Study on the influence factors of aging property of nano-modified asphalt

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Abstract. In order to study the aging property of nano-modified asphalt, the values of nano-modified asphalt like softening point, penetration, ductility and viscosity etc. before and after the aging test were measured by controlling the content and types of nanomaterial, and then the relevant aging property indexes were calculated, the aging property optimum of the modified asphalt was determined by scientific methods of mathematical statistics and analysis. The testing results show that nanomaterial can effectively improve the high-temperature stability, low-temperature crack resistance and viscoelasticity of nano-modified asphalt. The content and type of nanomaterial have a great influence on the aging property of modified asphalt, the anti-aging performance of nano-modified asphalt with 0.5% titanium dioxide content is better.

1. Introduction

In recent years, more and more nanomaterial and nanotechnology have been employed to various fields of transportation. As there are strong atomic activities and special interface effect at the nanomaterial surface, nanomaterial can easily combine with other atoms to achieve their own stable state, which can lead to big changes in the activated macroscopic material system [1]. High-temperature stability, anti-fatigue friction performance (anti-slip performance) and anti-aging performance of nano-modified asphalt will be greatly improved.

The nanomaterial changes asphalt properties from micro scale, its modification mechanism is very different from that of traditional polymer modified asphalt, which draws keen interest of researchers on it [2]. There are many common nanometer modifiers like nanocarbon, nanoclay, nanofibers, etc. in the market, nanoclay, among these nanomaterial, is often used in asphalt modification due to the low cost and abundant yield [3, 4], Baqersad [5] tested the aging property of Bentonite Nanoclay modified asphalt mixture, testing results showed that it had better rutting resistance and low-temperature durability. Yao [6] analyzed the effects of different nanomaterial on asphalt aging through infrared spectroscopy, and identified functional groups related to mixture fatigue.

Hassan [7] found that the incorporation of nano-titanium dioxide did not affect the conventional properties of the mixture by rheological tests, not only could titanium dioxide effectively remove nitrogen oxides from the air, but also it could prevent aging effect of ultraviolet rays on asphalt.
pavement. Tin antimony oxide (ATO) and cesium tungsten oxide (GATO) have excellent performance of near infrared absorption and refraction effect, but studies on anti-aging performance of ATO and GATO modified asphalt are not extensive, therefore, the modified asphalt of them are studied so as to provide reference for relative direction.

2. Materials and methods

2.1. Materials

(1) Matrix asphalt:
Among many factors that can affect the properties of modified asphalt, matrix asphalt is important one, 70# matrix asphalt produced by Shandong Qilu Petrochemical Engineering Co. Ltd is employed to this study. Relevant performance tests are conducted according to Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering (JTG E20-2011) (hereinafter referred to as the Methods), and test results are shown in table 1.

| Test index               | Unit       | Technical requirements | Test results | Test method |
|-------------------------|------------|------------------------|--------------|-------------|
| Penetration             | 15℃, 100g, 5s | 0.1 mm                 | 32           | T0604       |
|                         | 25℃, 100g, 5s | 60~80                  | 62           |             |
|                         | 30℃, 100g, 5s | —                      | 99           |             |
| Softening point (R&B)  | ℃          | ≥46                    | 47.5         | T0606       |
| Ductility (15℃, 5cm/min)| cm         | ≥100                   | 104          | T0605       |
| Density (25℃)          | g/cm³      | Actual measurement    | 0.988        | T0603       |
| RTFOT (163℃, 300min)   | %          | ≤±0.8                  | 0.01         | T0610       |
| Penetration ratio (25℃)| %          | ≥61                    | 70           | T0604       |
| Ductility (10℃, 5cm/min)| cm        | ≥6                     | 6.73         | T0605       |

(2) Nanomaterial:
Matrix asphalt with nano-titanium dioxide material can better prevent asphalt aging caused by ultraviolet light, and can remove nitrogen and oxygen pollutants in the air. ATO and GATO can effectively absorb or reflect near infrared ray, the technical indexes of the three kinds of nanomaterial are shown in table 2.

| Nanomaterial       | Partial size (nm) | Purity (%) | Surface area (m²/g) | Packed density (g/cm³) | Appearance   |
|--------------------|-------------------|------------|---------------------|------------------------|--------------|
| Titanium dioxide   | 15-18             | ≥99.2      | 98                  | 0.24                   | White powder |
| ATO                | 5-15              | ≥99.9      | 50                  | 0.70                   | Blue powder  |
| GATO               | 30-40             | ≥99.0      | 89                  | 0.34                   | Black powder |

2.2. Preparation of nano-modified asphalt
High speed shear method is usually used to prepare modified asphalt. Firstly, 70# asphalt is heated to 150±5℃ in the oven (the holding time should not exceed 1h after reaching the temperature), then a certain amount of nanometer titanium dioxide (or ATO, GATO) is weighed and added to the pre-made asphalt by stirring until there is no nanomaterial floating at asphalt surface, finally, the nano-modified asphalt is shore at a speed of 5000rpm for 1h.

