Introduction

Asphalt is an organic matter of complex chemical composition, and a complex colloidal system, similar to polymer solution. It consists of mineral oil whose relative molecular weight is between 470 and 980, such as saturates and aromatics, resins whose relative molecular weight is between 780 – 1400, and asphaltenes whose relative molecular weight are 800 – 3500. Among them, asphaltenes with high molecular weight are wrapped by resins, which form micelles and are dispersed in oil media. This kind of colloidal system has a unique liquidity and typical rheological properties.

This model is confirmed by some experimental results. For example, small angle X-ray scattering (SAXS) and small angle neutrons scattering (SANS) confirm that asphaltenes form micelles in asphalt. It was also shown that the diffusion pattern observed in SAXS or SANS experiments, disappeared once the asphaltenes were removed from the asphalt. The atomic force microscopy (AFM) shows a peculiar “bee” structure that was initially only found for a “gel” bitumen. The same “bee” structure (also called catana phase) was repeatedly observed in other works with an average height between 22 and 85 nm and a typical distance between strips of order 150 nm. The link between the extent of “bee” phase and the asphaltene has been confirmed in one study when it was discarded and a correlation was instead proposed with the metal content of the bitumen in another one. The SEM observation of the same “gel” bitumen that gave “bee” structure in AFM, showed connecting aggregates of what was believed to be asphaltene particles of diameter around 100 nm. However, it is still difficult to make an exact description of the colloidal system and there are a few studies of the relationship between colloidal structure and chemical composition and performance indexes of asphalt. The reason is that the chemical composition of asphalt is complicated and it is difficult to describe the colloidal structure quantitatively.

Attenuated total reflection (ATR) technology can be used to analyse the difference between the structure of the surface and the interior. Therefore, by using ATR, the aromatic nucleus content of asphalt at different depths with changing the incident angles was taken as the index of colloid structure. Furthermore, the correlation of this index and chemical composition and performance of the asphalt was
analysed to confirm which component and performance index has good correlation. In this paper, SARA fractions of asphalt and part of the high and low temperature performance indexes were chosen for study.

Materials and experimental procedure

Materials
Four different types of asphalt, such as Japan 70, Huanxiling 130, Kelamayi Basic and Zhenhai 90 were chosen. They have different grades and are commonly used in asphalt industry.

ATR test
Nicolet Magna IR 560 with attenuated total reflection (ATR) attachment was used to measure the spectrum of four kinds of asphalt. The incident angle was 40°, 50°, 60° respectively. The revolution was four (4) and the scan times 20.

DMTA test
The DuPont DMTA 983 was used. The heating rate was 2 °C min⁻¹, scanning frequency was 10 Hz and the measuring temperature ranged 30 – 100 °C.

DSC test
The Netzsch DSC 204 was used. The heating rate was 10 °C min⁻¹ and the measuring temperature ranged from −120 to 120 °C.

Penetration test
Penetration test was carried out according to ASTM D5-73 (100 g, 5 s, 25 °C)

Softening point test
Softening point test was carried out according to ASTM D36.

SARA fraction method
According to ASTM D4425, SARA method was used to separate the four fractions of asphalt.

Results and discussion

Colloidal structure characteristic analysis
With regard to ATR test, the incident angles of 40°, 50° and 60° were chosen. It is known that the incident depth decreases as the incident angle increases, which means more surface information can be obtained with a smaller incident angle. Generally, the absorbance peak of aromatic nucleus of asphalt appears around 1600 cm⁻¹, and by comparing the intensity of the 1600 cm⁻¹ region \( A_{1600} \) to that of 1455 cm⁻¹ \( A_{1455} \), which is attributed to saturated C–C vibrations, the relative degree of aromatic nucleus content can be estimated. The peak area ratio of four kinds of asphalt in different incident angles is shown in Fig. 1.

As shown in Fig. 1, the relative peak intensity of aromatic nucleus becomes weak with increasing incident angle, which means less aromatic nucleus content on the surface. This result is in accordance with the general view on colloidal structure model of asphalt. In this model, asphaltene with more aromatic structure are in the centre and absorb some micelles to form the disperse phase. The aromatic content becomes lower and the polarity becomes weaker as distance from the centre increases. When the distance continues to increase, the main substances become aliphatic oil of lower polarity as dispersion medium.

The aromatic content of each fraction in asphalt has great impact on the colloidal structure. It can form colloidal structure only if the aromatic content of maltene matches the dispersion phase. Sufficient aromatic content in maltene easily forms sol type asphalt but deficient aromatic content will form gel type asphalt. Therefore, in this paper, the relative aromatic nucleus content at the incident angles of 60 degrees and 40 degrees are respectively considered as the representative values of aromatic nucleus content of surface and interior. The ratio of the surface representative values to the interior representative value is taken as an evaluation index of asphalt colloidal structure. Table 1 lists the ratio \( A_{1600}/A_{1455} \) at the incident angle of 60 degrees to that at the incident angle of 40 degrees of four kinds of asphalt.

