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# Effect of chemical composition and structure of asphalt binders on self-healing

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## HIGHLIGHTS

- The self-healing ability of asphalt is sensitive to the content of aromatics.
- The self-healing ability of asphalt is sensitive to the content of small molecule.
- Molecule structure has a greatest impact on the self-healing ability of asphalt.

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## ABSTRACT

Asphalt binders have the self-healing ability to repair fatigue cracking automatically, and therefore the fatigue life can be extended. The extended fatigue life depends on the coupling effect between the chemical kinetics of asphalt molecules at cracking surfaces and the rate of the crack growth under fatigue loading. Obviously, the chemical characteristics of asphalt determine its inherent self-healing ability. However, uncertainty still remains in the effect of the chemical composition and structure of asphalt on the inherent self-healing ability. In this paper, four different Pen grade asphalt binders were characterized by Thin Layer Chromatography (TLC), Gel Permeation Chromatography (GPC), Fourier Transform infrared spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR), and the self-healing abilities of asphalt binders were investigated by a fatigue-rest-fatigue test with DSR. It was found that asphalt with a higher small molecule content/large molecular content ratio combined with higher aromatics content has a greater self-healing ability. In addition to the chemical composition of asphalt, its molecule structure also plays an important role in determining its self-healing ability. A higher $I_{1460}/I_{1376}$, $S/Ar$ ratio and $H_{ar}$ value, indicating a lower branched-chain and higher long and thin molecule content in asphalt, could promote self-healing. Based on Grey relational analysis, the microstructure of asphalt has a greater impact on the self-healing ability of asphalt binder compared with other factors.

## 1. Introduction

Under the action of repeated vehicular loading and the deterioration of the asphalt materials, fatigue cracking gradually generates due to the growth and the accumulation of micro and macro cracks [1]. Fatigue cracking is the main damage form of asphalt pavement, which influences the pavement performance significantly [2–4]. Fortunately, asphalt materials were found to have the self-healing ability to repair fatigue cracking automatically and then the fatigue life can be extended. In the 1960s, Deacon [5] first provided the evidence to show the self-healing process in asphalt. He found that with the increase of the resting time, the lifetime of asphalt concrete can be extended. The findings have been confirmed by other researchers [6–11].

Since the self-healing behavior of asphalt was found, it has aroused extensive attention in relevant research. Three self-healing mechanism, surface energy theory [12], capillary flow theory [13,8,14,15], and molecular diffusion theory [16–18], were developed to explain the self-healing behavior. Surface energy theory shows that the self-healing nature of asphalt is wetting, adsorption and diffusion across crack interface to reduce the surface energy. The energy comes from the formation of Van Der Waals force and hydrogen bond on the interface of the crack. The second theory holds the point that when the temperature is higher than the glass transition temperature of asphalt material, the capillary phenomenon occurs. Pressure difference exists between the

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contact points on microcracks, with the flow and diffusion of asphalt, the number of contact points increases gradually, leading to the healing of microcracks. The last one proposed by Wool and O'Connor maintains that the self-healing process can be divided into five steps: rearrangement, surface approach, wetting of the surface, low level diffusion between crack surfaces, and randomization. Bhasin and Little argued that the short-term healing of asphalt is due to "wetting" and long-term healing is attributed to "diffusion".

The above theories indicate that the chemical composition and structure of asphalt determine its inherent self-healing ability. Kim [19] introduced an index, the molar ratio of hydrogen atom and carbon atom in methyl and methylene (MMHC), to explain the effect of chemical composition on the self-healing ability of asphalt. He found that high level of MMHC would decrease the self-healing ability of asphalt. Santagata [20] employed saturate/aromatic ratio ($S/Ar$) to analyze the influence of chemical composition on the healing ability of asphalt. He believed that saturates frequently contain long aliphatic chains and the aromatics mainly have compact ring structures. With the increase of $S/Ar$ ratio, the ability of the oil phase of the bitumen to heal microcracks tends to increase. Another conclusion is that the fatigue life of asphalt binders is directly linked to the colloidal instability index. Based on the molecular dynamics simulation, Bommavaram and Bhasin [21,22] noticed that the molecular diffusion rate is positively correlated with the ratio of methylene and methyl ($CH_2/CH_3$). Obviously, a higher molecular diffusion rate implies a higher self-healing ability of asphalt. Actually, this finding is consistent with Kim, namely the chemical composition and structure have a great influence on self-healing ability. However, indications such as $S/Ar$ or $CH_2/CH_3$ are not enough to estimate the self-healing ability of asphalt binders.

