Study on the adhesion between activated kaolin modified asphalt and mineral materials

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Abstract: The mass fraction of kaolin was 3%, 5%, 7%, 9%, 11%, 13% and 15%, respectively. The three indexes of kaolin were tested. The results showed that after kaolin was added, the penetration, softening point, ductility and deformation resistance of matrix asphalt were decreased. In addition, indoor adhesion test was conducted to analyze the adhesion of modified asphalt of granite and limestone with different kaolin contents, and the adhesion of modified asphalt in distilled water and 5%NaCl solution were compared. It is found that adding kaolin can improve the adhesion between asphalt and aggregate. Through a comparison of properties, it is suggested that the content of kaolin should be 5% rather than more than 7%.

1. Introduction

Kaolin is a very important and widely used non-metallic mineral. It is a mixture of hydrous aluminosilicates composed of a variety of minerals, of which kaolinite, montmorillonite, and hydromica are the basic components. Kaolin is widely used in dozens of industries and departments, such as papermaking, ceramics, plastics, rubber, chemicals, electronics, coatings, refractory materials, medicine, cosmetics, textiles, national defense, and atomic energy, due to its plasticity, adhesion, dispersibility, adsorption and chemical stability[1].

Kaolin is an important clay composed mainly of kaolin minerals. Kaolin is a 1:1 layered octahedral silicate mineral. Its basic constituent units are silica-oxygen tetrahedron and alumina-oxygen octahedral. The former forms hexagonal grid layers along two-dimensional plane direction by sharing apex angles. The tip oxygen of each silicon-oxygen tetrahedron that is not shared faces to one side. Silicon-oxygen tetrahedrons are joined into layers along with two-dimensional directions in a common way[2].

Kaolin has remarkable advantages in production technology, price, properties, and reserves, but the application of kaolin as a modifier in petroleum asphalt is rarely reported. Previous studies have been mostly applied in coal asphalt. For example, Liya Gao[3] et al. modified coal asphalt by intercalating kaolin with dimethyl sulfoxide (DMSO) and found that thin flake kaolin improved the thermal stability of coal asphalt. Yunting Chen[4] are handled in dimethyl sulfoxide (DMSO) intercalated kaolin clay, coal tar/modified kaolin composites, was prepared by X-ray diffractometer and scanning electron microscopy (SEM) analysis method, found that the modified kaolin dosage was 5%, of coal tar/modified kaolin composite material of high-temperature properties and aging properties, improved, softening point is 55.2 °C, penetration of 29.4 mm, 15 °C ductility is 116.1 cm. Shuangfu Han[5] et al. used the same method to discuss the influence of kaolin on the anti-aging performance of coal asphalt. In addition, Chunfa Ouyang[6] et al. studied the influence of kaolin on the high-temperature storage
stability, mechanical properties, dynamic rheological properties and phase morphology and structure of SBS modified asphalt. Although kaolin is applied to asphalt, the types and action modes of asphalt are different. The research on kaolin as modifier applied to petroleum asphalt is only reflected in the literature of Huiming Bao’s team[7].

Based on the existing research, this paper uses kaolin with a fineness of 200 to modify petroleum asphalt. In the reference book "Research on Pavement Performance of Kaolin Modified Asphalt Mixture"[7], only the pavement performance of Kaolin Modified Asphalt is studied, but the research on the adhesion between modified asphalt and aggregate is not in-depth. The adhesion between asphalt and aggregate is the key factor affecting the quality and stability of the asphalt mixture. Asphalt pavement diseases mostly occur at the asphalt-stone interface where the adhesion is not strong[8-9]. In order to better promote kaolin modified asphalt, it is necessary to study the adhesion between kaolin modified asphalt and aggregate. Therefore, the adhesion test of limestone and granite aggregates in two different liquid environments was carried out to explore the adhesion effect between kaolin modified asphalt and aggregate.