<table>
<thead>
<tr>
<th>Asphalt</th>
<th>Kelamayi Basic Asphalt</th>
<th>Japan 70#</th>
<th>Zhenhai 90#</th>
<th>Huanxiling 130#</th>
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</thead>
<tbody>
<tr>
<td>ratio omjer</td>
<td>0.377</td>
<td>0.376</td>
<td>0.497</td>
<td>0.764</td>
</tr>
</tbody>
</table>

Four fractions of asphalt
Table 2 lists the content of four fractions. It can be seen that there is an apparent difference in the content of the four fractions because of different source, which might affect the performance of asphalt colloid.
Table 2 – Content of four fractions of different asphalt

<table>
<thead>
<tr>
<th>Asphalt Asphalt</th>
<th>Saturates Zasićeni</th>
<th>Aromatics Aromatski</th>
<th>Resins Smole</th>
<th>Asphaltenes Asfalteni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huanxiling 130#</td>
<td>32.00</td>
<td>31.40</td>
<td>33.20</td>
<td>3.40</td>
</tr>
<tr>
<td>Kelamayi Basic Asphalt</td>
<td>31.10</td>
<td>32.80</td>
<td>36.10</td>
<td>0</td>
</tr>
<tr>
<td>Japan 70#</td>
<td>19.10</td>
<td>48.40</td>
<td>22.00</td>
<td>10.50</td>
</tr>
<tr>
<td>Zhenhai 90#</td>
<td>24.90</td>
<td>40.50</td>
<td>28.30</td>
<td>6.30</td>
</tr>
</tbody>
</table>

Analysis on high temperature performance

Pavements withstand repeated and continuous traffic loads. Therefore, to know the true mechanical response of asphalt binder, it is necessary to study the deformation behaviour under dynamic loading conditions, which is the dynamic viscoelastic behavior. Therefore, Dynamic Mechanical Thermal Analysis (DMTA) was used to analyse the dynamic viscoelastic behaviour of asphalt.

Two parameters, complex modulus $G'$, the tangent of the phase angle $\tan \delta$ were adopted to described the dynamic viscoelastic behaviour of asphalt. Among them, $G'$ represents the ability to resist deformation, $\tan \delta$ represents the relative contribution of elastic and viscous part of asphalt, and higher $G'$ or lower $\tan \delta$ is beneficial to resist rutting. In this paper, $G'$ and $\tan \delta$ are thought as two separate high temperature performance indexes.

Fig. 2 shows the complex modulus $G'$ of the different kinds of asphalt at temperatures between 30 to 100 °C. It can be seen from Fig. 2 that the complex modulus changes slightly from 30 to 70 °C, but slopes downwards when the temperature exceeds 70 °C, indicating that the ability to resist high temperature deformation drops.

Analysis of low temperature performance

Generally, asphalt with higher penetration has better crack resistance at low temperature. Some researchers have pointed out that the asphalt has a glass-transition temperature ($t_g$). Asphalt has a larger viscosity between the soft point temperature and $t_g$ but becomes stiff and brittle under $t_g$. Therefore, $t_g$ can be taken as a evaluation index of low temperature performance.

In Fig. 4, an endothermic peak appears at $-50^\circ C$ to $-10^\circ C$, which means that the asphalt changes from glassy state to viscous liquid state. The endothermic peak at $-50^\circ C$ to $-10^\circ C$ is related to the dissolution of some ingredients in the asphalt. Also, a peak appears at 5 °C, which is caused by some wax existing in the asphalt. The data of $t_g$ and penetration value of four kinds of asphalt are listed in Table 3.
Correlation analysis of four fractions of asphalt

The ratio of aromatic nucleus content of surface to interior, and the content of four fractions was taken as reference sequence and comparative sequence respectively. The initial results analysed by correlation method are shown in Table 4. Table 5 lists the calculation results of difference value for each influence factor. Table 6 shows the calculation results of gray correlation coefficient. As shown in Table 6, the content of resin has the greatest correlation degree, followed by that of saturate, aromatics and asphaltene.

From the above analysis, it can be concluded that saturates and resins have high correlation and play an important role in balancing the colloid structure of asphalt. The reason being that the content of saturates has a relationship with the content of C—C on the surface, and resin is like a bridge in forming the colloid structure. The content of resins decides how much the content of aromatics and saturates is needed to maintain the colloid structure. In addition, the characteristic of asphaltene is not only affected by the colloid characteristic, but also by the content of polar group, so the correlation degree of asphaltene content and colloid characteristics is the lowest.
Correlation of high temperature performance

In the analysis of grey correlation, the index of colloidal structure was chosen as reference sequence, and the complex $G^*$ and tan $\delta$ as comparative sequence. Among them, the respective average value of $G^*$ and tan $\delta$ ranging from $30\,^\circ C$ to $70\,^\circ C$ was taken as reference sequence, which represents one performance index of asphalt under this temperature range. The average of $G^*$ and tan $\delta$ between $30\,^\circ C$ to $70\,^\circ C$ can reflect the average performance of asphalt in this temperature range. The curve rises to the temperature of $70\,^\circ C – 90\,^\circ C$, so the slope of $G^*$ and tan $\delta$ at $70\,^\circ C – 90\,^\circ C$ was considered as another performance index of asphalt. The slope of $G^*$ and tan $\delta$ can reflect the changes of asphalt performance at high temperatures.

