Mechanical properties of gutta-percha sulfide modified asphalt

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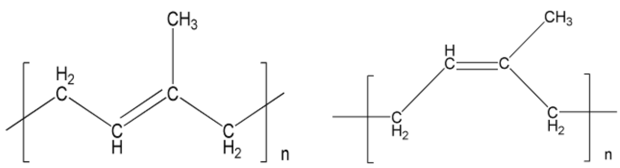
Abstract. Gutta-percha is the isomer of caoutchouc and can be used to enhance the performance of asphalt. In this paper, the produce proceedings of gutta-percha sulfide and gutta-percha sulfide modified asphalt are introduced. The performance indices of gutta-percha sulfide modified asphalt samples with different proportions are examined based on laboratory tests and the optimum ratio of gutta-percha and sulfur is decided.The micromechanism, temperature sensitivity, high and low temperature properties and viscoelasticity of the polymer modified asphalt are analyzed to discuss the modified mechanism and to decide the optimal polymer content. Low temperature bending tests are carried out to verify the low temperature performance of gutta-percha sulfide modified asphalt mixture. Research results showed that gutta-percha sulfide modified asphalt has good low temperature performance and a promising application prospect in the cold regions.

Keywords: gutta-percha sulfide, polymer modifier asphalt, vulcanization, micromechanism, viscoelasticity, ductility.

1. Introduction

Nowadays modified asphalt has been widely applied in surface course and middle course of pavement with the rapid development of China's social economy as well as heavy traffic. Because of its superior low-temperature performance and elastic recovery capability, styrene-butadiene-styrene (SBS) has been widely used in asphalt modification [1-4]. However, the cost of SBS modified asphalt remains high and SBS does not have a good compatibility with asphalt [5-6]. Taking saving social resources and mitigating the conflict between supply and demand into account, it is of great importance to find new asphalt modifiers.

Gutta-percha tree is a kind of propolis plant which grows only in the semitropical and warm temperature regions of China. Gutta-percha is the isomer of caoutchouc:gutta-percha is trans-polyisoprene, while caoutchouc is cis-polyisoprene [7] (Figure 1).



Trans-polyisoprene (Gutta-percha) Cis-polyisoprene (Caoutchouc)

Figure 1. Molecular structure of gutta-percha and caoutchouc.

The objective of this paper is to explore the mechanism and application of gutta-percha in asphalt modification. This was accomplished by conducting an indoor tests to evaluate the performance of modified asphalt.

2. Vulcanization mechanism of gutta-percha

The glass transition temperature of gutta-percha is -70℃, which is close to that of caoutchouc. Gutta-percha does not take on elasticity under normal temperature because of its crystallizability. So the elasticity of its molecular chain can not be released until its crystallization is restrained.

Similar to caoutchouc, there are plenty of double bonds in gutta-percha molecule chains. So gutta-percha has the potential to be vulcanized. During the vulcanization process, the planar structure of double bonds are broken up and then connected by a chemical bond and form a new cross linked structure, therefore vulcanization is a kind of cross link reaction. Two broken bonds from two different chains can link the two chains by forming a junction. Along with the vulcanization process, more and more junctions turn separated chains into a network structure. Consequently crystallization in gutta-percha is restrained and elasticity is gained.

According to the different degrees of cross linking, vulcanization of gutta-percha is commonly divided into three phases [8] and three different materials:

Phase A: zero cross linking degree, gutta-percha sulfide in this phase is thermoplastic material.

Phase B: low cross linking degree, gutta-percha sulfide in this phase is thermoelastic material.

Phase C: high cross linking degree, gutta-percha sulfide in this phase is rubbery material.

When all crystals are broken up, the sulfide becomes typical rubber. Under this circumstance, cross link junctions will become closer with further vulcanization. This structure will prevent the movement of gutta-percha molecular chains; therefore the rigidity of the chains is enhanced while the flexibility is lost. As a result, to choose a reasonable cross linking degree in vulcanization imposes a great effect on the low temperature performance of modified asphalt.

3. Materials preparation and methods

High speed sheering, a common laboratory modified asphalt preparation method, is employed in the present study to prepare the modified asphalt test samples.

3.1. Instruments and materials

Matrix asphalt made by Ningbo Baoying Asphalt Storage Co. Ltd. is used in this study. Its performance indices are outlined in Table 1:

Table 1. Main performance indices and technical requirements of the matrix asphalt.

