The Effect of Zinc Stearate Modification on Aging Characteristics of Asphalt Binder

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Abstract. Different types of modifiers have been investigated to improve aging characteristics of asphalt binders. In this research, the effect of zinc stearate modification has been studied on aging resistance of asphalt binder. For this purpose, viscous flow properties and other rheological characteristics of neat and modified asphalt binders have been evaluated by using conventional experimental tests and superpave protocol test. In order to evaluate rheological behavior of asphalt binder in presence of zinc stearate, a neat asphalt binder sample with three modified samples containing 0.5, 1 and 2 wt% of zinc stearate were aged by means of the Rolling Thin Film Oven Test (RTFOT). The Brookfield rotational viscosity (RV) was implemented at six different temperatures from 100 to 200 degree of centigrade. Furthermore, the dynamic shear rheometer (DSR) was used for evaluating complex modulus (G*) and phase angle (δ) of all neat and modified samples at 10, 20, 30, 40, 50 and 60°C in frequency sweep mode. To evaluate effect of adding zinc stearate by using viscosity results, proportion of asphalt binder’s viscosity after aging to its viscosity before aging was defined as viscosity aging index (VAI). Results showed that adding zinc stearate to neat asphalt binder reduces the viscosity aging index. Results of frequency sweep test indicated that zinc stearate causes the values of complex shear modulus in aging asphalt binder approach to neat state which means the effect of zinc stearate modification is positive for improving aging resistance of asphalt binder.

1. Introduction
Aging of asphalt binder during its life cycle from mixing with aggregates to fully destruction has always been one of the main concerns of researchers in the field of pavement’s materials and design [1,2]. With respect to such a phenomenon, the initial rheological characteristics of asphalt binder will be changed which in some cases improves and in some other cases weakens the performance of the asphalt pavement [3]. For example, loss of volatile and light oils at high service temperatures leads to hardening asphalt binder due to aging and increases the rutting resistance of asphalt binders. However, at low service temperature the asphalt binder becomes harder and more brittle and the risk of cracking increases [4]. Generally, controlling and decreasing the effect of aging on rheological characteristics...
of unaged asphalt binder were topics of numerous researches in the field of asphalt binder modification.

Numerous modifiers have been carried out to increase aging resistance of asphalt binder. Some of these modifiers have been used as a rejuvenator of recycled asphalt mixture and some others as an anti-aging to enhance asphalt binder’s rheological and mechanical performance. Zinc dialkyldithiophosphate (ZDDP), carbon black, octabenzone (UV531) and bumetrizole (UV326) are some well-known substances that have been used as an anti-aging agent. However, the effect of these anti-aging agents is not significant on the properties of asphalt binders [5]. Nanotechnology has been gradually penetrated into the field of asphalt modification [6]. Fini et al. proved that the addition of bio-binder which was derived from waste swine manure can reduce the viscosity of the asphalt binder. Furthermore, they indicated that bio-binder has the potential to improve thermal cracking performance of conventional asphalt binders [7].

In this research, zinc stearate was used as an additive to enhance anti-aging properties of original asphalt binder. For this purpose, one neat asphalt binder sample and three modified ones containing 0.5, 1 and 2 wt% of zinc stearate were aged by means of the rolling thin film oven test (RTFOT) and then two classical tests were performed including penetration test and softening point. The Brookfield rotational viscosity (RV) was also carried out on these samples. Generally, the viscosity of aged asphalt binder is greater than un-aged asphalt binder. In this paper, the viscosity index has been calculated by dividing viscosity of aged asphalt on viscosity of un-aged asphalt which obviously increases due to the loss of volatile and light oils. This index will be somewhat larger than one. Therefore, observing the viscosity index can be a suitable method for assessing the effect of zinc stearate on the aging characteristics of asphalt binder. In addition, investigation of rheological behavior of modified asphalt binder can provide useful information on the behavior of asphalt binder in presence of zinc stearate. For this purpose, the dynamic shear rheometer (DSR) was used at test temperatures between 10 and 60°C.

2. Experimental program

2.1. Materials
In this study samples were prepared using asphalt binder with penetration grade of 60/70 (the common asphalt binder in Iran) acquired from the Tehran Petroleum Refinery of Pasargad Oil Company located in Tehran, Iran. The Zinc Stearates (ZS) is a micronized and hydrophilic white powder that used in its formal sense is soap. This industrial-grade material is derived from the reaction of fatty acids with a combination of zinc metal. This material widely used in industrial, which derived from the reaction of fatty acids with a combination of zinc. Stearates are used as a lubricant for the polymer industries. Polymers are long chain molecules that are viscous and sticky in their high melting points. The friction force between polymer-polymer, polymer-metal, polymer-fillers, fillers-fillers and fillers-metal causes difficulty for polymers flow. The appropriate solution for aforementioned problem is reducing the coefficient of surfaces friction. Among several types of lubricants, zinc stearate is an important additive in the process of polymers production. It is used as an internal lubricant for molding. Figure 1 shows appearance shape at the room temperature and the molecular structure of zinc stearates.