2. Test raw materials

2.1. Nature of main raw materials

Base asphalt is made of "Donghai Branch" 70 # A grade road asphalt produced by Maoming Branch of Sinopec. According to the requirements of "Test Rules for Asphalt and Asphalt Mixture in Highway Engineering JTG E20-2011"[10] (hereinafter referred to as "Rules"), the basic performance indexes of base asphalt are shown in Table 1.

| Item                      | Technical Requirements | Result | Experimental Method       |
|---------------------------|------------------------|--------|---------------------------|
| Penetration(25℃)/(mm)     | 6-8                    | 6.5    | T0604-2011                |
| Ductility(15℃)/cm         | ≥100                   | 104.52 | T0605-2011                |
| Softening Point /℃        | ≥46                    | 48.5   | T0606-2011                |
| Flash Point /℃            | ≥260                   | 299    | T0633-2011                |
| Solubility/%              | ≥99.5                  | 99.88  | T0607-2011                |

The kaolin produced by Jinhai Kaolin Co., Ltd. in Hepu County of Guangxi was tested. The main components are SiO2, Al2O3, Fe2O3, etc. The mass fraction of SiO2 is 68.68%, Al2O3 is 20.52%, and Fe2O3 is 0.8%.

Limestone and Granite with a particle size of 13.2~19mm are selected as mineral aggregates, and the relevant technical indexes are shown in table 2 and table 3.

Table 2 Technical specifications and requirements for limestone coarse aggregate

| Item                                      | Result | Technical Requirements |
|-------------------------------------------|--------|------------------------|
| Crushed stone value (%)                  | 18.5   | ≤28                    |
| Flat and elongated particle in coarse aggregate (%) | 6.4    | ≤18                    |
| Apparent specific gravity (g/cm³)         | 2.716  | ≥2.5                   |
| Water absorption (%)                      | 0.5    | ≤3                     |
| Particle content <0.075mm (wash method) (%) | 0.42   | ≤1                     |
Table 3 Technical specifications and requirements for granite coarse aggregate

| Item                                           | Result | Technical Requirements |
|------------------------------------------------|--------|------------------------|
| Crushed stone value (%)                       | 6.1    | ≤28                    |
| Flat and elongated particle in coarse aggregate (%) | 4.7    | ≤18                    |
| Apparent specific gravity (g/cm³)              | 2.868  | ≥2.5                  |
| Water absorption (%)                           | 0.4    | ≤3                    |
| Particle content <0.075mm (wash method) (%)    | 0.37   | ≤1                    |

As can be seen from table 1, table 2 and table 3, the performance indexes of the selected test materials all meet the requirements of the specification.

2.2 Activation of Kaolin and Preparation of Modified Asphalt

First of all, kaolin needs to be activated. The specific method is as follows:

1. The kaolin was dried in a constant temperature drying box at 100°C for 24 hours, and the free water was removed.
2. After grinding and sieving the dried kaolin, the kaolin fineness of 200 meshes or less is selected for the next step.

The larger the number of grinding details, the finer the kaolin powder particles, the larger the relative surface area, the more oil in the asphalt adsorbed, and the more obvious the modification effect.

![Fig.1 Kaolin](image1)

Secondly, the asphalt samples are prepared according to the T0602 method in the rules. Heating asphalt in the oven to about 150°C (with asphalt completely softening as standard, specific temperature varies with the selected base asphalt).

![Fig.2 Modified Asphalt](image2)
Then, weighed and completely softened base asphalt and kaolin were dissolved by mechanical stirring and then injected into the high shear emulsifier rapidly. The asphalt and kaolin were sheared for 30 minutes at a speed of 10000 r/min at 150°C. The mass fractions of kaolin are 3%, 5%, 7%, 9%, 11%, 13%, and 15% respectively. The dissolution state of kaolin is judged by the criterion that kaolin is fully integrated into the asphalt under the shear condition and swelling occurs. The indexes of modified asphalt were tested and compared with base asphalt. The experimental results are shown in Fig. 3.