Test Items		Performance Index	Technical Requirements
Penetration(25℃)/0.1mm		65.3	60～80
Penetration Index		-1.92463	-1.5～+1.0
Ductility(10℃)/cm		57.5(>150)	≮20
Ductility(15℃)/cm		71.5(>100)	≮100
Softening Point TR&B /℃		47.8	≮46
RTFOT (163℃,5h)	Weight Loss/%	-0.0543	±0.8
	Penetration Ratio/%	61.26	≮61
	Ductility(10℃)/cm	>100	≮15
	Ductility(15℃)/cm	12.75	≮6
Dynamic Viscosity(60℃)/Pa.s		197.13	≮180
PG Grade		64-22	—

Parts of the modifiers and instruments used in this study are outlined in Table 2:

Table 2. Trademark and manufacturer of materials and instruments.

Name	Trademark/Type	Manufacturer
Styrene-butadiene Block Copolymer	SBS/YH-791	Baling petrochemical Corp.
Gutta-percha	—	—
Mixer	—	Brabender
High Speed Sheering Machine	L4RT	Silverson machine Inc.

3.2. Vulcanization process of gutta-percha

The Brabender mixer is used to blend sulfur and gutta-percha in this study (Figure 2). The compatibility between gutta-percha and the matrix asphalt is not so good, so direct blending of sulfur and gutta-percha does not enhance the performance of asphalt significantly [9]. When a few of asphalt is mixed, the compatibility turns much better. In this way, the asphalt added plays the role of compatibilizer here. This method is similar to the matrix method in production of modified asphalt.

Vulcanization process is as follows: turn on the mixer and warm it up till the temperature of feed tank reaches 80℃. Put small pieces of gutta-percha into the feed tank, heat and soften these pieces and then blend them slowly. Then load sulfur and asphalt, close the feed tank and blend at a speed of 60r/min and keep the temperature at 80℃. After 5 minutes' blending, peel off the gutta-percha sulfide from the mixer.

Figure 2. The Brabender mixer.

Figure 3. High speed shearing machine.

3.3. Preparation process of modified asphalt

The L4RT high speed shearing machine (Figure 3) is used to prepare the modified asphalt samples in this study with an electric furnace and an infrared thermometer which can measure the liquid surface temperature are needed as well.

Put the pieces of gutta-percha sulfide into an oven with a set temperature of 60℃ for 15 to 20 minutes until they are soft, and then cut them into small pieces. Put the iron barrel filled with matrix asphalt into the oven of 120℃ for one hour to make it free-pouring.

Place the barrel on the electric furnace, put modifier slices inside and then hand mix for about 20 minutes to make the modifier swollen in the matrix asphalt. Make sure to keep the temperature of the asphalt below 170℃ by infrared thermometer. After hand mixing, place the barrel and the furnace below the shearing machine for two hours with the shearing speed slowly reaching 6000r/min and the temperature around 170℃.

3.4. Decision of optimal ratio

When SBS is the modifier and its content is low, to increase the content of SBS can apparently promote the performance of modified asphalt; however with a high content, the change of SBS content has little influence on the performance of modified asphalt. Exsisting studies show that the most reasonable content of SBS exits [10, 11]. It refers to a critical state when SBS in asphalt begins to turn from a disperse phase to a continuous phase. Test results indicate that the most reasonable content weights approximate 5% of asphalt.

By the same token, it is hypothesized that there may be an optimal ratio for gutta-percha sulphide in asphalt. According to the most reasonable content of SBS, set the content of gutta-percha to 5 wt% of the matrix asphalt, and prepare samples containing 0.1 wt%, 0.4 wt% and 0.6 wt% sulfur. The Softening Point and ductility (5℃ and 10℃) are tested which represent the high and low temperature performance of the asphalt. The results of the performance indices are outlined in Table 3.

Table 3. Main performance indices of gutta-percha sulphide.

Matrix Asphalt	Gutta-percha /wt %	Sulfur /wt %	Softening Point TR&B /℃	Ductility(5℃) /cm	Ductility(10℃) /cm
100	0	0	47.8	0	57.5
100	5	0	52.4	6.05	11.25
100	5	0.1	50.1	19	53
100	5	0.4	50.1	35.2	66.8
100	5	0.6	49.2	10	38.5

Figure 4 and Figure 5 are illustrated to present the results. As the sulfur content increased, ductility of both 5℃ and 10℃ went up and then down. When the sulfur content was 0.4%, ductility got its maximum value. However, to change the sulfur content had little effect on softening point. Hence, the optimal ratio of gutta-percha and sulfur is 5:0.4.