2.3. Performance index test
(1) Basic technical property index test
According to T0604-2011, T0606-2011 and T0605-2011 of the Methods, respectively, penetration test (mm), softening point test (℃) and ductility test (cm) are conducted strictly. Repeatability test allows error is controlled, the test data are recorded down.

(2) Brookfield viscosity test
The viscosity is tested at 135℃ according to T0625-2011 of the Methods, temperature error within 1℃ is ensured, torque count should be kept at around 50%. The data should be recorded every 1min at constant temperature and the mean value of three times repeating test should be taken.

(3) Rotating thin film oven test (RTFOT)
RTFOT shall be conducted according to T0610-2011 of the Methods. After aging for 5h, the performance indexes are tested. During this period, the asphalt shall be stirred every 1h, and all tests shall be completed within 72h after heating.

3. Study on aging property

3.1. Orthogonal test scheme
The main influencing factors to determine the aging property of nano-modified asphalt are the content and type of nanomaterial, factor A (content of nanomaterial) has three level (0.5%, 2.0%, 3.5%), factor B (type of nanomaterial) has three level (Titanium dioxide, ATO, GATO). Orthogonal table \( L_9 (3^4) \) is taken to arrange the test, as shown in table 3.

| Specimen | A: Content of nanomaterial (%) | B: Type of nanomaterial |
|----------|-------------------------------|------------------------|
| 1        | 1 (0.5)                       | 1 (Titanium dioxide)   |
| 2        | 1                             | 2 (ATO)                |
| 3        | 1                             | 3 (GATO)               |
| 4        | 2 (2.0)                       | 1                      |
| 5        | 2                             | 2                      |
| 6        | 2                             | 3                      |
| 7        | 3 (3.5)                       | 1                      |
| 8        | 3                             | 2                      |
| 9        | 3                             | 3                      |

3.2. Aging property index
Researches indicated that same modified asphalt sample would crust on the asphalt surface if TFOT was adopted, which would worsen the aging condition and hindered the aging process. Therefore, the RTFOT is adopted in this study, the rotation and agitation state are always maintained during the test so as to better simulate the actual situation of aging.

The aging property indexes like penetration ratio, softening point increment, etc. can objectively reflect aging property of asphalt. Penetration ratio is the ratio of penetration value between aging asphalt and original asphalt. Softening point increment is the softening point difference between aging asphalt and original asphalt. Orthogonal test results are shown as figure 1.

From the perspective of technical property index, the higher the softening point, the better the high-temperature stability of asphalt, the lower the penetration, the higher the viscoelasticity, the higher the ductility, the better the low-temperature crack resistance. From the perspective of aging property index, the larger the penetration ratio before and after aging, the larger the softening point increment, the better the overall anti-aging performance of the asphalt. As can be seen from figure 1, the order of penetration ratio is: specimen 1 > specimen 3 > specimen 4 > specimen 2 > specimen 5 > specimen 7 > specimen 8 > specimen 6 > specimen 9, the order of softening point increment is: specimen 1 > specimen 3 > specimen 6 > specimen 2 > specimen 9 > specimen 5 > specimen 8 > specimen 4 >
specimen 7, it can be seen that specimen 1 has better anti-aging performance, followed by specimen 3, although the order of aging ductility is: specimen 4 > specimen 6 > specimen 7 > specimen 9 > specimen 1 = specimen 8 > specimen 3 > specimen 2, the technical property index of specimen 1 are relatively superior before aging, which indicates that specimen 1 has been barely effected by aging test.

![Figure 1](image1.png)

**Figure 1.** Orthogonal test results of nano-modified asphalt. (a) Ductility test. (b) Softening point test. (c) Penetration test. (d) Brookfield viscosity test.

It can be preliminarily seen that nano-material can slow down the reduction of penetration and ductility after aging, improve softening point by compared technical property index of matrix asphalt after aging test, therefore anti-aging performance of nanomaterial asphalt has been effectively enhanced and the anti-aging performance of specimen 1 is relatively excellent than other specimen.