Fig.3 Test results of basic properties of kaolin modified asphalt with different contents

From Figure 3, we can see: (1) On the one hand, the penetration of kaolin modified asphalt with different content is lower than that of base asphalt at the same temperature, and the penetration reaches the minimum when the content of kaolin is 13%. Among them, the needle penetration decreased by 31% at 30°C. On the other hand, for modified asphalt with the same kaolin content, the penetration degree increases with the increase of temperature at different test temperatures, and the greater the temperature difference is, the greater the difference is. This indicates that at the same temperature, the higher the kaolin content is, the larger the relative specific surface area will be, the greater the absorption of asphalt oil will be, and the greater the internal friction of asphalt fluid will be\cite{11}. External performance is to enhance the asphalt resistance to deformation. At the same time, with the increase in temperature, the activity of kaolin increases. Due to the nature of asphalt itself, the penetration at higher temperature is greater than that at a lower temperature. The higher the temperature, the larger the content of kaolin, the softer the modified asphalt, and the worse the resistance to high-temperature deformation. (2) After adding kaolin, the softening point of modified asphalt is significantly increased, reaching the highest value of 62.5°C when the kaolin content is 13%, which is about 27.5% higher than that of base asphalt. The softening point of modified asphalt tends to decrease when the content of kaolin is more than 13%. (3) The ductility of asphalt is greatly reduced by the addition of kaolin. However, the ductility value of kaolin content tends to be the same after 5%, and the reduction range is not obvious.

In summary: After kaolin modification, asphalt becomes hard and its resistance to deformation
increases. However, when the content of kaolin is too high and the temperature rises, the activity of kaolin and asphalt increases, and the high-temperature performance become worse. Therefore, the content of kaolin should not be too high, and comprehensive consideration should be given to the coordination of high and low-temperature properties.

2.3. Adhesion test design of kaolin modified asphalt

(1) Determine the test indicators: In this experiment, the average adhesion of mineral powder was selected as the experimental index, and the average adhesion rate was taken as a reference.

(2) Selection of particle size: According to the method of T0616-1993 in the rules, coarse aggregate with maximum particle size greater than 13.2mm is adopted, and the shape must be regular, so as to ensure that the surface area of the aggregate is not too far from the same volume.

(3) Selection of ore powder: The mineral is limestone ore powder commonly used in asphalt mixture.

2.4. Adhesion Test of Kaolin Modified Asphalt

This experiment is based on the water boiling method in JTGE20-2011 "Test Rules for Asphalt and Asphalt Mixture in Highway Engineering", and refers to Zhen Li, Guangwen Fu [12-13] and other test methods of "the influence of salt-freezing cycle on asphalt performance", the specific process is as follows.

(1) The selected coarse aggregate particles are washed and then dried and heated in an oven at 105 ±5℃.

(2) Kaolin modified asphalt is heated to 140 ~ 160℃ and then the prepared coarse aggregate is immersed in kaolin modified asphalt for 45 seconds so that the surface of the coarse aggregate is completely covered by asphalt.

(3) Slip off the excess bitumen. When the aggregate coated with asphalt is cooled to room temperature, it is immersed in boiling distilled water or salt solution, and the distilled water or salt solution remains slightly boiling. After soaking for 3 minutes, take out the aggregate and hang it to dry.

(4) The air-dried aggregate was put into a 35℃ thermostat for 1 hour, and its quality (M0) was called after 1 hour. The samples were rolled in limestone powder aggregate basin with tweezers for one week and then weighed by electronic balance. This mass is denoted as M1. The accuracy of electronic balance was 0.001g. The mass difference between M0 and M1 is the adsorptive capacity of aggregate to fine aggregate. Parallel experiments were carried out. Evaluation of Adhesion between Asphalt and Coarse Aggregate by Mean Value of Adsorbed Mineral Powder Quality.

3. Test results and analysis

3.1. Test results

The test results are shown in figure 4 and figure 5.