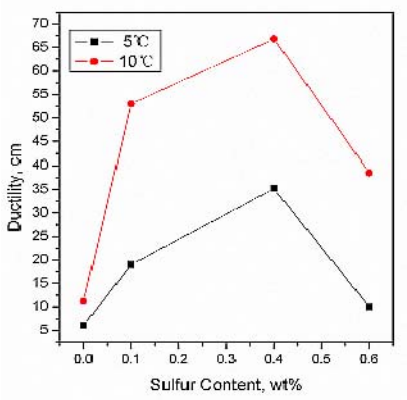


Figure 4. Ductility versus sulfur content.

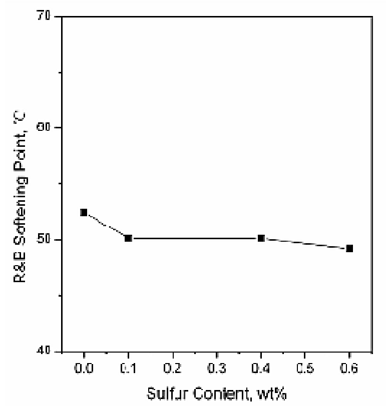


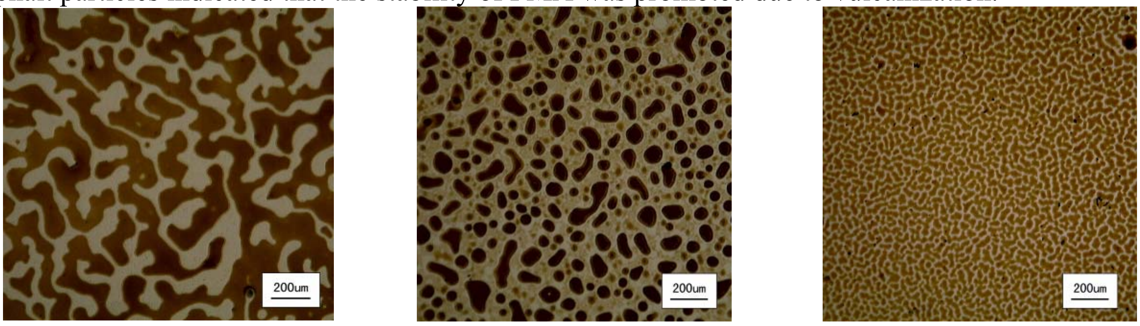
Figure 5. Softening point versus sulfur content.

4. Performance of gutta-percha sulphide modified asphalt

To explore the optimal content of gutta-percha sulfide, the performances of three modified asphalt samples designated as A, B and C were tested in every aspect. The three samples had respective gutta-percha sulfide contents, namely 3%, 5% and 7% with the same ratio of gutta-percha and sulfur (12.5:1) as previously concluded.

4.1. Micromechanism

Microscope was applied to study the micromechanism of the underlying polymer modifier asphalt(PMA). Figure 6 (a) ~ (c) shows the morphology of three samples with different polymer contents. In these pictures, the dark phase represents asphalt and the light phase polymer. The legends in these pictures represent 200 um. The particles of asphalt were big and that of the polymer phase seemed difficult to disperse in the asphalt as shown in Figure 6(a). As the sulfur content went up, the asphalt phase became increasingly small, and the polymer phase dispersed more uniformly. The decrease in asphalt particles indicated that the stability of PMA was promoted due to vulcanization.



(a) 3%Gutta-percha Sulfide (b) 5%Gutta-percha Sulfide (c) 7% Gutta-percha sulfide

Figure 6. Micrographs of gutta-percha sulfide modified asphalt.

4.2. Temperature sensitivity

Figure 7 shows the Penetration index of sample A, B and C. Penetration index (PI) reflects the temperature sensitivity and colloidal structure of asphalt. High PI value reflects temperature stability, while low PI value indicates instability as temperature changes. According to the asphalt colloid theory, asphalt containing high asphaltene and low oil is less sensitive to temperature. As shown in Picture 7 PI value went up as more sulfides were added. Gutta-percha is of weak polar, so it can be swollen by nonpolar molecules as saturated fragrance, therefore a colloidal like structure is formed and the asphaltene content is relatively increased. As a result, high Gutta-percha Sulfide content leads to higher temperature stability.