### 4. Analysis and discussion of test results

#### 4.1. Range analysis of orthogonal test

The range analysis of the above orthogonal test results is carried out to determine the influence degree of each factor level on the nano-modified asphalt. Given the range analysis result of the optimal test scheme (table 4), primary and secondary order and optimal level of factors are shown in table 5.

| Test index | Level 1’s test index sum K₁ | Level 2’s test index sum K₂ | Level 3’s test index sum K₃ | Level 1’s test index mean k₁ | Level 2’s test index mean k₂ | Level 3’s test index mean k₃ | Range | Optimal solution |
|------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-------|------------------|
| Penetration| A 163.00                    | 162.10                      | 166.00                      | 54.33                       | 54.03                       | 55.33                       | 1.30  | A₂               |
|            | B 170.20                    | 158.90                      | 162.00                      | 56.73                       | 52.97                       | 54.00                       | 3.77  | B₁               |
| Softening  | A 152.25                    | 153.70                      | 155.90                      | 50.75                       | 51.23                       | 51.97                       | 1.22  | A₁               |
| point      | B 153.50                    | 154.90                      | 153.45                      | 51.17                       | 51.63                       | 51.15                       | 0.48  | B₂               |
| Viscosity  | A 1326.00                   | 1423.50                     | 1389.20                     | 442.00                      | 474.50                      | 463.07                      | 32.50 | A₂               |
|            | B 1569.00                   | 1312.50                     | 1257.20                     | 523.00                      | 437.50                      | 419.07                      | 103.9 | B₁               |
| Ductility  | A 39.60                     | 35.40                       | 36.10                       | 13.20                       | 11.80                       | 12.03                       | 1.40  | A₁               |
|            | B 35.10                     | 38.30                       | 37.70                       | 11.70                       | 12.77                       | 12.57                       | 1.07  | B₂               |
| Penetration ratio| A 203.00             | 193.30                      | 186.70                      | 67.67                       | 64.43                       | 62.23                       | 5.43  | A₁               |
|            | B 199.50                    | 191.80                      | 191.70                      | 66.50                       | 63.93                       | 63.93                       | 2.60  | B₁               |
| Softening  | A 24.05                     | 20.20                       | 19.20                       | 8.02                        | 6.73                        | 6.4                         | 24.05 | A₁               |
| point      | B 19.15                     | 20.50                       | 23.80                       | 6.38                        | 6.83                        | 7.93                        | 19.15 | B₂               |
Table 5. Primary and secondary order and optimal level of factors in orthogonal test.

| Test index         | Primary and secondary order of factors | Optimal levels |
|--------------------|----------------------------------------|----------------|
| Penetration        | $B > A$                                | $A_3 B_1$      |
| Softening point    | $A > B$                                | $A_3 B_2$      |
| Viscosity          | $B > A$                                | $A_2 B_1$      |
| Ductility          | $A > B$                                | $A_1 B_2$      |
| Penetration ratio  | $A > B$                                | $A_1 B_3$      |
| Softening point increment | $A > B$                            | $A_1 B_3$      |
| Aging ductility    | $A > B$                                | $A_1 B_3$      |

As we can see from table 5, the primary and secondary order of factors is $A > B$, from the perspective of the level of factors, there are three level 1 of $A$ having a great influence among the seven indexes, there are four level 1 of $A$ having a great influence among the seven indexes, therefore the optimal combination is $A_1 B_1$.

4.2. Variance analysis of orthogonal test

Furthermore, the performance optimization evaluation of orthogonal schemes is conducted through variance analysis to determine the significance level of each factor. The result of variance analysis is shown in table 6.

Table 6. Variance analysis of orthogonal test.