Therefore, the objective of this study is to adopt suitable test methods and indexes to investigate the effect of chemical composition and structure on the self-healing ability of asphalt, and then find out the main factors affecting the self-healing ability of asphalt binders. Firstly, the self-healing ability of four different Pen grade asphalt binders was evaluated by the fatigue-rest-fatigue test. Then, the chemical composition and structure of asphalt were analyzed by Thin Layer Chromatography (TCL), Gel Permeation Chromatography (GPC), Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance (NMR) tests. Finally, the effect of chemical composition and structure of asphalt on its self-healing ability was discussed, and the grey relational analysis between chemical structure/composition and self-healing ability was implemented.

## 2. Materials and methodology

### 2.1. Materials

In order to highlight the effect of the variations of chemical composition and structure on self-healing ability, four base asphalt binders (Pen grades 20, 50, 70, 100) were selected. These asphalt binders were sampled from China Petrochemistry Company. The basic properties are listed in Table 1.

### 2.2. Methodology

#### 2.2.1. Fatigue-rest-fatigue test

By using a Dynamic Shear Rheometer (DSR, AR1500EX, TA Instruments Company, UAS), a fatigue-rest-fatigue test was put forward to investigate the self-healing ability of asphalt binders. The test method is shown in Fig. 1. The test condition is 3.0% strain, the temperature is 25 °C and the resting time is 3600 s. The healing index (HI) is used to evaluate the self-healing ability of asphalt.

#### 2.2.2. Thin-Layer Chromatography

Thin-Layer Chromatography (TLC) is a method to analyze a mixture by separating the compounds in it. TLC can be used to determine the content and the purity of components in a mixture. In the paper, three kinds of spreading agent including N-heptane containing a small amount of polar substances, analytical pure toluene, and dichloromethane-methanol (volume ratio is 95:5) were used. The ability of different component to adsorb spreading agent is quite different. Therefore, when the sample coated on the chromarod was put into spreading agent, its different components were separated. After the sample was dried, the hydrogen flame detector was used to scan the chromarod, and then the signal showing the chemical fractions was collected.

Four sharp peaks can be found in the chromatogram, which represent the four fractions of asphalt: asphaltenes (As), saturates (S), aromatics (Ar) and resins (R). By calculating the area of each peak and taking correction factor into account, the percentage of each fraction was acquired. Then $S/A_r$ ratio and the colloid instable index ($CII$) can be obtained as follows:

$$CII = \frac{A_s + S}{R + A_r} \tag{1}$$

where $A_s$, $S$, $R$ and $A_r$ respectively represent the weight percentage of asphaltene, saturate, resin and aromatic.

The $S/Ar$ ratio reflects the amount ratio of long molecules to ring shaped molecules. The molecule structure of asphalt with higher $S/Ar$ ratio is longer and thinner. The value of $CII$ characterizes the peptizing capability of asphalt. With a smaller $CII$, asphalt is more likely to be sol-type material and its colloidal structure is more stable.

#### 2.2.3. Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) was used to separate the molecules of asphalt samples depending on various sizes. Then a chromatogram displaying a clear depiction of the molecular weight distribution was obtained. The $y$-axis is the signal intensity, which is proportional to the concentration of molecule, and the $x$-axis is the elution time. The area under the curve represents the molecules injected into the GPC system. From left to right, the molecular size decreases gradually.

In the research, each curve was divided into 13 equal parts according to the elution time (see Fig. 2) [23]. Part 1 to part 5 are defined as the large molecular size ($LMS$), part 6 to part 9 are the middle molecular size ($MMS$), and part 10 to part 13 are the small molecular size ($SMS$).

**Table 1**
Performances of asphalt binders used in the investigation.

| Asphalt | Penetration (25 °C, 100 g, 5 s) 0.1 mm | Softening point (R&B) °C | Ductility (15 °C, 5 cm/min) cm | Viscosity (135 °C) mPa·s |
|---|---|---|---|---|
| 20# | 21.7 | 64.9 | – | 1581.6 |
| 50# | 43.2 | 52.5 | >100 | 557.3 |
| 70# | 68.4 | 46.2 | >100 | 436.5 |
| 100# | 108.8 | 43.0 | >100 | 301.3 |