4.3. High temperature property

Figure 8 and Figure 9 show the penetration and R&B softening point of the samples. The two indices represent the high temperature property in Chinese standard. As shown in the figures, gutta-percha slightly promoted high temperature property of asphalt, but as the content increased, the asphalt appeared to be softer. As previously mentioned, sulfuration is a cross link reaction, which makes the vulcanized material softer due to the restraint to crystallization, so it explains why asphalt became softer as gutta-percha sulfide content increased. The melting point of gutta-percha is only 65℃, while that of SBS is nearly 180℃, therefore particulates of gutta-percha are easy to be softened and lose binding force to asphalt particulates because of the increase of temperature. So gutta-percha sulfide can hardly improve the high temperature property.

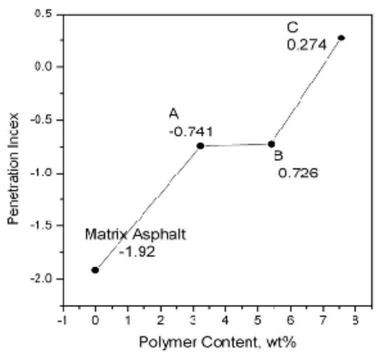


Figure 7. PI value of gutta-percha sulfide modified asphalt.

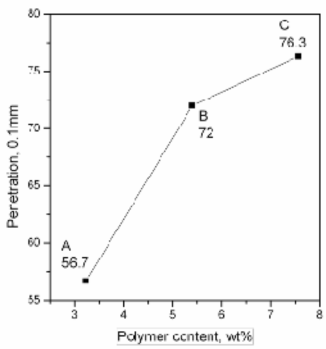


Figure 8. Penetration of gutta-percha sulfide modified asphalt.

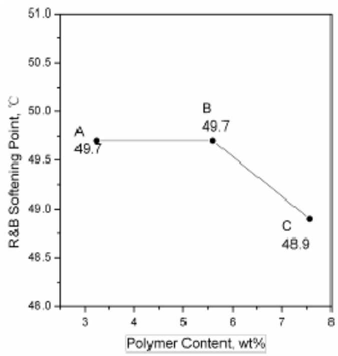


Figure 9. R&B softening point of gutta-percha sulfide modified asphalt.

4.4. Low temperature property

Figure 10 indicates that gutta-percha sulfide can improve low temperature property of asphalt. As the polymer content rose, 10℃ ductility kept elevating but the increase rate decreased when the polymer content reached 5.4 wt% of matrix asphalt. 5℃ ductility rose first and fell later at the turning point of 5.4 wt%. The glass state temperature of gutta-percha is -65℃, so when the temperature gets low, particles of gutta-percha can maintain at a certain elasticity to disperse the stress. Moreover, after the vulcanization, reticular structure is formed, which enables the gutta-percha an additional resilience capability. As is mentioned above, vulcanization can promote the compatibility of gutta-percha and asphalt; all these factors produce a significant promotion to the low temperature property of asphalt. If gutta-percha has been over cross-linked, the elasticity and ductility of the sulfide will drop, this can explain why the increasing rate of ductility slowed down when the polymer content increased.

4.5. Viscoelasticity property

As shown in Figures 11 and 12, the viscoelasticity of asphalt was slightly improved. As the gutta-percha sulfide content increased, the viscoelasticity of PMA kept rising. It proves that vulcanization can enhance the resilience and stretch property of gutta-percha, however under normal and high temperature, the promotion is not so marked at low temperature.

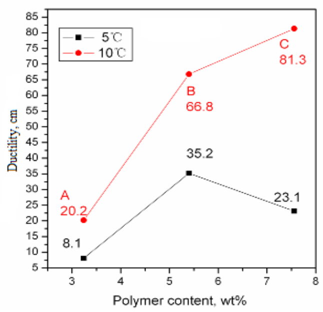


Figure 10. Ductility of gutta-percha sulfide modified asphalt.

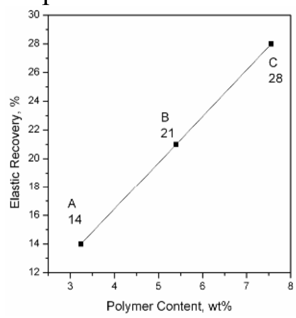


Figure 11. Elastic recovery of gutta-percha sulfide modified asphalt.

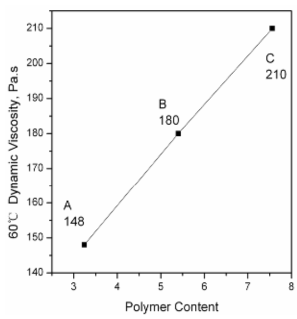


Figure 12. 60 ℃ Dynamic Viscosity of gutta-percha sulfide modified asphalt.

