhanced, gradually increasing the ductility. Ductility is used to evaluate the plasticity of asphalt. DCR disperses uniformly in asphalt, enhancing the cohesion and flexibility of asphalt, allowing it to withstand greater deformation without breaking when stretched by external forces, and thus increasing ductility.

As the degree of desulfurization of rubber powder increases, the elastic recovery of asphalt tends to decrease. The rubber molecular chains in CR form a stable cross-linked network structure through vulcanization, giving the rubber powder good elasticity. However, the desulfurization process reduces the crosslinking density of rubber. As the degree of desulfurization of CR increases, the crosslinking density of the prepared DCR continuously decreases. Rubber with a high crosslinking density can better maintain its elastic structure in asphalt, contributing more to the elastic recovery of asphalt. When the crosslinking density decreases, the elasticity of the rubber phase weakens, leading to a decrease in the overall elastic recovery ability of asphalt. The crosslinking density of vulcanized rubber powder is closely related to its swelling capacity. The higher the crosslinking density, the stronger its ability to absorb light components in asphalt. As the degree of desulfurization of rubber powder increases, its ability to absorb light components in asphalt weakens. The swelling effect of light components in asphalt on the rubber phase decreases, and the rubber phase cannot swell sufficiently to fully exert its elastic properties, thereby affecting the elastic recovery of asphalt. The desulfurization reaction causes the



(a) Softening point; (b) Penetration; (c) Ductility; (d) Elastic recovery

Figure 4 Conventional physical properties of PMA and SMA at different desulfurization speeds

rubber molecular chains to undergo de-crosslinking, forming more soluble molecules and increasing the sol content. The structure and properties of these molecular chains change, and their elasticity is inferior to that of rubber molecular chains in a crosslinked state. After being subjected to external forces, they are difficult to effectively recover to their original state like unsulfurized or low-desulfurized rubber powder, thus reducing the elastic recovery performance of asphalt.

3 Conclusion

(1) Using a twin-screw shearing desulfurization process to prepare desulfurized rubber, as the desulfurization temperature, rotational speed, and desulfurizing agent content increase, the sol content rises and the crosslinking density decreases. Loose particles in the DCR disappear, the surface becomes sticky and develops holes and gaps, and the internal crosslinking network of the DCR is destroyed.

(2) With the increase of desulfurization temperature and rotational speed, the ductility and penetration of crumb rubber modified asphalt (CMA) increase, but the softening point and elastic recovery decrease, resulting in improved comprehensive performance. Desulfurized rubber is highly environmentally friendly and economical.