The calculation process of grey correlation analysis is the same as above. The calculation results are shown in Table 7. It can be seen that $G^*$ and tan $\delta$ have good correlation with the index of colloidal structure at the temperature of $30\,^\circ C – 70\,^\circ C$ but poor correlation at $70\,^\circ C – 90\,^\circ C$. The analysis indicates that at high temperatures, it is necessary to search for other indexes to characterize the colloidal structure.

Correlation analysis of low temperature performance

The colloid characteristics are taken as reference sequence, and the data of penetration and $t_k$ are taken as comparative sequence. The analysis process is the same as above, and the results are shown in Table 8. It can be seen that the data of penetration and $t_k$ have a good correlation with colloidal characteristics index, which indicates that low temperature performance has a good correlation with colloidal characteristics index. Also, the $t_k$ value has higher correlation degree than penetration, which shows that $t_k$ can better reflect the structure characteristics of asphalt than penetration value.

Conclusion

The characteristics of colloidal structure of asphalt were analysed by ATR and the ratio of the aromatics content on the surface to that in the interior was taken as an evaluation index of colloidal structure. Gray correlation method was used to analyse the correlation degree of the index and chemical fraction and performance of asphalt. Conclusions can be drawn as follows:

The correlation degree of index of colloidal structure and the content of four fractions of asphalt from the largest to smallest is the content of saturates, resins, aromatics and asphaltenes, meaning that saturates and resins are an important factor in forming the colloidal structure.

The index of colloidal structure has a good correlation with $G^*$ and tan $\delta$ at the temperature of $30 – 70\,^\circ C$ but poor correlation at $70 – 90\,^\circ C$.

The index of colloidal structure has a good correlation with low temperature performance of asphalt, and the results show $t_k$ can better reflect the characteristics of colloidal structure than penetration value.

Part of chemical fraction and performance indexes has a good correlation with the index of colloidal structure, indicating that asphalt is a complex structure system and needs to be characterized by more evaluation indexes.
List of symbols and abbreviations

**Popis simbola i kratica**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>– apsorbance</td>
</tr>
<tr>
<td>B</td>
<td>– prigušena potpuna refleksija</td>
</tr>
<tr>
<td>C</td>
<td>– kompleksni modul, MPa</td>
</tr>
<tr>
<td>(t_g)</td>
<td>– glass-transition temperature, °C</td>
</tr>
<tr>
<td>(w)</td>
<td>– mass fraction, %</td>
</tr>
<tr>
<td>(\delta)</td>
<td>– phase angle, °</td>
</tr>
<tr>
<td>AFM</td>
<td>– mikroskopija atomoških sila</td>
</tr>
<tr>
<td>ATR</td>
<td>– prigušena potpuna refleksija</td>
</tr>
<tr>
<td>DMTA</td>
<td>– dinamomehanička termička analiza</td>
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<tr>
<td>DSC</td>
<td>– diferencijalna pretražna calorimetrija</td>
</tr>
<tr>
<td>SANS</td>
<td>– neutronsko raspršenje pod malim kutom</td>
</tr>
<tr>
<td>SARA</td>
<td>– odjeljivanje na zasićene spojeve, aromatske, smole i asfaltene</td>
</tr>
<tr>
<td>SAXS</td>
<td>– small angle X-ray scattering</td>
</tr>
<tr>
<td>SEM</td>
<td>– pretražna elektronska mikroskopija</td>
</tr>
</tbody>
</table>

**References**

SAŽETAK
Korelacijska analiza koloidne strukture
i kemijskog sastava asfalta te njegovih radnih svojstava

Yunbo Lei,a Xuejuan Cao b* i Yongjie Ding c

Asfalt se smatra koloidnim materijalom i zato je važno proučiti odnos između koloidne strukture, kemijskog sastava i svojstava. Kao indeks koloidne strukture uzet je sadržaj aromatskih jezgri asfaltnog gela te svojstava upotrijebljena je siva korelacija. Rezultati pokazuju da je korelacija između razina indeksa koloidne strukture, zasićenih ugljikovodika i smola visoka, što dokazuje da zasićenost i smole igraju važnu ulogu u koloidnoj strukturi asfaltnog gela. S obzirom na indeks svojstava asfaltnog gela, kompleksni modul \( G' \) i tangens faznog kuta dobro koreliraju s indeksom koloidne strukture pri temperaturama od 30 do 70 °C, ali loše koreliraju pri temperaturama od 70 do 90 °C. Svojstva na niskim temperaturama povezana su s indeksom koloidne strukture i staklište može bolje odražavati karakteristike koloidne strukture. Analiza pokazuje da je koloidna struktura asfaltnog gela kompleksan sustav, pa je za određivanje radnih svojstava potrebno upotrijebiti više višestrukih indeksa od jednog indeksa.

Ključne riječi
Asfalt, koloidna struktura, siva korelacija, kemijski sastav

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