5. Low temperature bending test of gutta-percha sulphide modified asphalt mixture

According to the testing results, gutta-percha sulfide can obviously improve the low temperature property of asphalt. Low temperature properties of the mixtures were also investigated to evaluate the modified effects of gutta-percha sulfide.

In this study, the low temperature bending beam test at -10 ℃ with a loading rate of 50 mm/min was used. The beam specimen size was 250mm×30mm×35mm. Tensile strength and maximum tensile strain of failure could be collected and calculated by the experimental data as well as bending stiffness modulus and strain energy density.

The aggregate gradation of the mixture is a NMAS of 13 mm labeled as AC-13 with the optimum asphalt content 5.1% and the performance of coarse aggregate and fine aggregate all meet the specification requirements. Test results are shown below as Table 4.

Table 4. Low temperature bending test results.

Asphlat mixture Type	Tensile strength /Mpa	Maximum tensile strain /με	Bending stiffness modulus /MPa	Strain energy density /KJ/m3
General Asphalt mixture	6.346	1774	5395	1.983
Gutta-percha sulphide modified asphalt mixture	8.763	3621	2420	2.602

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In China, the specification requirement for maximum tensile strain of low temperature bending test is no less than 3000με. Gutta-percha sulphide modified asphalt mixture have reached the requirement with higher tensile strength, higher strain energy density and much lower bending stiffness modulus, which means gutta-percha sulphide modified asphalt can greatly enhance the low temperature performance and anti-cracking abilities of the asphalt mixture.

6. Conclusions

According to the analysis, the main conclusions have been summarized as follows:

(1) Gutta-percha sulfide can obviously improve the low temperature property of asphalt, but only has a slight influence on the high temperature and viscosity properties, thus it possesses great application prospect in low temperature regions.

(2) Vulcanization enables gutta-percha a better performance on resilience and stretch. However, the breaking up of cross link due to vulcanization will reduce the rigidity of gutta-percha, and over vulcanization leads to the loss of elasticity.

(3) Taking consideration of all the factors, the optimal content is 5 wt% gutta-percha and 0.4 wt% sulfur of the matrix asphalt.

References

[1] Fu H, Xie L and Dou D Y 2007 Storage Stability and Compatibility of Asphalt Binder Modified by SBS Graftcopolymer *Construction and Building Materials* **21**(7) 1528-1533

[2] Cong Y, Liao K and Huang W 2006 Study on Techoical Parameters of SBS Modified Asphalt *Petroleum Science and Technology* **24**(5) 507-512

[3] Airey G D 2004 Fundamental Binder and Practical Mixture Evaluation of Polymer Modified Bituminous Materials *The International Journal of Pavement Engineering* **5**(3) 137-151

[4] Fawcett A H and McNally T 2003 Polystyrene and Asphaltene Micelles within Blends with a Bitumen of an SBS Block Copolymer and Styrene and Butadiene Homopolymers *Colloid and Polymer Science* **281**(3) 203-213

[5] Yildirim Y 2007 Polymer Modified Asphalt Binders *Construction and Building Materials* **21**(1) 66-72

[6] Liu Z, Xuan M, Zhao Z, Cong Y and Liao K 2003 A Study of the Compatibility Between Asphalt and SBS *Petroleum Science and Technology* **21**(7) 1317-1325

[7] Yan R 1995 Prospects and Research Progress on Eucommia Ulmozdes Gum *Progress in Chemistry* **7**(1) 65-71

[8] Xue Z, Xie L and Yan R 1992 Study on NR/Gutta-Percha and PB/Gutta-Percha Bends *Journal of China Elastomerics* **2**(1) 12-17

[9] Chen J S and Huang C C 2006 Fundamental Characterization of SBS Modified Asphalt Mixed with Sulfur *Journal of Transportation Research Board* **103**(5) 2817-2825

[10] Zhao K and Yuan J 2001 The Study on the Mechanism of Polymer Modified Asphalt (Part 1) ——Absorbing-action of Modifier to Light Constituent in Asphalt and the State of Aggregation *Journal of Xi'an Highway University* **21**(2) 34-37

[11] Zhao K and Yuan J 2001 The Study on the Mechanism of Polymer Modified Asphalt (part2) --Summarizing on the Submicroscopic Shape of Modifier Particles *Journal of Xi'an Highway University* **21**(3) 21-24