| Performance index | Variation source | Degree of freedom | Sum of squares | Mean squares of dispersion | $F$ value | Critical value |
|-------------------|------------------|-------------------|----------------|---------------------------|-----------|----------------|
| Penetration       | Content of nanomaterial (A) | 2           | 2.78           | 1.39                      | 0.05      | $F_{0.05}(2,4) = 6.9$ |
|                   | Type of nanomaterial (B) | 2           | 22.73          | 11.37                     | 0.44      | $F_{0.05}(2,4) = 18.0$ |
|                   | Error (E)         | 4           | 102.65         | 25.66                     |           |                |
|                   | Total (T)         | 8           | 128.16         |                           |           |                |
| Softening point   | A                 | 2           | 2.25           | 1.13                      | 4.79      | $F_{0.05}(2,4) = 6.9$ |
|                   | B                 | 2           | 0.45           | 0.23                      | 0.96      | $F_{0.05}(2,4) = 18.0$ |
|                   | E                 | 4           | 0.94           | 0.24                      |           |                |
|                   | T                 | 8           | 3.65           |                           |           |                |
| Viscosity         | A                 | 2           | 1630.78        | 815.39                    | 0.63      | $F_{0.05}(2,4) = 18.0$ |
|                   | B                 | 2           | 18452.18       | 9226.09                   | 7.15      | $F_{0.05}(2,4) = 18.0$ |
|                   | E                 | 4           | 5162.75        | 1290.69                   |           | $F_{0.05}(2,4) = 18.0$ |
|                   | T                 | 8           | 25245.70       |                           |           |                |
| Ductility         | A                 | 2           | 3.38           | 1.69                      | 0.45      | $F_{0.05}(2,4) = 6.9$ |
|                   | B                 | 2           | 1.93           | 0.97                      | 0.26      | $F_{0.05}(2,4) = 18.0$ |
|                   | E                 | 4           | 15.00          | 3.75                      |           | $F_{0.05}(2,4) = 18.0$ |
|                   | T                 | 8           | 20.30          |                           |           |                |
| Penetration ratio | A                 | 2           | 44.82          | 22.41                     | 6.73      | $F_{0.05}(2,4) = 6.9$ |
|                   | B                 | 2           | 13.35          | 6.68                      | 2.01      | $F_{0.05}(2,4) = 18.0$ |
|                   | E                 | 4           | 13.31          | 3.33                      |           | $F_{0.05}(2,4) = 18.0$ |
|                   | T                 | 8           | 71.48          |                           |           |                |
When the factor degree of freedom is 2 and the error degree of freedom is 4, critical $F$ value is $F_{0.05}(2,4)=6.9$, it is 95% sure that this factor is the critical value of significant factor, if the $F$ value of the factor is less than 6.9, it indicates that this factor has no significant influence on the performance index of nano-modified asphalt, critical $F$ value is $F_{0.01}(2,4)=18.0$, it is 99% sure that this factor is the critical value of the significant factor, if $6.9 < F$ value $< 18.0$, it demonstrates that this factor has a significant influence on the performance index of nano-modified asphalt, if the $F$ value is greater than 18.0, the influence of this factor on its performance index is extremely significant.

As can be seen from table 6, the content and the type of nanomaterial have no significant influence on penetration. As indicated by the fact that both $F_A$ and $F_B$ of softening point are less than $F_{0.05}(2,4)$, however, $F_A$ is close to $F_{0.05}(2,4)$, which can be considered as that the content of nanomaterial has a more obvious effect on softening point and the type of nanomaterial has no significant effect on it. That $F_A$ of viscosity is less than $F_{0.05}(2,4)$ and $F_B$ of viscosity is larger than $F_{0.05}(2,4)$ indicates the content of nanomaterial has no significant effect on viscosity and the type of nanomaterial has a significant effect on it. The content and type of nanomaterial have no significance effect on ductility.

It can be seen that the content and type of nanomaterial have no significant effect on penetration ratio and softening point increment, however, $F_A$ of the penetration ratio is slightly less than $F_{0.05}(2,4)$, so it can be considered as that the nanomaterial content has a more obvious effect on the penetration ratio. The content and type of nanomaterial have an extremely significant effect on the aging ductility. From the overall situation, most $F$ value of technical property index are less than 1 while all $F$ value of aging performance index are great than 2 at least, which indicates that the addition of nanomaterial can greatly improve the anti-aging performance of asphalt.

5. Conclusion
Nano-modified asphalt has high development potential and many advantages, the influence factors of nano-modified asphalt aging property and its optimum proportion were analyzed through orthogonal design study, the main conclusions are as follows:

(1) The result of the orthogonal test shows that the nanomaterial can effectively slow down the reduction of asphalt penetration and ductility after aging, the high-temperature stability, low-temperature crack resistance and viscoelasticity of nano-modified asphalt are improved.

(2) The result of range analysis and variance analysis of orthogonal test indicates that the content and type of nanomaterial have a more obvious effect on the aging property indexes compared with technical property indexes, therefore, the nanomaterial can effectively improve anti-aging performance of asphalt.

(3) According to technical property indexes and aging property indexes, the nano-modified asphalt prepared by adding 0.5% titanium dioxide has high viscoelasticity, good high-temperature stability, rutting resistance and excellent low-temperature anti-cracking performance, its anti-aging performance is optimal, compared with other test specimens.

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