2.2. Preparation of the samples
In this research, there are four different asphalt samples including BASE, ZS05 (0.5%), ZS1 (1%) and ZS2 (2%) which are fabricated at 140°C by mixing neat asphalt binder and specified percentage of zinc stearate for 45 min with a low shear mixer.
To simulate the short-term aging (hardening or oxidation) characteristics of the asphalt binders’ samples, the RTFO test was used. Therefore, two samples of asphalt binder, including neat and RTFO-aged asphalt were obtained. In the RTFO test, the asphalt binder specimens should be heated inside the main container so that the temperature does not exceed 150°C. Then pour 35 g of asphalt with a precision of 0.001 into eight sample bottles. The asphalt binder samples are heated up in a 163°C oven until it is completely fluid and pourable. The samples are kept in the oven, on temperature, with air flow of 400 min/ml and the carriage rotating for 85 min. When mass-change bottles have cooled to a safe handling temperature, their weights are measured to the nearest 0.001 g and recorded.

2.3. Test methods
In this study, the most important classical tests, including the ASTM D5 test (penetration point) and softening point Test (ASTM D36), which are well-known and used in the industrial literature and consultants and contractors have been performed on all samples. These experiments were carried out on unaged samples. In addition to the conventional tests, the superpave protocol experiments included rolling thin film oven test (RTFOT) and rotational viscosity (RV) were implemented at 100, 120, 135, 160, 180 and 200°C. Furthermore, the dynamic shear rheometer (DSR) was used for evaluating complex modulus (G*) and phase angle (δ) of all neat and modified samples in frequency sweep mode from 0.1 to 100 Hz. The diameter of the test sample was 25 mm with thickness of 1 mm. Both experiments were carried out in two cases of aged and unaged neat and modified samples.

3. Results and Discussion

3.1. Conventional experimental tests
Table 1 indicates results of conventional experimental tests. As it can be seen adding zinc stearate has no significant effect on physically characteristics of asphalt binder including its penetration grade and softening point. Therefore, it can be concluded that addition of stearates does not change physical properties of asphalt binder including consistency and heat sensitivity.
Table 1. Penetration and softening point of neat and modified asphalt binders

| Sample Code | Penetration (0.1 mm) | Softening Point (°C) |
|-------------|----------------------|----------------------|
| BASE        | 61                   | 48.4                 |
| ZS05        | 60                   | 48.5                 |
| ZS1         | 64                   | 48.7                 |
| ZS2         | 59                   | 49.5                 |

3.2. Superpave protocol test

Figure 2 depicts results of rotational viscosity test based on the viscosity aging index (VAI). This index can be calculated according to the following equation:

\[
\text{Viscosity Aging Index} = \frac{\text{Viscosity}_{\text{Aged Binder}}}{\text{Viscosity}_{\text{Unaged Binder}}} \tag{1}
\]

Figure 2. Viscosity versus temperature for neat and zinc stearate modified asphalt binder

Figure 2 illustrates that the addition of zinc stearate can reduce the viscosity aging index. It is apparent that increasing the percentage of ZS causes further reduction of VAI. For 2% of ZS this index becomes less than 1. These results proved that introducing ZS to neat asphalt binder can control and reduce the effects of aging and cracking. On this basis, it can be concluded that ZS as a modifier can enhance the aging characteristics of asphalt binder.

The dynamic shear rheometer (DSR) was used for evaluating complex modulus (G*) and phase angle (δ) of all neat and modified samples at 10, 20, 30, 40, 50 and 60°C in the frequency sweep
mode. The results clearly showed in figure 3, 4, 5 and 6. These figures illustrate that increasing of temperature led to decreasing of complex modulus ($G^*$). As it can be seen in these figures, the graph of unaged binder and RTFO aged modified samples converge to each other that means the positive effect of this modifier on the hardening control of asphalt binder.

**Figure 3.** The complex shear modulus versus frequency for neat asphalt binder

**Figure 4.** The complex shear modulus versus frequency for asphalt binder modified with 0.5% of zinc stearate
Figure 5. The complex shear modulus versus frequency for asphalt binder modified with 1% of zinc stearate

Figure 6. The complex shear modulus versus frequency for asphalt binder modified with 2% of zinc stearate

For example in figure 5 which is related to the addition of 1% by weight of stearates to neat asphalt binder, it is clearly visible that for three temperatures of 10, 20 and 30°C, the complex shear modulus of neat sample and modified samples containing 0.5% of ZS approach to each other that confirms the results of the rotational viscosity test. Furthermore, according to the set of figures it is clear that the addition of stearates, particularly at 1% and 2%, causes the graphs to shift upwards which means
increasing the stiffness and the complex shear modulus of the modified sample relative to neat asphalt binder.

4. Conclusion
The effect of zinc stearate as a modifier on aging resistance of asphalt binder was discussed in this paper. The following conclusions can be drawn:

- Zinc stearate as a modifier can be concluded that addition of stearates does not change physical properties of asphalt binder including consistency and heat sensitivity.
- Addition of zinc stearate can reduce the viscosity aging index. It means that positive effect of this modifier on aging characteristics of asphalt binders.
- Results of frequency sweep test indicated that zinc stearate causes the values of complex shear modulus in aging asphalt binder approach to neat state which means the effect of zinc stearate modification is positive for improving aging resistance of asphalt binder.
- the results of a complex shear modulus illustrate that adding zinc stearates, especially in 1 and 2% by weight increases the asphalt binder stiffness

5. References

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