![Adhesion curve of coarse aggregate in distilled water with different kaolin content](image-url)
3.2. Analysis of test results

3.2.1 Trend of Adhesion of Coarse Aggregate in Distilled Water with Different Kaolin Contents

As can be seen from Figure 4, in distilled water, under the same conditions: (1) The adhesion of kaolin modified asphalt is higher than that of base asphalt, which indicates that the addition of kaolin can improve the adhesion between base asphalt and aggregate. (2) Whether it is granite or limestone, the adhesion of mineral powder increases first and then decreases. The content of kaolin is different when the adhesion reaches its peak value. Granite reaches its maximum when the content of kaolin is 3%, and limestone reaches its maximum when the content of kaolin is 5% Afterward, with the increase of kaolin content, the adhesion decreases. When the kaolin content is 11%, the adhesion is similar to that of base asphalt. (3) The changing trend of adsorption rate of two kinds of ore aggregates is the same as that of adsorption amount, but there is no significant difference.

3.2.2 Adhesion change trend of coarse aggregate in 5% NaCl solution with different kaolin content

It can be clearly seen in Fig. 5 that the adhesion of limestone to modified asphalt is greater than that of granite and kaolin modified asphalt at any kaolin content and the minimum difference of adsorption capacity to minerals is also above 6%. This shows that the bonding force between limestone and modified asphalt is far greater than that of granite.

In the case of salt solution, the adhesion of granite to mineral powder first increases and then decreases, reaching the maximum when the kaolin content is 5%, and the average adsorption of mineral powder is 0.0913g. After that, with the increase of kaolin content, the bond strength between granite and asphalt gradually decreases. The cohesive force between limestone and asphalt has no obvious regularity in this solution. The relatively stable adsorption capacity of mineral powder is between 5% and 9% of kaolin content.

3.2.3 Comprehensive evaluation and analysis

The cohesion between limestone and kaolin modified asphalt is much better than that of granite.

(1) According to the analysis of the chemical composition of aggregate, SiO2 is the main chemical composition of granite, while CaCO3 is the main chemical composition of limestone. According to acidity, that is, SiO2 content, the granite used in this test is weak acid stone, while the limestone is alkaline. The cohesive force between asphalt and alkaline aggregate is greater than that between asphalt and acid aggregate.

(2) Microstructure analysis of coarse aggregates shows that different minerals have different physical properties. Different mineral compositions lead to changes in rock texture, which directly affects the mechanical properties of aggregates. Lixin Gan[14] and Lu Wang[8] of Chang'an University...
have scanned two kinds of rock aggregates by electron microscopy, which has been confirmed by fractal theory. The scanning electron microscopy figure is shown in Fig. 6. Through comparison, it can be seen that the surface texture of granite limestone is more fully developed. In the original state, the surface texture of limestone is more complex than that of granite, and the structural depth and folding degree are greater than that of granite. When limestone aggregate contacts with asphalt, the asphalt at the contact interface will be filled with tiny pits and cracks on its surface. At the same time, the uneven surface of the limestone is conducive to the adsorption of asphalt, and the texture of asphalt adsorbed in the concave interlocking with the convex texture, thus improving the cohesion between asphalt and aggregate. Although asphalt also adheres to every part of the granite surface, its texture development is relatively low, and its adhesion is worse.

![Fig.6 1000 times coarse aggregate surface texture map](image)

(3) From the analysis of the aggregate environment, the adhesion of limestone to kaolin modified asphalt in two kinds of solutions (distilled water, 5% NaCl solution) is better than that of granite. Combining the adhesion curve of limestone to kaolin modified asphalt in two kinds of solutions and the basic property index of kaolin modified asphalt, it is suggested that the best content of kaolin is around 5% and not more than 7%. According to the technical indexes of two kinds of coarse aggregates, the crushing value of limestone is 18.5%, while that of granite is only 6.1%, which is one-third of that of limestone. Therefore, considering water loss, we can try to find better aggregates or optimization measures to improve its road performance.

4. Conclusions
1) The addition of kaolin can improve the consistency of asphalt and increase its resistance to deformation. But the content of kaolin should not be too high.
2) The adhesion between kaolin modified asphalt and limestone is greater than that between matrix asphalt and limestone. It shows that the modification of base asphalt by kaolin is effective.
3) The adhesion between kaolin modified asphalt and aggregate first increases and then decreases. It is meaningless that the output of kaolin is too high.
4) In order to improve the adhesion between asphalt and aggregate, it is suggested that the content of kaolin in kaolin modified asphalt should be 5% and should not exceed 7%.

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